WATER TECHNOLOGY

Unit V: Hard water – Reasons for hardness – units of hardness - Boiler troubles –Priming and Foaming, Scale formation, Boiler corrosion, Caustic embrittlement – Internal treatments - Softening of Hard water: Lime – Soda process, Zeolite process and numerical problems based on these processes and Ion Exchange process - Water for drinking purposes- Purification – Sterilization and disinfection: Chlorination, Break point chlorination and other methods – Reverse Osmosis and Electro Dialysis.

Introduction:

Water is one of the abundant available substances in nature. Water forms about 75% of the matter on earth's crust. It is an essential ingredient to both plant and animal life. Water is not only essential for human beings, plants and animals for sustaining life but is also equally important for agricultural, industrial and other purposes.

Without food human being can survive for a number of days, but water is such an essential thing without it one cannot survive. Probably it's most important use as an engineering material is in the steam generation. Water is also used as a coolant, in power, and chemical plants. In addition to it, water can also be used in the production of steel, rayon, paper, textiles, chemicals, irrigation, drinking etc.

Sources of water: The chief sources of water fall in two main groups,

1. Surface water, 2. Underground water

Impurities in water: The main impurities present in water are classified into three types.

1. Physical impurities, 2. Chemical impurities, 3. Bacteriological impurities

**Types of water:** Water is classified into two types based on the property of it with soap solution.

- Soft water
- Hard water.

Soft water: Soft water is one that gives good lather readily with soap solution.

Hard water: Water that does not produce lather with soap readily is called as hard water. This is due to the presence of certain salts of calcium, magnesium and other heavy metals dissolved in water. A sample of hard water when treated with soap, (sodium or potassium salt of higher fatty acid such as oleic, palmatic or stearic) does not produce lather, but on the other hand

forms a white scum or precipitate. This precipitate is resulted due to the formation of insoluble salts of calcium and magnesium.

When water with such hardness is used for washing, large amount of soap is consumed. Thus hardness of water can be defined as the soap consuming capacity of water. The reaction can be explained as follows,

$$2RCOONa + M^{2+} \rightarrow (RCOO)_2\, M + 2Na^+$$
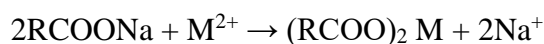
Insoluble soap

where   R =   long chain fatty acid like palmitic, oleic and stearic acid.

$M^{2+} = Ca^{2+}, Mg^{2+}$
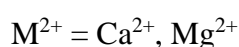
Common hardness producing salt present in water are chlorides, sulphates and bicarbonates of Calcium and Magnesium. i.e., $CaCl_2$, $CaSO_4$, $MgCl_2$, $MgSO_4$, $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$. Their quantity only decides the extent of hardness of water.

Classification of hardness of water: Hardness of water can be classified into two categories.

1. **Temporary hardness:** This is caused by the presence of dissolved bicarbonates of calcium and magnesium. Temporary hardness is mostly destroyed by simple boiling of water.
2. **Permanent hardness:** This is due to the presence of dissolved chlorides and sulphates of calcium and magnesium. Unlike temporary hardness, permanent hardness is not destroyed on boiling.

<u>Units of hardness:</u>

Hardness of water is expressed in terms of equivalents of $CaCO_3$. The choice of $CaCO_3$ in particular is due to

- $CaCO_3$ is the most insoluble salt which can be precipitated in water treatment.
- Molecular weight of $CaCO_3$ is 100 which is easy for calculations.

If water contains $CaCO_3$ alone the hardness is a measure of equivalents of $CaCO_3$. Usually, water contains some other salts. The amount of these salts is converted in to their $CaCO_3$ equivalent.

$$\text{CaCO}_3 \text{ equivalent} = \frac{\text{Weight of hardness producing salt}}{\text{Molecular weight of the salt}} \times \text{Molecular weight of CaCO}_3$$

(OR)

$$\text{The equivalents of CaCO}_3 = \frac{\text{Mass of hardness producing substance} \times \text{Equivalent Weight of CaCO}_3}{\text{Equivalent Weight of hardness producing substance}}$$

$$= \frac{\text{Mass of hardness producing substance} \times 50}{\text{Equivalent Weight of hardness producing substance}}$$

Parts per million (ppm): It is the number of parts of $CaCO_3$ equivalent hardness per million (10^6) parts of water.

Milligram per Litre (mg/L): It is the number of milligram of $CaCO_3$ equivalent hardness present per litre of water.

Boiler Feed Water:

Most of the water used in industry and power houses is in the form of steam. For steam generation, boilers are employed. The water fed into the boiler for the production of steam is called boiler feed water. Water used in boilers should be free from dissolved calcium and magnesium salts and dissolved gases such as oxygen (O_2) and carbon dioxide (CO_2).

Boilers are generally classified according to their pressures into three categories.

- Low-pressure boilers: Up to 15 kg/cm^2
- Medium-pressure boilers: 15 to 30 kg/cm^2
- High pressure boilers: Over 30 kg/cm^2

Disadvantages of using hard water in boilers:

If the boiler feed water contains impurities (or) if the hard water obtained from natural sources is fed directly to the boilers, the following troubles may arise:

1. Scale and Sludge formation
2. Boiler corrosion
3. Caustic embrittlement
4. Priming and foaming

1. Scale and Sludge formation in boilers:

In boilers, water evaporates continuously and the concentration of the dissolved salts increases progressively. If the precipitated matter is soft and slimy, it is called sludge. While the precipitate forms an adherent coating on the inner walls of the boiler, it is called scale.

Sludge Formation   **Scale Formation**
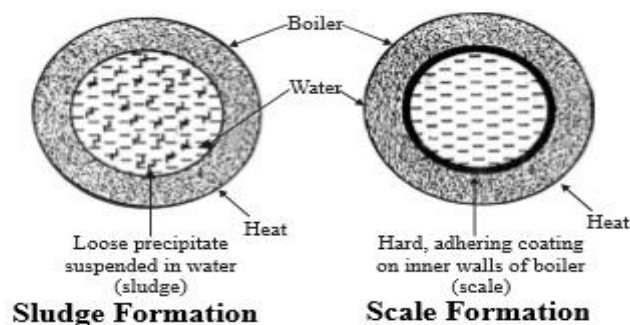
Scale is a hard, adherent coating forms on the inner walls of the boiler during steam generation. The main scale forming substances are $Ca(HCO_3)_2$ and $MgCl_2$, $CaSO_4$.
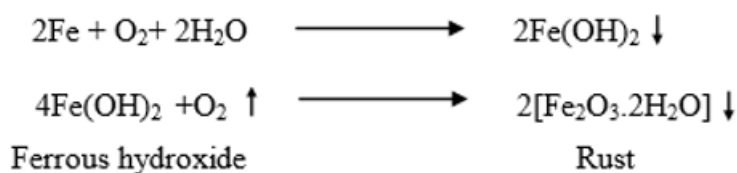
Disadvantages of scale and sludge: Wastage of fuel, Decrease in efficiency, Danger of Explosion.
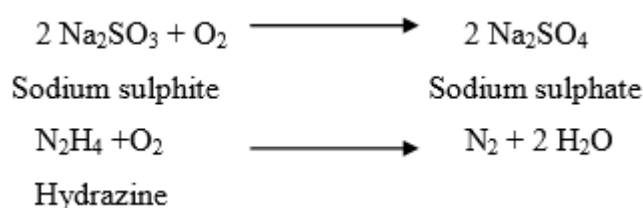
2. Boiler corrosion:

The decay of boiler material by its environment is termed as boiler corrosion. Corrosion in boilers is due to the presence of

(i)   Dissolved oxygen, (ii) Dissolved carbon dioxide, (iii) Dissolved salts

i) Dissolved Oxygen (DO): When water containing dissolved oxygen is heated in the boiler, the dissolved oxygen gets liberated and corrodes the boiler material as follows
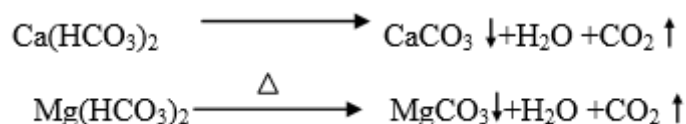
$$2Fe + O_2 + 2H_2O \longrightarrow 2Fe(OH)_2 \downarrow$$

$$4Fe(OH)_2 + O_2 \uparrow \longrightarrow 2[Fe_2O_3.2H_2O] \downarrow$$

Ferrous hydroxide   Rust

Removal of DO: Sodium sulphite and hydrazine are some of the chemicals used for removing oxygen.

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

Sodium sulphite   Sodium sulphate

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

Hydrazine

ii) Dissolved carbon dioxide: Dissolved carbon dioxide in water produces carbonic acid, which is acidic.

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

Carbon dioxide is also released inside the boiler, if water used for steam generation contains bicarbonates of Calcium and Magnesium

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$
$$Mg(HCO_3)_2 \xrightarrow{\Delta} MgCO_3 \downarrow + H_2O + CO_2 \uparrow$$

Removal of dissolved carbon dioxide: Carbon dioxide may be removed by adding calculated amount of NH_4OH into water.

$$2NH_4OH + CO_2 \longrightarrow (NH_4)_2CO_3 + H_2O$$

iii) Dissolved salts: 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.

$$Fe + 2HCl \longrightarrow FeCl_2 \downarrow + H_2 \uparrow$$
$$FeCl_2 + 2H_2O \longrightarrow Fe(OH)_2 \downarrow + 2HCl$$
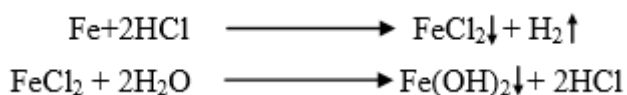
Thus presence of even a small amount of $MgCl_2$ will cause corrosion of iron to a large extent. **Removal of acids:** Corrosion by acids can be avoided by the addition of alkali to the boiler water.

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

3. Caustic embrittlement:

Caustic embrittlement is the phenomenon in which the material of a boiler becomes brittle due to the accumulation of caustic substances, such as sodium hydroxide and sulphuric acid. Caustic embrittlement is a type of boiler corrosion, caused by using highly alkaline water in the boiler. Boiler water usually contains a certain proportion of sodium carbonate, added for

water softening purposes. In high pressure boilers, Na_2CO_3 decomposes to give sodium hydroxide and carbon dioxide, and this makes the boiler-water "caustic".

$$Na_2CO_3 + H_2O \longrightarrow 2NaOH + CO_2 \uparrow$$

Alkaline water enters hair cracks, joints, rivets bends and when water evaporates it leaves NaOH behind in the cracks/spot. This NaOH when reacts with iron (usually boiler wall materials are iron alloys), it dissolves iron and yield sodium ferrate.

$$Fe + 2NaOH \longrightarrow Na_2FeO_2 + H_2$$
$$\text{Sodium Ferroate}$$
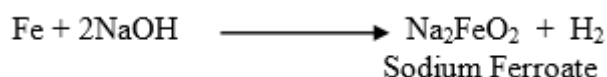
This causes embrittlement of boiler parts, particularly at bends, joints, rivets etc

Prevention: It can be prevented by

- Adding sodium sulphate (or) sodium phosphate as softening reagent instead of Na_2CO_3.
- Adding tannin, lignin to the boiler water which blocks the hair cracks.

4. Priming and Foaming (Carry Over Process):

Sometimes, steam may be associated with small droplets of water. Such steam containing liquid water is called wet steam. These droplets of water may carry with them some dissolved salts and sludge materials present in water. This phenomenon is called Carry Over Process. This occurs mainly due to Priming and Foaming. Priming and foaming usually occur together.

Priming: It refers the formation of wet steam by rapid boiling of water at the heating surface. Priming may be caused by

i) High steam velocity

ii) Very high water level in the boiler

iii) Improper boiler design

iv) Sudden boiling of water

Prevention: Priming can be controlled by controlling the velocity of steam, keeping the water level lower and good boiler design.

Foaming: The formation of stable bubbles above the surface of water is called foaming. These bubbles are carried along with steam leading to excessive priming. Foaming may be caused by presence of oil, grease in water and finely divided sludge particles.

Prevention: Foaming can be prevented by adding coagulants and anti-foaming chemicals.

Softening methods:

The process of removing hardness producing salts from water is known as softening of water. Softening of water can be done by the two ways

I. External treatment:

It involves the removal of hardness producing salts from the water before feeding into the boiler. The external treatment can be done by the following methods.
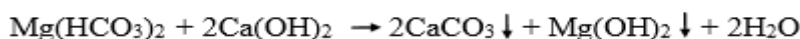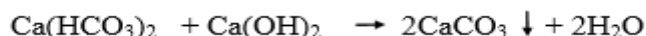
(a) Cold and hot lime-soda process, (b) Zeolite process, (c) Ion-Exchange process
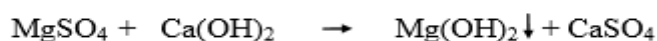
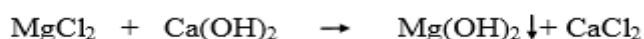**a) Cold and hot lime-soda process:**

The lime-soda process involves the chemical conversion of all the soluble hardness-causing salts by the addition of soda and lime into insoluble precipitates which could easily be removed by settling and filtration. In this process, water to be softened is treated with calculated amounts of lime $Ca(OH)_2$ and soda Na_2CO_3.

Functions of lime: Lime removes temporary hardness, permanent magnesium hardness, dissolved iron and aluminium salts, dissolved CO_2 and H_2S gases and free mineral acids present in water.
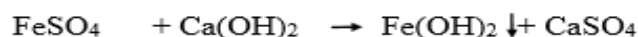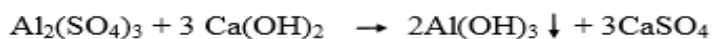
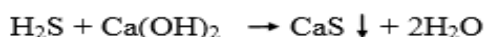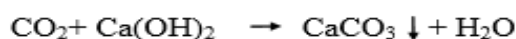1. *Removal of temporary calcium and magnesium hardness*

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

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

2. *Removal of permanent magnesium hardness*

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

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

3. *Removal of dissolved iron and magnesium salts*

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

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

$$2Fe(OH)_2 + H_2O + 1/2 O_2 \rightarrow 2Fe(OH)_3 \downarrow$$

4. *Removal of dissolved CO_2 and H_2S*

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

$$H_2S + Ca(OH)_2 \rightarrow CaS \downarrow + 2H_2O$$

5. *Removal of free mineral acid*

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

$$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2H_2O$$
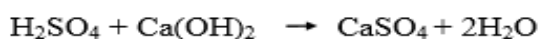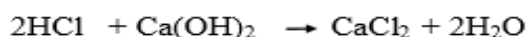
Functions of soda: During the removal of Mg^{2+}, Fe^{2+}, Al^{3+}, HCl and H_2SO_4 by lime, permanent calcium hardness is introduced in the water due to formation of calcium salts. The permanent hardness present in water is removed by soda.

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

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + Na_2SO_4$$
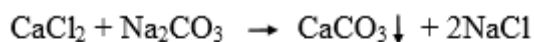
The process carried out at room temperature is called cold lime-soda process and that carried out at 94°-100°C is called hot lime-soda process.

1. Cold Lime-Soda process: In this method, water to be softened is treated with calculated quantities of lime and soda at room temperature. Small amounts of a coagulant such as alum, aluminium sulphate, sodium aluminate etc., are also added. The coagulant helps the finely divided precipitate formed in the process to flocculate.

Method: The mixture of water, calculated quantities of lime and soda and a small amount of a coagulant is fed from the top into inner chamber of a vertical circular tank (Figure). The chamber is provided with a vertical rotating shaft carrying a number of paddles to ensure vigorous stirring and continuous mixing of water with the chemicals added.


cold lime-soda softener.
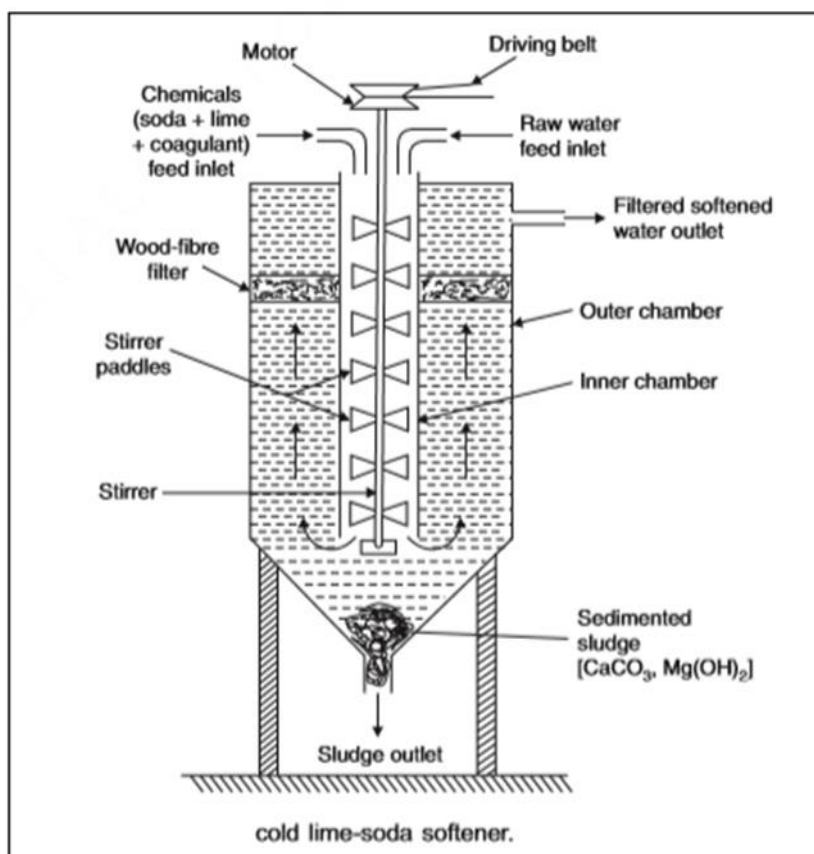
The chemical reactions take place and the hardness producing salts get converted into insoluble precipitates which accumulate in the form of a heavy sludge. The softened water rises upwards and is filtered by a wood-fibre filter and finally taken out from an outlet provided at the top of the outer cylinder. The heavy sludge settles down at the bottom of the outer chamber and is taken out through an outlet. The softened water obtained from this process contains calcium hardness about 40 ppm and magnesium hardness is brought down to almost zero.

2. Hot Lime-Soda process: This process is similar to cold lime-soda process. In this process, water is treated with the softening chemicals at a temperature of 94°-100°C. As the reaction takes place at high temperature, this process has some advantages.

- The precipitation reaction becomes almost complete
- The reaction takes place faster
- The sludge settles rapidly
- No coagulant is needed
- Dissolved gases are removed
- Viscosity of soft water is lower, hence filtered easily
- Residual hardness is low compared to the cold process

Hot lime-soda process consists of three parts:

- Reaction tank-in which complete mixing of the ingredients takes place
- Conical sedimentation vessel-where the sludge settles down
- Sand filter-where sludge is completely removed
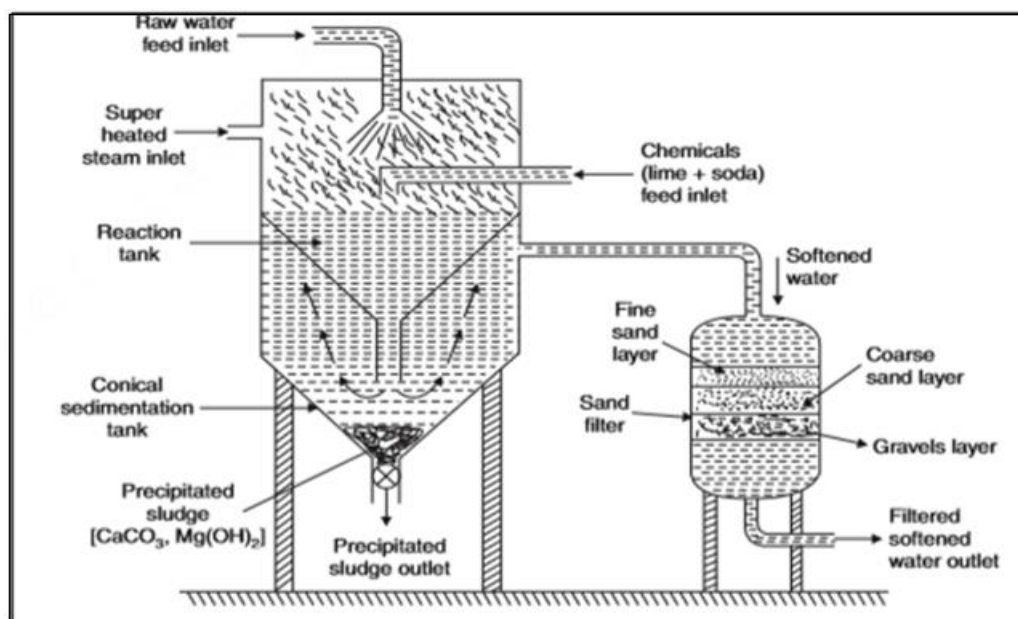
Raw water is fed from the top into the reaction tank where it is thoroughly mixed with calculated quantities of softening chemicals and is agitated with superheated steam. The reactions take place and water gets softened. The softened water containing sludge then enters into the sedimentation vessel where sludge settles down. The softened water rises up in the vessel, while precipitated sludge is taken out through an outlet provided at the bottom of the vessel. The softened water is then taken to a sand filter which ensures the complete removal of the sludge from softened water. The softened water obtained from this process contains a residual hardness of 15-30 ppm.

Advantages of lime-soda process:

- Economical
- Improves the corrosion resistance of the water and
- Mineral content of the water is reduced.
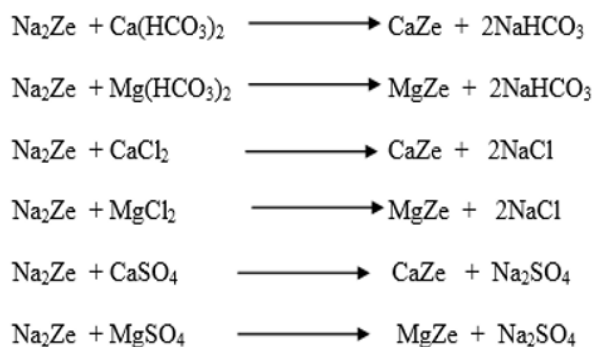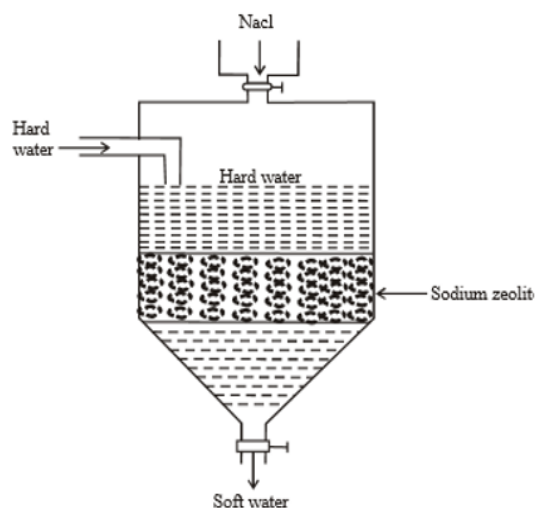
Disadvantages:

- Disposal of large amounts of sludge formed in the process poses problems.
- The treated water obtained by this process is not completely softened. Due to residual hardness, water is not good for high pressure boilers.
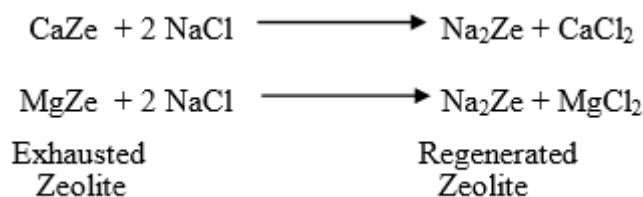
b) Zeolite (or) Permutit process:

Zeolites are naturally occurring hydrated sodium aluminium silicate, $Na_2O. Al_2O_3. xSiO_2 yH_2O$ where x = 2 to 10 and y = 2 to 6. The synthetic form of zeolite is known as permutit. Synthetic zeolite is represented by Na_2Ze. The sodium ions which are loosely held in Na_2Ze are replaced by Ca^{2+} and Mg^{2+} ions present in the water.
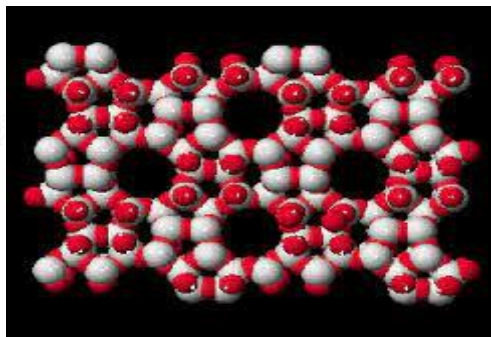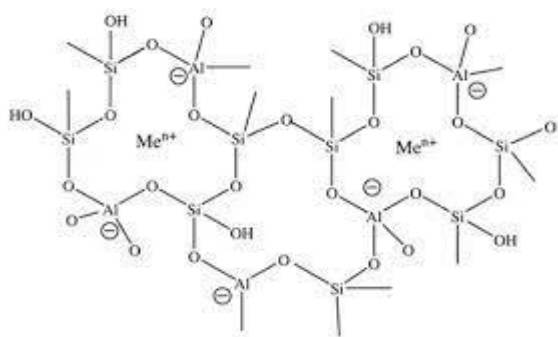
Process: In this process, the hard water is passed through a bed of sodium zeolite (Na_2Ze). The hardness causing ions (Ca^{2+}, Mg^{2+}) in hard water is replaced by loosely held sodium ions in zeolite bed. The outgoing soft water contains only sodium ions.

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

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

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

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

$$Na_2Ze + CaSO_4 \longrightarrow CaZe + Na_2SO_4$$

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

Regeneration: After the softening process, the zeolite is completely converted into calcium and magnesium zeolites and it gets exhausted. At this stage the hard water supply is stopped and the exhausted bed is regenerated by treating with a concentrated 10% brine (NaCl) solution.

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

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

Exhausted   Regenerated
Zeolite   Zeolite

Advantages:

- This process removes hardness up to 10ppm.
- Operational cost is less
- Requires less time for softening
- Maintenance and operation is easy

Limitations:

- The process exchanges only Ca^{2+} and Mg^{2+} ions with Na^+ ions. It does not remove the acidic ions like bicarbonate and carbonate ions. Water containing such ions is not much suitable for boilers as it may cause corrosion of boilers.
- Turbid water, if used clog the pores of the Zeolite bed, making it inactive.
- Highly acidic or alkaline water destroy the Zeolite bed.

c) Ion-exchange process:

In this method ion exchange resins are used as softening material. In this process cations like Ca^{2+}, Mg^{2+} and anions like Cl^-, SO_4^{2-} which are responsible for hardness are removed respectively by cation exchange resins and anion exchange resins.

Ion exchange resins are insoluble, cross linked, long chain organic polymers with a micro porous structure. The functional groups attached to the chains are responsible for the ion exchanging properties.

Cation exchange resins (RH^+): Resin containing acidic functional groups (-COOH, -SO$_3$H) are capable of exchanging their H^+ ions with cations of hard water.
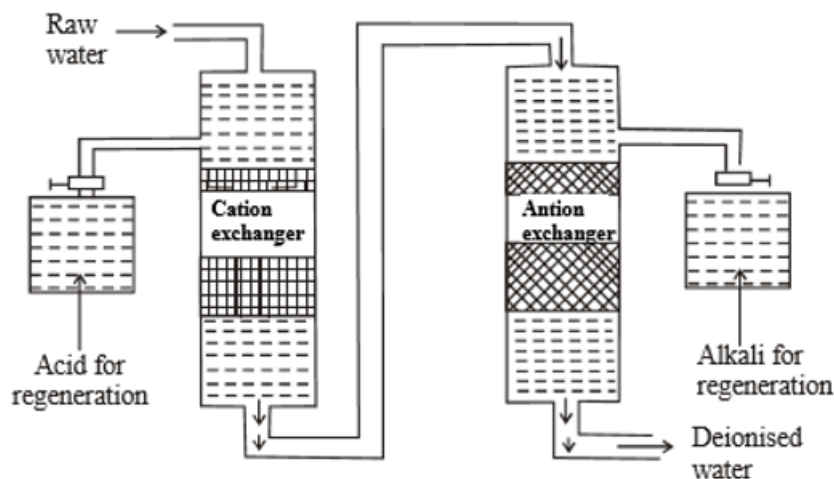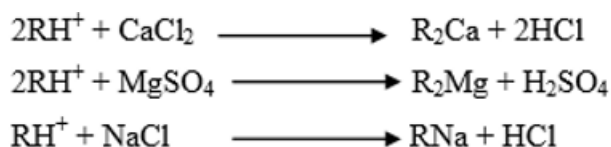
Ex: Sulphonated polystyrene
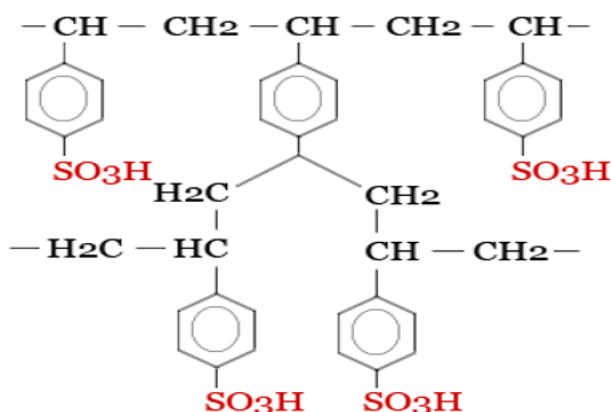
Anion exchange resins (ROH^-): Resins containing basic functional groups (-NH$_2$, -OH) are capable of exchanging their OH^- ions with the anions of hard water.

Ex: Cross-linked quaternary ammonium salts
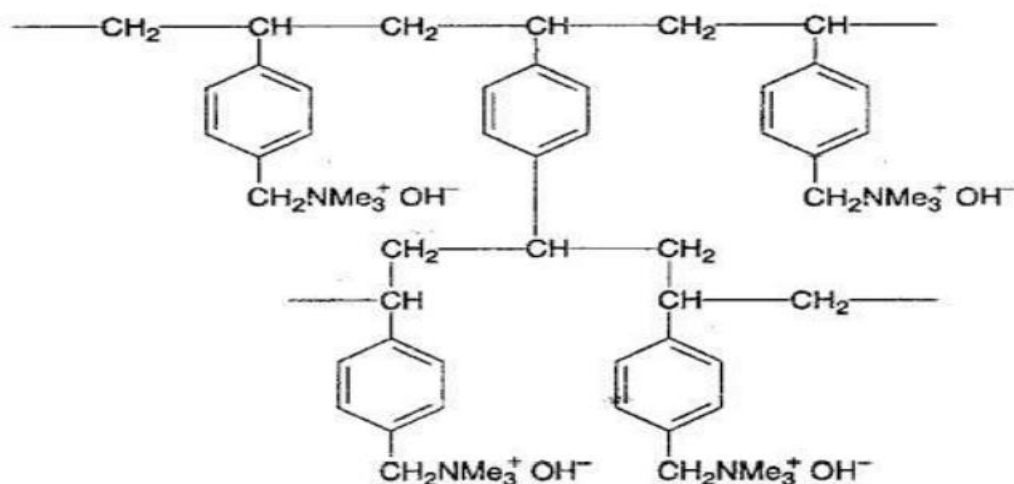
Process: The hard water first passed through a cation exchange column which absorbs all the cations like Ca^{2+}, Mg^{2+}, K^+, Na^+ etc., present in the hard water.

$$2RH^+ + CaCl_2 \longrightarrow R_2Ca + 2HCl$$
$$2RH^+ + MgSO_4 \longrightarrow R_2Mg + H_2SO_4$$
$$RH^+ + NaCl \longrightarrow RNa + HCl$$

The cation free water is then passed through an anion exchange column, which absorbs all the anions like Cl^-, SO_4^{2-} etc., present in the water.

$$2ROH^- + 2HCl \longrightarrow 2RCl + 2H_2O$$
$$2ROH^- + H_2SO_4 \longrightarrow R_2SO_4 + 2H_2O$$
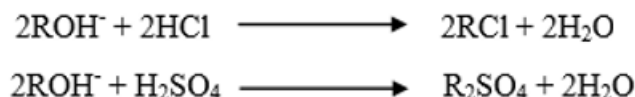
Thus the water coming out from the anion exchange is free from both cations and anions. This water is known as ion free water (or) deionised (or) demineralised water.

Regeneration: When the cation exchange column is exhausted, it can be regenerated by passing a solution of dil. HCl (or) dil.H_2SO_4.

$$R_2Ca + 2HCl \longrightarrow 2RH^+ + CaCl_2$$
$$R_2Mg + H_2SO_4 \longrightarrow 2RH^+ + MgSO_4$$
$$RNa + HCl \longrightarrow RH^+ + NaCl$$

When the anion exchange column is exhausted, it can be regenerated by passing a solution of dil. NaOH.

$$2RCl + 2NaOH \longrightarrow 2ROH^- + 2NaCl$$
$$R_2SO_4 + 2NaOH \longrightarrow 2ROH^- + Na_2SO_4$$
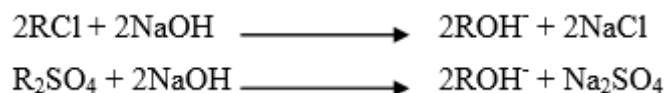
Advantages:

- The process can be used to soften highly acidic (or) alkaline water.
- It produces water of very low hardness (2ppm).

Disadvantages:

- The equipment is costly and more expensive chemicals are needed.
- If the water contains turbidity, the output is low due to clogging.
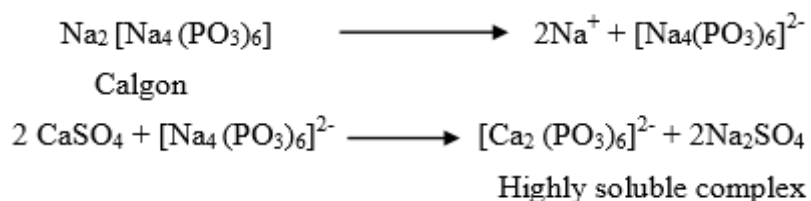
II. Internal treatment:

This process involves the adding of chemicals directly to the water in the boilers for removing dangerous, scale-forming salts which were not completely removed by the external treatment for water softening. This method is used to convert scale forming substances into sludge.

i) Colloidal conditioning: Scale formation can be avoided by adding organic substances like tannin, agar-agar (a gel), gelatin, glue etc., which get coated over on the scale forming precipitate, thereby, yielding non-sticky and loose deposits. This can be removed easily.

ii) Carbonate conditioning: Scale formation due to $CaSO_4$ in high pressure boilers can be avoided by adding Na_2CO_3 to the boiler water.

$$CaSO_4 + Na_2CO_3 \leftrightarrow CaCO_3 + Na_2SO_4$$
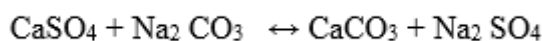
iii) Calgon conditioning: Calgon is sodium hexa metaphosphate, $Na_2[Na_4(PO_3)_6]$. In Calgon conditioning, the added Calgon forms soluble complex compound with $CaSO_4$, thereby it prevents the scale and sludge formation in water. Since the complex is highly soluble, there is no problem of sludge disposal.

$$Na_2[Na_4(PO_3)_6] \longrightarrow 2Na^+ + [Na_4(PO_3)_6]^{2-}$$
$$\text{Calgon}$$
$$2\,CaSO_4 + [Na_4(PO_3)_6]^{2-} \longrightarrow [Ca_2(PO_3)_6]^{2-} + 2Na_2SO_4$$
$$\text{Highly soluble complex}$$

iv) Phosphate conditioning: In high pressure boilers, $CaSO_4$, can be converted into soft sludge by adding excess of soluble phosphates.

$$3CaSO_4 + 2Na_3PO_4 \xrightarrow{pH = 9.5 - 10.5} Ca_3(PO_4)_2 + 3\,Na_2SO_4$$
$$\text{Soft sludge}$$
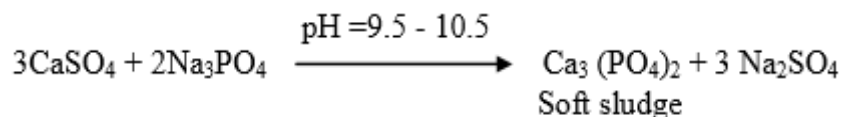
There are 3 types of phosphates employed for this purpose

1. Trisodium phosphate (Na_3PO_4, too alkaline)-used for too acidic water.

2. Disodium hydrogen phosphate (Na_2HPO_4, weakly alkaline)- used for weakly acidic water.

3. Monosodium dihydrogen phosphate (NaH_2PO_4, acidic)-used for alkaline water in boilers.

Numerical problems:

Lime requirements: Lime, i.e. $Ca(OH)_2$ is required for

- Temporary calcium hardness Ca $(HCO_3)_2$.
- Temporary magnesium hardness, $Mg(HCO_3)_2$. Lime requirement for temporary Mg-hardness is double that required for Ca-hardness.
- Lime eliminates permanent magnesium hardness but introduces an equivalent permanent calcium hardness.
- Lime also reacts with dissolved CO_2, iron and aluminium salts, free acids and introduces an equivalent Ca-hardness.
- NaCl, KCl and SiO_2. Do not contribute to hardness.

Since 100 parts of $CaCO_3$ is equivalent to 74 parts of $Ca(OH)_2$,

Lime required for softening,

$$= \left\{ \frac{74}{100} \times \text{[where Lime required]} \times \frac{\text{litres of waer}}{10^6} \times \frac{100}{\% \text{ purity}} \right\} Kg$$

$$= \frac{74}{100} \begin{bmatrix} \text{Temp. Ca hardness} + 2 \times \text{temp. Mg hadness} \\ + \text{perm. (Mg + Fe + 3Al) hardness} \\ \frac{1}{2} HCl + H_2SO_4 \\ \text{all in terms of } CaCO_3 \text{ equivalents} \end{bmatrix} \times \frac{\text{litres of waer}}{10^6} \times \frac{100}{\% \text{ purity}} \quad Kg$$

Soda requirement:

Soda is required for eliminating salts of calcium other than temporary hardness. Since 100 parts of $CaCO_3$ is equivalent to 10^6 parts of sodium carbonate.

Soda required for softening,

$$= \left\{ \frac{106}{100} \times \text{[where Soda required]} \times \frac{\text{litres of waer}}{10^6} \times \frac{100}{\% \text{ purity}} \right\} \text{Kg}$$

$$= \frac{106}{100} \begin{bmatrix} \text{Perm. Ca hardness + Perm. (Me + Fe + 3Al) hardness} \\ \frac{1}{2} \text{HCl} + \text{H}_2\text{SO}_4 \\ \text{all in terms of CaCO}_3 \text{ equivalents} \end{bmatrix} \times \frac{\text{litres of waer}}{10^6} \times \frac{100}{\% \text{ purity}} \text{Kg}$$

Problems:

(1) Calculate amount of lime and soda required for softening of 50,000 litres of water containing following salts. (Purity of lime = 95% and soda = 93%)$CaCO_3$ = 3.5 mg/lit, Mg $(HCO_3)_2$ = 29.2 mg/lit, Mg $(NO_3)_2$ = 29.6, $MgSO_4$ = 36.0 ms/lit, $CaSO_4$ = 27.2 mg/lit, $MgCl_2$ = 47.5 mg/lit, SiO_2 = 105 mg/lit, NaCl = 52 mg/lit, H_2SO_4 = 9.8 mg/lit.

Calculations for CaCO₃ equivalents:

Impurity	Amount	Mol.wt.	$CaCO_3$ equts. $= \dfrac{Amt \times 100}{Mol.wt}$
$CaCO_3$	35.0	100	35
$Mg(HCO_3)_2$	29.2	146	20
$Mg(NO_3)_2$	29.6	148	20
$MgSO_4$	36.0	120	30
$MgCl_2$	47.5	95.2	50
$CaSO_4$	27.2	136	20
H_2SO_4	9.8	98	10
SiO_2			
NaCl		Do not contribute to hardness	

$$\text{Amt. of lime required} = \frac{74}{100} [\text{Temp Ca}^{+2} + 2 \times \text{Temp Mg}^{+2} +$$

$$\text{Perm Mg} + \text{H}_2\text{SO}_4] \times 50,000 \times \frac{1}{10^6} \times \frac{100}{95}$$

$$= \frac{74}{100} [35 + 2 \times 20 + 100 + 10] \, 50,000 \times \frac{1}{10^6} \times \frac{100}{95}$$

$$= 7.205 \text{ kg}$$

$$\text{Soda required} = \frac{106}{100} [\text{Perm (Ca + Mg)} + \text{H}_2\text{SO}_4 \times 50,000 \times \frac{1}{10^6} \times \frac{100}{93}]$$

$$= \frac{106}{100} [20 + 100 + 10] \times 50,000 \times \frac{1}{10^6} \times \frac{100}{93}$$

$$= 7.408 \text{ kg}$$

6. Calculate the quantity of lime and soda required for softening 50,000 liters of water containing the following salts per liter: $Ca(HCO_3)$ = 8.1mg ; Mg $(HCO_3)_2$ = 7.5mg ; $CaSO_4$ = 13.6 mg; $MgSO_4$ = 12.0 mg; $MgCl_2$ = 2.0 mg; and NaCl = 4.7 mg.

Ans 1.0134 kg (Lime) ; 0.9068 kg(Soda).

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

Ans. 166.5 ppm or mg/L (Lime): nil (Soda).

(2) Calculate amount of lime and soda required for softening of 20,000 litres of water containing following salts in ppm. $CaSO_4 = 13.6$, $Ca(HCO_3)_2 = 16.2$, $MgCO_3 = 16.8$, $HCl = 36.5$, $AlCl_3 = 13.5$, $KCl = 5.1$

Calculations for CaCO$_3$ equivalents.

Impurity	Amount	Mol.wt.	CaCO₃ equts
$CaSO_4$	13.6	136	10
$MgCO_3$	16.8	84	20
$AlCl_3$	13.5	133.5	10
$Ca(HCO_3)_2$	16.2	162	10
HCl	3.65	36.5	10
KCl	5.1	Do not conibute hardness.	
Reaction →	$2\,AlCl_3 + 3\,Ca(OH)_2$	→	$2Al(OH)_3\downarrow + 3CaCl_2$

Amount of lime required $= \dfrac{74}{100}$ [Temp Ca + 2 (Temp Mg) + Perm 1.5 Al + 1/2 HCl]

$$\times\,20{,}000 \times \dfrac{1}{10^6}$$

$$= \dfrac{74}{100}\,[10 + 2\times 20 + 1.5 \times 10 + 1/2 \times 10] \times 20{,}000 \times$$

$$\dfrac{1}{10^6} = 1.036\ \text{kg}$$

Amount of soda required $= \dfrac{106}{100}$ [Perm Ca⁺ Perm (1.5 Al) + 1/2 HCl]

$$\times\,20{,}000 \times \dfrac{1}{10^6}$$

$$= \dfrac{106}{100}\,[10 + 1.5 \times 10 \times 1/2 \times 10] \times 20{,}000 \times \dfrac{1}{10^6}$$

$$= 0.636\ \text{kg}$$

3 1000 litres of hard H_2O is softened by zeolite process. The zeolite was regenerated by passing 20 litres of sodium chloride solution containing 1500 mg/lit. of NaCl. Calculate hardness of H_2O.

Solution:

20 litres of NaCl contain $= 1.5 \times 20 = 30$ gm of NaCl
We have to convert it in terms of $CaCO_3$ equivalent.

$$2\ \text{NaCl} = \text{CaCO}_3$$

$$2 \times 58.5\ \text{gm} = 100\ \text{gm}$$

$$58.5 = 50\ \text{gm}$$

Thus, 30 gm of NaCl equivalent to $30 \times \dfrac{50}{58.5} = 25.64$ gm of $CaCO_3$

10.00 litres of H_2O contains 25.64 gm of NaCl as $CaCO_3$

1 litre of H_2O contains $\dfrac{25.64}{1000} = 0.02564$ gm of NaCl as $CaCO_3$

Thus, 1 litre water contains $= 0.02564 \times 1000$ mg of NaCl as $CaCO_3$

$$= 25.64\ \text{mg 1 litres or ppm}$$

4 By passing 50 litres of NaCl solution containing 250 gm/litre of NaCl, a exhaust zeolite softener bed was regenerated. Calculate the litres of hard H_2O sample (hardness equal to 200 ppm as $CaCO_3$) which can be softened by regenerated bed of zeolite softener.

Solution:

First, we have to calculate total NaCl in terms of $CaCO_3$ equivalent, used for the regeneration of zeolite.

50 litres of NaCl solution contain = 50×250 = 12,500 gm of NaCl

$$CaCO_2 = 2\ NaCl$$

$$100 = 2(58.5)$$

$$50 = 58.5$$

$\therefore$ $CaCO_3$ equivalent would be = $12,500 \times \dfrac{50}{58.5}$ = **10,683.7** gm

As the hardness is 200 ppm, i.e., 200 mg/lit. of $CaCO_3$

0.2 gm/lit. of $CaCO_3$

10,683.7 gm will be present in ....

$$\dfrac{10,683.7}{0.2} = 53,418.80 \text{ lit. of water.}$$

The zeolite bed can soften 53,418.80 lit. of H_2O.

5. How many litres of 10% Brine solution will be required to regenerate an exhausted zeolite bed after softening of 10 litres of hard water of 750 ppm hardness.

Solution:

Hardness of water 750 ppm

Total quantity 10 litres = 750×10

= 7500 mg of $CaCO_3$ equivalent

50 gm $CaCO_3$ =   58.5 g NaCl

7.5 g of $CaCO_3$ equivalent   =   ?

$(7.5/50)X\ 58.5 = 8.775$ g of NaCl

NaCl used is 10%, i.e., 10 gm/100 ml

10 g NaCl = 100ml

8.775 g of NaCl =   ?

$(8.775/10)\ X\ 100 = 87.75$ ml of NaCl

$\therefore$ Volume of NaCl required = 87.75 ml

Water for drinking purposes:

* Drinking water, also known as potable water, is water that is safe to drink or use for food preparation.

* The amount of drinking water required to maintain good health depends on physical activity level, age, health-related issues, and environmental conditions.

* The human body contains 50 % to 78 % of water according to the size of the body. Humans need to drink 7 litres of water every day to avoid dehydration.

* It plays an important role in digestion and other biological processes that occur in living organisms.

* It plays an important role in maintaining the pH of the body.

* It helps in regulating the body temperature.

* Water provides the necessary cooling effect to the body.

* Water removes harmful toxins from the body through sweat and urination.

* As per Indian standards, safe drinking water should meet the following requirements for water quality.

As per Indian Standards (IS: 10500-1983)

Sr. No.	Characteristics	Desirable limit
1.	pH value	6.5 to 8.5
2.	Odour	unobjectionable
3.	Colour (Hazon unit), maximum	10
4.	Test	Agreeable
5.	Turbidity (NTU) maximum	5
6.	Total dissolved solids (TDS) ppm	500
7.	Total hardness maximum as ($CaCO_3$ ppm)	300
8.	Calcium (ppm)	75 – 200
9.	Magnesium (ppm)	30 – 150
10.	Iron as Fe (ppm)	0.1 – 1.0
11.	Chloride (as Ci) ppm	200 – 600
12.	Nitrate (as NO_3^-) ppm	45
13.	Sulphate as (SO_4) ppm	200 – 400
14.	Phosphate as (PO_4) ppm	10 – 15
15.	Organic matter (ppm)	0.2 – 1.0

Purification:

- Water purification means freeing water from any kind of contaminants.
- Impurities are removed from water by sedimentation, filtration, chlorination etc.
- Various salts and metals cause hardness in water. Hardness may be removed by boiling, by adding sodium carbonate and lime or by filtering through natural or artificial zeolites.
- Water is also purified by processes such as sterilization and disinfection, reverse osmosis, electrolysis, chlorination etc.

Disinfection and sterilization:

- Disinfection and sterilization are the two common methods of killing or inhibiting the growth of microorganisms.
- Microbes can cause a number of diseases in humans and animals. They are also responsible for food spoilage. Therefore, it is necessary to kill or inhibit their growth. This is achieved by sterilization or disinfection.
- However, both these processes are based on different principles.

Sterilization:

- Sterilization is a process mainly used to kill all forms of microorganisms.
- This process is carried out to maintain a germ-free environment.
- It is usually done through combinations of heat, irradiation, filtration, high pressure etc.

Disinfection:

- Disinfection is a chemical process used to eliminate or inhibit the growth of bacteria and other pathogens that may cause infectious diseases in humans and animals.
- Disinfectants are the chemical solutions used to make substance infection-free. These include alcohol, iodine, chlorine, etc.

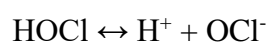*Similarities between disinfection and sterilization:*

- Both are used to decontaminate objects and surfaces
- Both processes can kill harmful microbes.

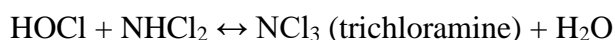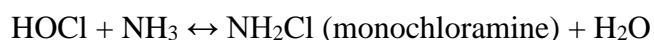*Difference between disinfection and sterilization:*

Disinfection	Sterilization
In this, the number of harmful microbes is minimized to a negligible level.	In this, the medium is made completely free from all microbes.
It kills only vegetative cells and not the spores.	It kills both vegetative cells and spores.
Wounds are disinfected – with agents such as hydrogen peroxide or rubbing alcohol.	Wounds cannot be sterilized – as it may kill surrounding healthy cells.
Disinfection only reduces the effect of microbes.	Sterilization completely rids microbes from the surface
Chemical methods are used for disinfection	Combination of heat, irradiation, high pressure, chemical and physical methods are used for sterilization
Phenol, alcohol, chlorine, iodine are some of the disinfecting agents.	High temperatures, steam, radiation, filtration are some of the sterilization techniques.
Only adequate cleanliness	Extreme cleanliness
Used in daily life.	Used primarily for medical and research purposes.
For eg., pasteurization, disinfecting urinals, etc.	For eg., sterilization of instruments used during surgery by autoclaving.

Chlorination:

- Chlorination is one of many methods that can be used to disinfect water.
- Water chlorination is the process of adding small quantities of chlorine or chlorine compounds to water.
- This method is used to kill bacteria, viruses and other microbes in water. In particular, chlorination is used to prevent the spread of waterborne diseases such as cholera, typhoid.
- Chlorine hydrolyses in water to form hypochlorous acid (HOCl) and further produce hypochlorite ion (OCl$^-$). The HOCl and OCl$^-$ together are known as free available chlorine.
- If Ammonia is also present in water, chlorine reacts to form chloramines (monochloromine, dichloramine and trichloramine). The chlorine existing in the form of chloramines is called as combined available chlorine.
- Total = Free chlorine + Combined chlorine
- Free chlorine: hypochlorous acid + hypochlorite ion

$$HOCl \leftrightarrow H^+ + OCl^-$$

- Combined chlorine (chloramines):

$$HOCl + NH_3 \leftrightarrow NH_2Cl \text{ (monochloramine)} + H_2O$$

$$HOCl + NH_2Cl \leftrightarrow NHCl_2 \text{ (dichloramine)} + H_2O$$

$$HOCl + NHCl_2 \leftrightarrow NCl_3 \text{ (trichloramine)} + H_2O$$

- These resulting chlorine compounds in water interfere with certain enzymes in the bacterial wall forming a toxic chloro-compounds thus destroying bacteria completely.

- The killing power of chlorine as disinfectant is proportional to the product of contact period and chlorine concentration in water.

- Chlorine can be applied by any of the following methods:
  - As dry chlorine gas
  - As chlorine liquid/ solution
  - In powder form (bleaching powder, $CaO(Cl)_2$/sodium hypochlorites, $NaOCl$)

- Too little chlorine is ineffective and too much chlorine cause taste and odours. So the amount of chlorine required to be added should be determined. It can be determined in the laboratory.

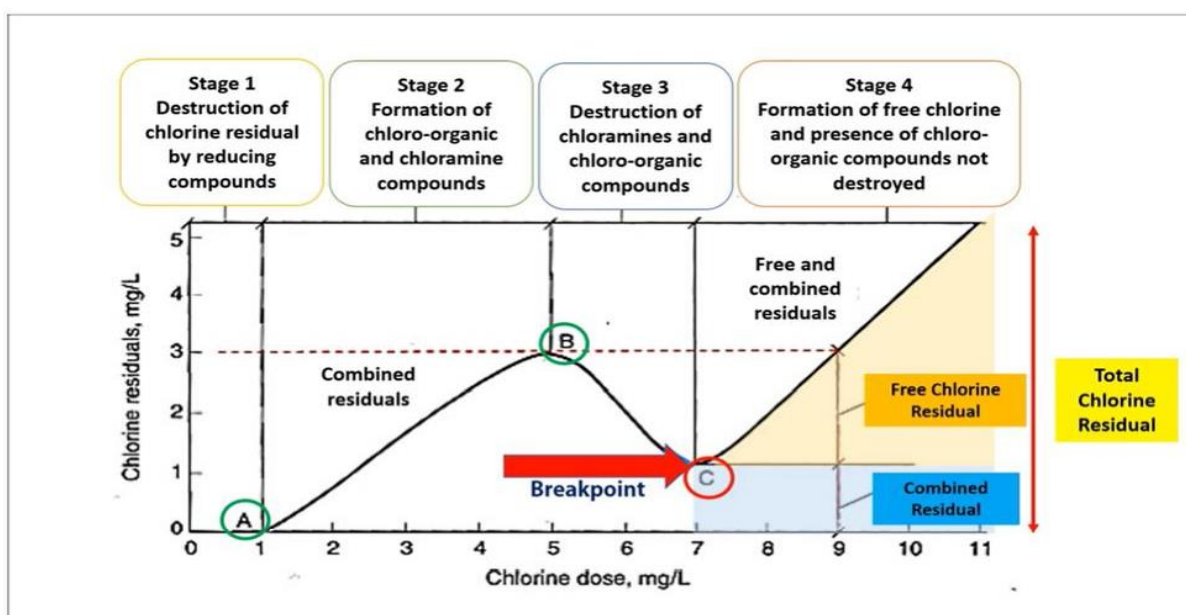- Chlorine dosage can be calculated with help of following formula:

Dosage in kg. of chlorine $= \dfrac{\text{volume of water in lit.X dosage in mg/L}}{1,000,000}$

The typical amount of chlorine gas required for water treatment is 1-16 mg/L of water.
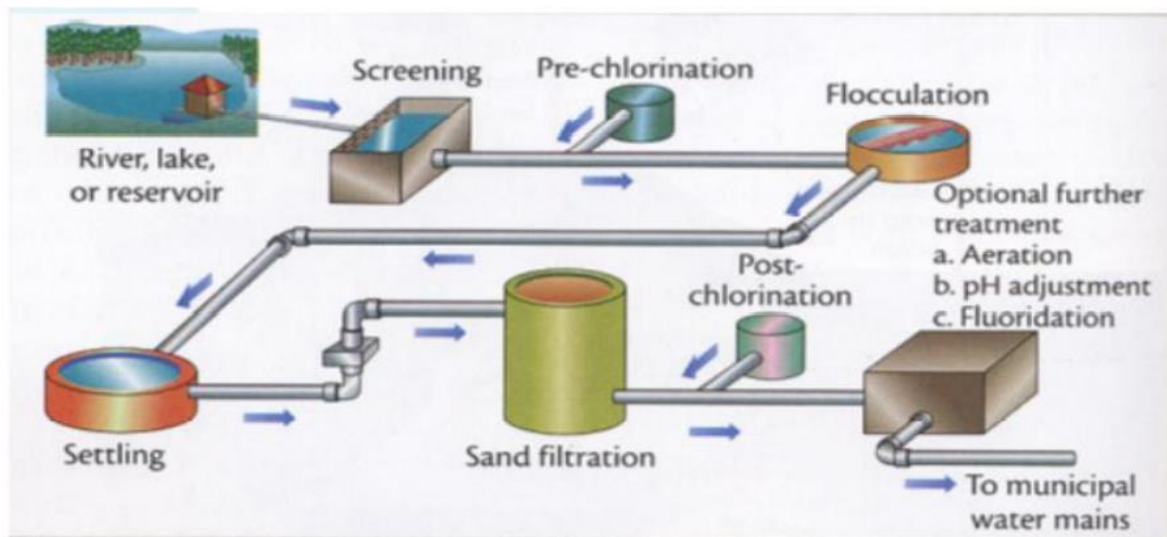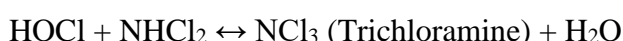

Break point chlorination:

- The graph below shows what happens when chlorine (either chlorine gas or a hypochlorite) is added to water.

- **Stage I (up to A):** Chlorine reacts with reducing compounds in the water, such as hydrogen sulfide, Fe^{2+}, Mn^{2+}, complete oxidize all these reducing compounds. No residual chlorine.

- **Stage II (A to B):** As the applied chlorine increases, chlorine reacts with organic impurities and nitrogen compound like ammonia naturally found in the water, to form chloro-organics and chloramines (combined chlorine residuals). The process would be stopped at point B.

$$HOCl + NH_3 \leftrightarrow NH_2Cl \text{ (Monochloramine)} + H_2O$$

$$HOCl + NH_2Cl \leftrightarrow NHCl_2 \text{ (Dichloramine)} + H_2O$$

$$HOCl + NHCl_2 \leftrightarrow NCl_3 \text{ (Trichloramine)} + H_2O$$

  Chloramines are an effective disinfectant against bacteria but not against viruses.

- **Stage III (B to C):** When the dose of chlorine increases, destruction of chloro-organics and chloramines take place. Chloramines are broken down and converted in to nitrogen gas which leaves the system.

$$2NH_3 + 3Cl_2 \rightarrow N_2 + 6HCl$$

$$2NH_2Cl + HOCl \rightarrow N_2 + 3HCl + H_2O$$
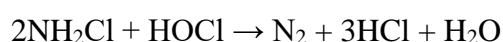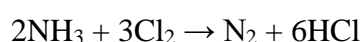
- **Breakpoint (Point C):** Finally, the water reaches the breakpoint, shown at point C. The breakpoint is the point at which the chlorine demand has been totally satisfied - the chlorine has reacted with all reducing agents, organics, and ammonia in the water and

further residual chlorine acts as disinfectant to destroy the pathogens. The breakpoint chlorination confirms the destruction of organic compounds and disease producing micro-organisms.

- **Stage IV (Beyond C):** When more chlorine is added beyond the breakpoint, the chlorine reacts with water and forms hypochlorous acid in direct proportion to the amount of chlorine added. Free available residuals formed and some chloro-organics still remain as combined residuals. Total residual chlorine [90% free residual chlorine (HOCl & OCl$^-$) and 10% combined chlorine] acts as disinfectant.

- Advantages:
  - It oxidizes completely organic compounds, ammonia and other reducing compounds.
  - It removes colour, odour and taste in water, due to organic matter.
  - It destroys completely all the disease-producing bacteria.
 - It prevents the growth of any weeds in water.

Reverse Osmosis:

- When two solutions of unequal concentrations are separated by a semi permeable membrane, flow of solvent takes place from dilute to concentrate sides, due to osmosis.
- Semi-permeable is defined as the membrane being permeable to some material but impermeable to others.
- The membrane will allow small molecules and ions to pass through it but acts as a barrier to larger molecules or dissolved substances.
- Let's assume the membrane is permeable to water, but not to salt.
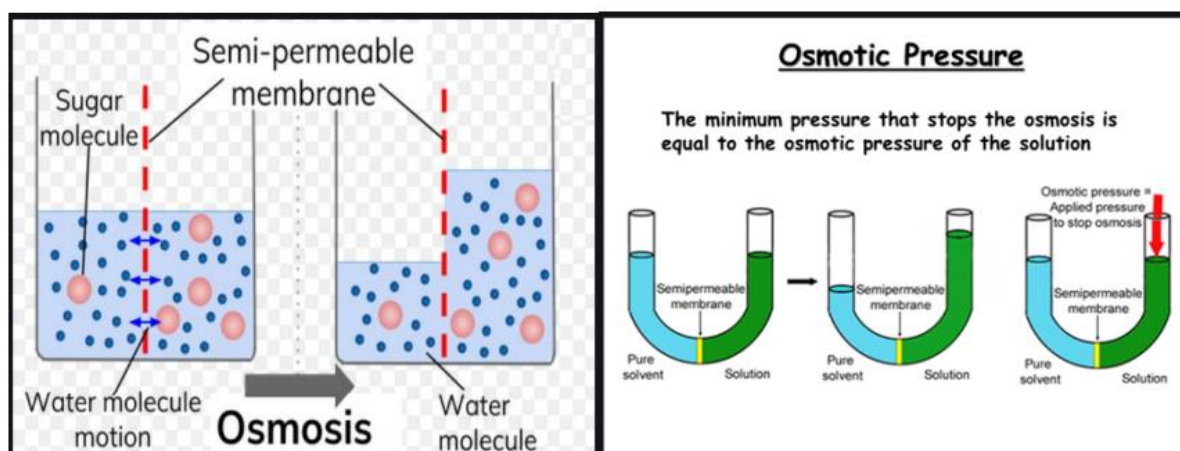
- Osmotic pressure is the minimum pressure which needs to be applied to a solution to prevent the inward flow of its pure solvent across a semipermeable membrane.

- If a pressure higher than the osmotic pressure is applied on the solution, the solvent (pure water) will flow reverse, higher concentration solution to low concentration solution across the membrane. This is the principle of reverse osmosis.

- Thus in reverse osmosis method, pure solvent is separated from its contaminants, rather than removing contaminants from the water.

- In reverse osmosis process, pressure is applied to the sea water or impure water to force the pure water content of it out the semi-permeable membrane, leaving behind the dissolve solids. The principle of reverse osmosis is applied for treating saline/sea water.

- The membrane consists of very thin film of cellulose acetate. However, more recently superior membranes made of polymethacrylate and polyamide polymers have come into use.
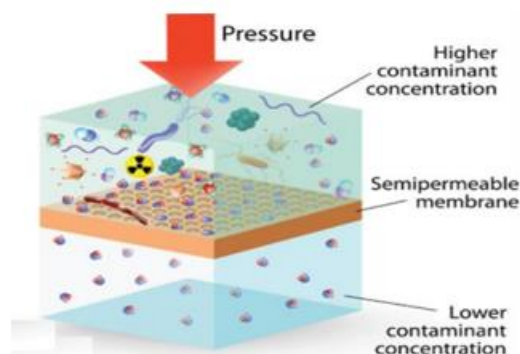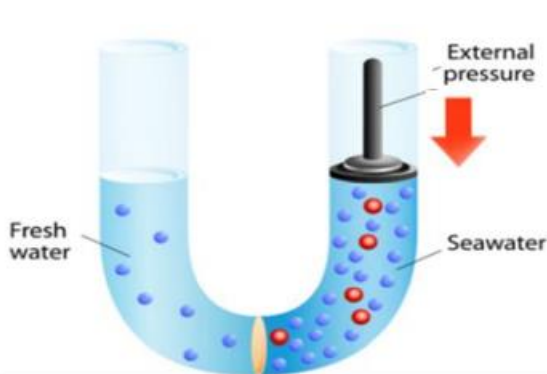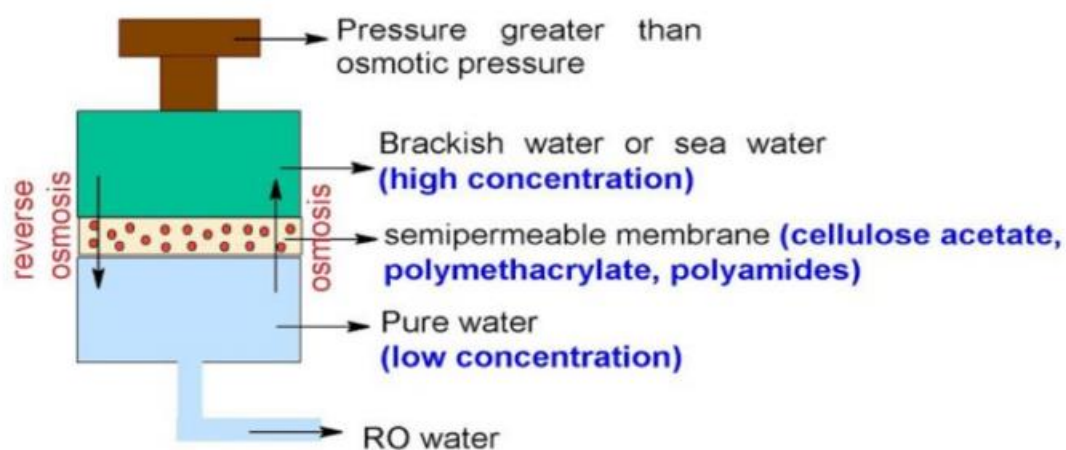
- Advantages:
  - Removes ionic, non-ionic, colloidal and high molecular weight organic matter.
  - The life time of membrane is quite high, about 2 years.
  - The maintenance cost is entirely on the replacement of the semi permeable membrane.
  - Due to low capital cost, simplicity, low operating cost and high reliability, the reverse osmosis is become more popular.

Electro dialysis:

- Electro dialysis is an electrochemical process whereby electrically charged particles (ions), are transported through ion-selective membranes by applying an electric field.

- In order to separate salts from a solution, ion-selective membranes, through which only one type of ions can permeate are arranged in the solution.

- When a salt solution is under the influence of an electric field the charge carriers in the solution come into motion. This means that the negatively charged anions migrate towards the anode and the positively charged cations migrate towards the cathode.

- The negatively charged particles (anions) can pass through an anion exchange membrane on their way to the anode but are retained by the cation exchange membrane. Similarly, positively charged particles (cations) can pass through cation exchange membrane on their way to the cathode but are retained by the anion exchange membrane.

- This separation results in a concentration of electrolytes in the concentrate loop and a depletion of charge carriers in the dilute loop.

- So, in one compartment of the cell, the salt concentration decreases while in the adjacent compartment it increases. Thus, we get alternative stream of pure water and concentrated water.

- Electrodialysis membranes are comprised of polymer chains - styrene-divinyl benzene made anionic with quaternary ammonium groups and made cationic with sulphonic groups.

- Applications:
    - Nitrogen removal from drinking water (nitrate, ammonium)
    - Relatively low energy consumption
    - The product water needs only limited pre-treatment.
    - Suitable for separating non-ionized components from ionized components.
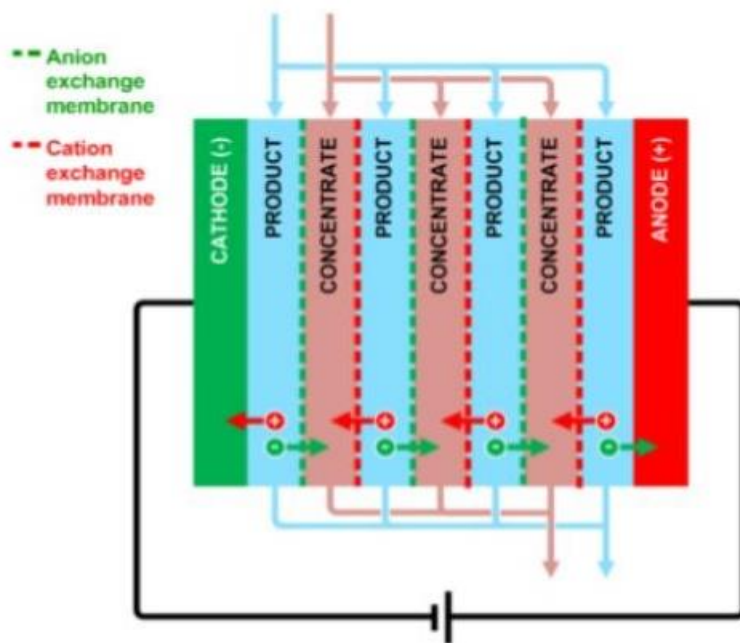
• Water flows parallel to the membranes.
• Positive ions flux through cation exchange membranes towards negatively charged cathode.

• Negative ions flux through anion exchange membranes towards positively charged anode.

• Water does not flux through the membranes.
• Product stream becomes purer while concentrate stream becomes more concentrated with ions.