WATER TECHNOLOGY

Introduction

- For existence of all living beings (animals, humans, plants) water is very important.
- Almost all human activities, domestic, agricultural and industrial purpose water is used.
- Without food, human can survive for a number of days, but water is such an essential that without it one cannot survive
- Although water is nature's most abundant compound but only less than 1% of the world's water resources are available for ready use.

Importance of water

It is an important engineering material

- In steam generation
- Coolant in power and chemical plants
- water widely used in Steel, plastic, atomic energy and textile industries.
- Other fields such as drinking, bathing, sanitary, washing irrigation etc.

- The major cationic species are **Sodium (Na^+)**
- The major anionic species are **Chlorides (Cl^-)**
- The major cationic species are **Calcium (Ca^{2+})**

- The major anionic species are
  - **Carbonates,**
  - **Sulphates and**
  - **Silicates.**
- Fresh water contains lesser amount of dissolved salts than Oceans & Seas.

About 97% of water is present in Oceans. It's salty hence it can't be used.

Oceans & Sea Water

Of the remaining 3%, 2% is locked in the form of ice caps and glaciers. It is not available for human

Ice Caps & Glaciers

Only 1% of water is pure water in liquid form, of which 0.9% is present as

Ground Water

Balance 0.1% of water is available as surface water in rivers, lakes, steams, reservoirs.

River Water

Where does the water come from?

I. Surface waters:

River water: This fed by rain water. Water flows over surface, dissolves salts of soil and suspended organic matter.

Lake water: Contain much lower amount of dissolved salts and organic matter.

Sea water: Most impure form of water. River water throws salts and matter. Continuous evaporation makes sea water more concentration.

II. Underground water: water percolates into earth. During its journey it comes contact with minerals get concentrated.

How is the Available Water Used in the World?

Agriculture Sector

The 70% of water is used for irrigation.

Industrial things

The 20 % of water is used for industrial things.

Examples: Power plants,

Oil refineries

Power Generation

Hydropower is the production of electrical power through the use of the gravitational force of falling or flowing water.

Domestic use

The 10 % of water is used for domestic uses.

- Drinking
- Bathing
- Cooking
- Sanitation
- Gardening

Other Uses are

- Recreation purpose
- Creating Artificial Environment

Impurities in water

Impurities in water classified into following types.

1. **Dissolved impurities:** Dissolved salts like carbonates, bicarbonates, chlorides and sulphates of Ca, Mg, Fe and Na. Dissolved gasses like O2 and CO2.
2. **Suspended impurities:** inorganic impurities like clay and sand, organic impurities like oil globules, animal and plant matter.
3. **Colloidal impurities:** products from organic waste, finely divided silica and clay.
4. **Microorganisms:** Bacteria, fungi and algae.

HARDNESS OF WATER

- Hardness of water is characteristic which prevents the lathering of soap. (or) The soap consuming capacity of water sample.
- When hard water when treated with soap do not produces lather, but forms insoluble precipitate which do not possess any detergent action.
- This is due to presence of certain salts of calcium, magnesium and other heavy metals dissolved in water .

- **Na - stearate + H_2O → NaOH + Stearic acid**
  Stearic acid + Na-stearate → formation of lather

- **2 Na- stearate + Hard water → $(\text{Stearate})_2\text{Ca}\downarrow + 2\text{Na}^+$**

Soft water

- Water that gives lather with soap easily and readily is known as Soft water.
- Soft water does not contain dissolved salts.
- In soft water cleaning quality of soap is not depressed and so soap not wasted.
- Less fuel are required for cooking in soft water.

Hard water

- Water which does not give lather with soap solution, but forms a white scum is called hard water.
- Hard water contains dissolved Ca and Mg salts.
- Cleaning capacity of soap depressed and lot of soap wasted.
- The boiling point of water elevated. Consequently, more fuel required for cooking.

Typical reactions of soap (sodium stearate) with Calcium chloride and magnesium sulphate:

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

Calcium Stearate

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

Magnesium Stearate

TYPES OF HARDNESS

I. Temporary hardness:

- It is caused by the presence of dissolved bicarbonates of calcium and magnesium and carbonates of Iron.
- Temporary hardness is easily removed by boiling, on boiling bicarbonates are decomposed into insoluble carbonates or hydroxides.

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

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

- It is also known as carbonate (or) alkali hardness.

II. Permanent hardness

- It is caused by the presence of dissolved chlorides, and sulphates of the calcium and magnesium and iron.
- The dissolved salts are $CaCl_2$, $MgCl_2$, $CaSO_4$, $MgSO_4$, $FeSO_4$, Al_2,$(SO_4)_2$ etc.
- Unlike temporary hardness, permanent hardness is not destroyed on boiling.
- It is also known as non carbonate (or) non alkaline hardness.
- The difference between the total hardness and alkaline hardness give the non-alkaline hardness.

Degree of Hardness:-

- The hardness of water is expressed in terms of calcium carbonate equivalents.
- The weights of different salts that causing hardness are converted to weight equivalent to that of calcium carbonate.
- The reason for choosing $CaCO_3$ as standard for reporting hardness is ease in calculations as its molecular weight is exactly 100 and is insoluble in water.

$$\text{Eq.of } CaCO_3 = \frac{\textit{mass of hardness causing salt}}{\textit{mol.wt of hardness causing salt}} \times 100$$

$$= \text{mg (or) ppm}$$

Units for Hardness:-

Parts per million(ppm):-The number of parts by weight of $CaCO_3$ present per million (10^6) parts by weight of water.

1ppm = 1 part of $CaCO_3$ equivalents in 10^6 parts of water.

Degree Clarke(°Cl):- Parts of $CaCO_3$ equivalents of hardness per 70.000 parts of water.

1°Cl = 1 part of $CaCO_3$ per 70,000 parts of water.

Degree French(^{0}Fr):- The parts of $CaCO_3$ equivalents of hardness per 10^5 parts of water.

1°Fr = 1 part of $CaCO_3$ per 10^5 parts of water.

10^6 ppm = 10^5 r = 70.000 °Cl

Hence 1 ppm = 0.1 r = 0.07l = 1mg/L

- A sample of water on analysis is found to contain the following impurities.

Impurity	$Ca(HCO_3)_2$	$Mg(HCO_3)_2$	$CaSO_4$	$MgSO_4$
Quantity mg/L	4	6	8	10
M.wt	162	146	136	120

Calculate the temporary, permanent and total hardness of water in ppm, °Fr and °Cl.

Solution:

Constituent	mg/L	100/M.wt	$CaCO_3$ equivalent
$Ca(HCO_3)_2$	4	100/162	0.617 X 4 = 2.47 mg/L
$Mg(HCO_3)_2$	6	100/146	0.684 X 6 = 4.11 mg/L
$CaSO_4$	8	100/136	0.735 X 8 = 5.58 mg/L
$MgSO_4$	10	100/120	0.833 X 10 = 8.33 mg/L

Determination of temporary Hardness:-

THS is due to presence of bicarbonates of Ca and Mg

THS = 2.47+ 4.11 =6.58 mg/L (or) ppm

As 1mg/L = 1ppm = 0.1 °Fr = 0.07 °Cl

Temporary hardness = 6.58 *mg/L (or) ppm*

= 6.58 x 0.1 =0.658 °Fr

= 6.58 x0.07= 0.46 °Cl

Determination of permanent hardness:-

PHS is due to presence of $CaSO_4$ and $MgSO_4$

Permanent hardness = 5.88 + 8.33 = 14.21 mg/L

= 14.21ppm

= 14.21 x 0.1 = 1.421 **°Fr**

= 14.21x 0.07 = 0.995**°Cl**

Total hardness = Temporary Hardness + permanent Hardness

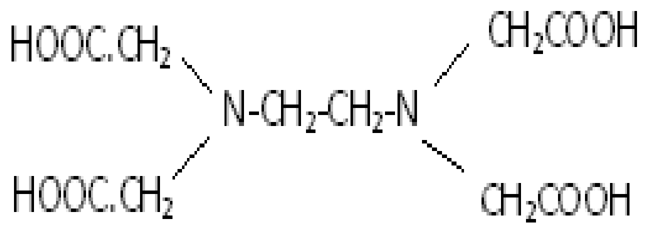
=6.58 + 14.21 = 20.79 mg/L

= 20.79 ppm

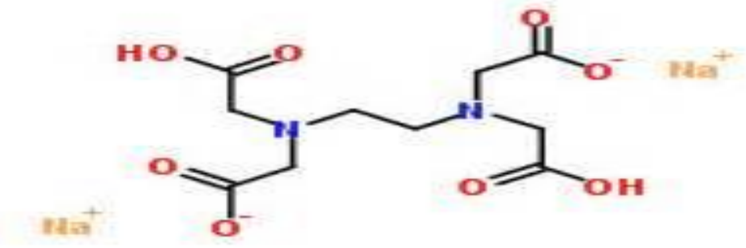
= 20.79 x 0.1 = 2.079 °**Fr**

= 20.79 x 0.07 = 1.4553 °**Cl**

Determination of hardness of water by EDTA method



EDTA



Di Sodium Salt Of EDTA

Ethylene diamine tetra acetic acid (EDTA) in the form of di sodium salt yields the anion of Ethylene diamine tetra acetate which forms complex ions with Ca^{+2} and Mg^{+2}

Principle of EDTA method for the determination of hardness of water

- In order to determine the equivalence point , indicator eriochrome black – T (EBT) is employed.
- EBT forms unstable wine red complex with Ca^{+2} and Mg^{+2} ions

$$\mathbf{M^{+2} \quad + \quad EBT \quad \rightarrow \quad [\ M\text{-}EBT\ ]\ complex}$$

(Ca^{+2} and Mg^{+2} ions

of hard water)

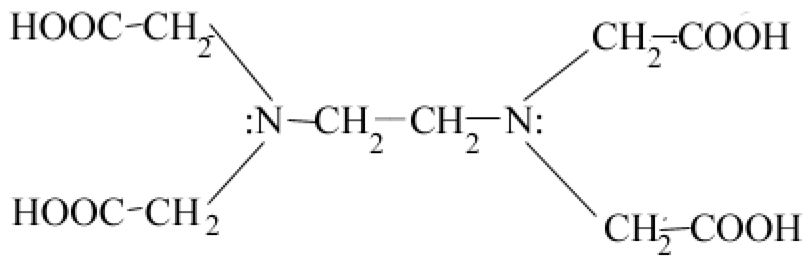
wine red

- During titration EDTA combines with Ca^{+2} or Mg^{+2} ions and forms stable [M-EDTA] blue coloured complex.

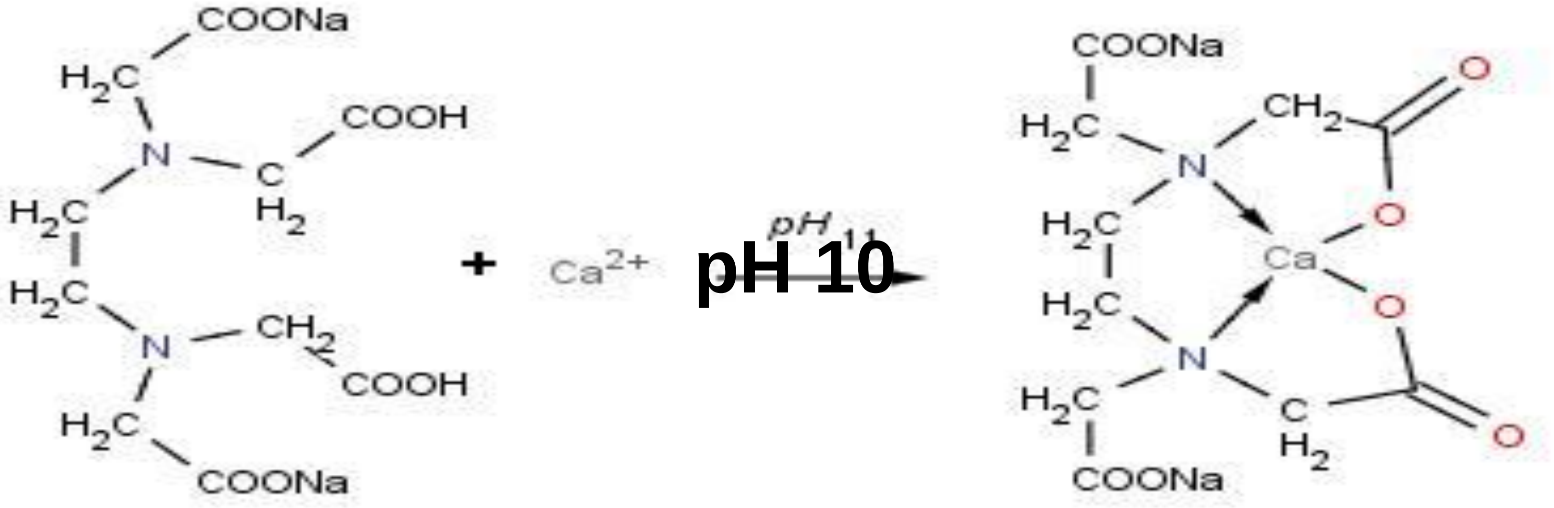
[M-EBT] complex + EDTA → [M-EDTA]complex + EBT

wine red blue

The change of wine red colour to distinct blue colour marks the end point of titration.



structure of EDTA



Di sodium salt of EDTA

Metal–EDTA complex

PROCEDURE:

I. Preparation of Standard Hard water:

- Transfer 1gm of $CaCO_3$ into a 100ml volumetric flask + 50 ml water + dil.HCl + Make up to the mark by adding water.

Molarity of $CaCO_3$ (M_1) = $\dfrac{wt}{M.wt} \times \dfrac{1000}{V_{ml}}$

II. Standardization of EDTA:

- 10ml of Standard hard water in conical flask + 5ml buffer + few drops Eriochrome black-T indicator. The solution attains wine-red colour.
- Titrate the contents against EDTA solution. Stop the addition, when the colour of solution changes from wine-red to blue.

- Note the burette reading and repeat. Let the volume of EDTA consumed in this titration be '**V1**' ml.

$$M_1 V_1 = M_2 V_2$$

(SHW) (EDTA)

III. Determination of Total Hardness of Unknown Water Sample:

- 10ml of Standard hard water in conical flask + 5ml buffer + few drops Eriochrome black-T indicator. The solution attains wine-red colour.
- Titrate the contents against EDTA solution. Stop the addition, when the colour of solution changes from wine-red to blue.
- Note the burette reading and repeat. Let the volume of EDTA consumed in this titration be '**V2**' ml.

$$M_2V_2 = M_3V_3$$

(EDTA) (UWS)

The total hardness of the test sample of water is calculated as follows:

$= M3 \times 100 \times 1000 =$ ppm

IV. Determination of Permanent Hardness of Unknown Water Sample:

- 10ml of boiled water in conical flask + 5ml buffer + few drops Eriochrome black-T indicator. The solution attains wine-red colour.
- Titrate the contents against EDTA solution. Stop the addition, when the colour of solution changes from wine-red to blue.

- Note the burette reading and repeat. Let the volume of EDTA consumed in this titration be ‘**V2**’ ml.

$$M_2 V_2 = M_4 V_4$$

(EDTA) (BWS)

Permanent hardness = $M_4 \times 100 \times 1000 =$ ppm

Total hardness = Temporary hardness + permanent hardness.

Temporary hardness = Total Hardness – permanent Hardness.

Alkalinity of Water

- Alkalinity is a measure of the capacity of water to neutralize acids.
- The presence of anions, such as OH^- , HCO_3^- CO_3^{2-} results in alkalinity of water due to their basic nature.
- Carbonate anion concentration is counted twice due to its ability to neutralize two protons.
- While bicarbonate is counted once as it can neutralize one proton.

- Out of the three anions OH^-, HCO_3^-, and CO_3^{2-} any two of them can exist in water together.
- OH^- and HCO_3^- cannot be together because H^+ ion of HCO_3^- neutralises OH^-

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

$$\mathbf{H^+ + OH^- \longrightarrow H_2O}$$

$$\mathbf{HCO_3^- + OH^- \longrightarrow CO_3^{2} + H_2O}$$

- Estimation of alkalinity in water is done by titrating water sample against standard acid using phenolphthalein and methyl orange as indicators.

- In this titration, two indicators are used as the different anions give end points at different pH values

$$\left.\begin{array}{l} \text{i. } OH^- + H^+ \longrightarrow H_2O \\ \\ \text{i. } CO_3^{2-} + H^+ \longrightarrow HCO_3^- \end{array}\right\} P$$

$$\left.\begin{array}{l} \text{iii.} HCO_3^- + H^+ \longrightarrow CO_2 + H_2O \end{array}\right\} M$$

- P- pink in basic, clear in acidic(8.3 to 10 pH), M-Yellow to orange (below 7 pH).
- If there is no pink colour after adding phenolphthalein to the water, alkalinity is not present due to OH^- and CO_3^{2-}.

- If CO_3^{2-} is present in sample, CO_3^{2-} consume one H^+ when the solution is titrated to pH 8.3, and it will consume another H^+ during further titration from pH 8.3 to pH 4.5.
- If the volume of acid required to get pH 8.3 is equal to the volume of acid used from pH 8.3 to pH 4.5, sample contained only CO_3^{2-} (no OH^-) as the major alkalinity component.
- If the pH of your sample is below 8.3, and a certain amount of acid is required to reach pH 4.5, your sample contained only HCO_3^- (no OH^- and CO_3^{2-}).
- If your sample requires a certain amount of acid to reach pH 8.3, but no acid is required from pH 8.3 to pH 4.5, your sample contained only OH^-.

Determination of alkalinity used in

- In Corrosion control,
- In calculating the amount of lime and soda needed for water softening,
- Internal conditioning of boiler feed water
- In controlling caustic embrittlement, Sludges and Scales

Total dissolved solids(TDS)

- All inorganic and organic substances contained in water that can pass through a filter are TDS.
- In general TDS is the sum of the cations and anions in water.
- Carbonates, bicarbonates, chlorides, fluorides, sulphates, phosphates, nitrates, calcium, magnesium, sodium and potassium any ion present contribute to TDS.
- Organic ions include pollutants, herbicide and hydrocarbons and soil particles.

Determination of TDS

- First remove suspended matter by filtration of selected water sample.
- Then evaporate water at 180^0C in a pre weighed dish until the dish weight no longer changes.
- The increase in weight of the dish represents TDS.
- TDS is a non specific, quantitative measure of the amount of dissolved chemicals but does not tell us anything about nature of it.
- TDS used as an indication of aesthetic characteristics of drinking water and a broad indicator of an array of chemical contaminants.

Specifications for water:

Different uses of water demand different specifications

I. Food Industry:

1. Poor quality water is responsible for diseases.
2. Free from microorganisms such as viruses, protozoa and bacteria.
3. Free from toxic chemicals like heavy metals and radio active compounds.

II. Laundries:

Require soft water, free from Mn and Fe salts. Hard water consume more soap, Fe and Mn import grey or yellow shade to the fabric.

III. Textile industry:

a) If hard water used, uniform dyeing not possible,
b) Hard water decreases solubility of acidic dyes,
c) Basic dyes precipitated by hard water,
d) Organic matter imparts foul smell,
e) Fe and Mn salts leaves stains on fabrics,

It should be from above impurities.

IV. In cooking:

If hard water used, fuel required is high. More time is required for cooking. Imparts unpleasant taste and muddy looking.

V. Pharmaceutical industries:

Require pure water , should be colourless, tasteless, odourless and free from pathogenic organisms.

VI. Sugar industry:

If hard water is used, results in deliquescent sugar. Impurities cause difficulty in crystallization.

VII. Paper industry:

- Should free from SiO_2, Fe and Mn salts.
- SiO_2 produces cracks and Fe, Mn imparts colour to paper.

VIII. In Cooling systems:

Impure water leads corrosion, microbiological growth, scale formation and fouling in cooling systems.

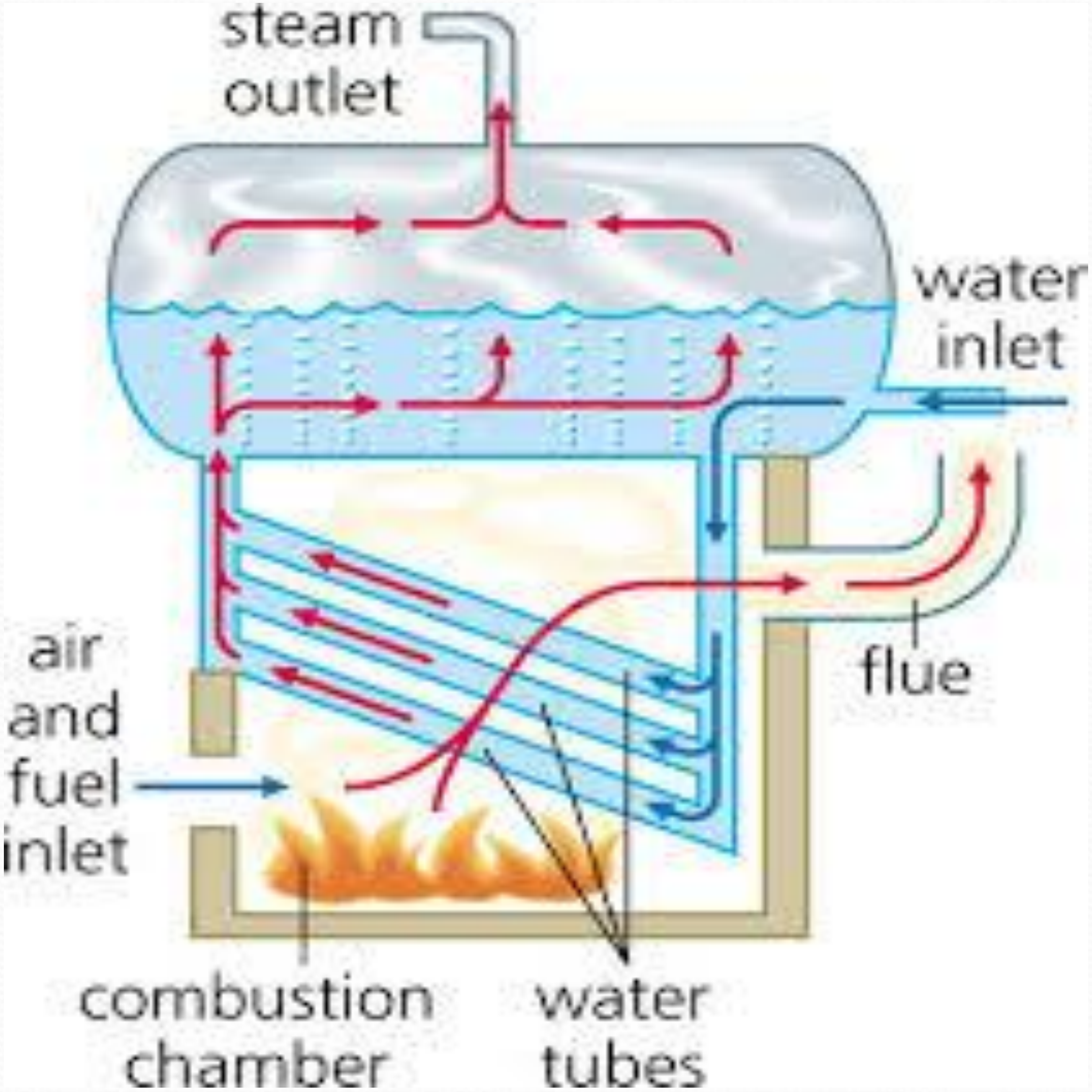
IX. In Steam generation:

Require water of low hardness.

- Otherwise efficient heat transfer is prevented by scale formation,
- Untreated water leads to corrosion of boiler material,
- Even explosion can also occurs.

BOILER


Steam Boilers


steam outlet
water inlet
flue
air and fuel inlet
combustion chamber
water tubes

Boiler troubles:

- Boilers are employed in industries for generation of steam.
- When raw water is directly feed into the boilers various physical changes and chemical reactions are induced in the boiler with the action of the heat.
- The ultimate result being the problem such as
  1. **Carry over,**
  2. **Boiler corrosion,**
  3. **Caustic embrittlement and**
  4. **Sludge and Scale formation.**

1.Carry over:

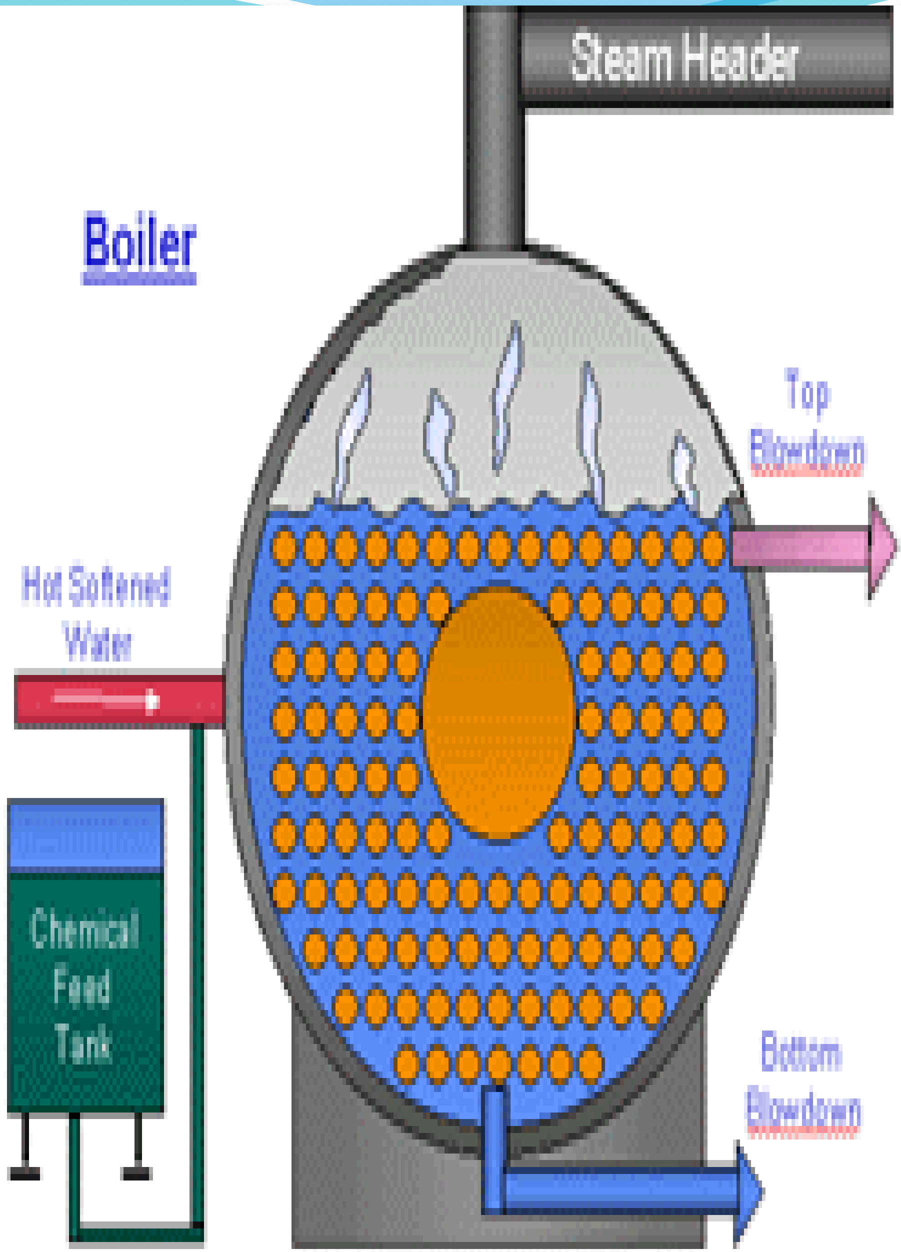
The process of carrying of water with impurities by steam is called carry over.

a) **PRIMING**: When boiler is steaming rapidly, some droplets of liquid water carried along with the steam. This process of wet steam formation is called priming.

- It is caused by the presence of large amount of dissolved salts,
- Improper boiler design,
- High steam velocities and sudden boiling.

Priming can be avoided

- ★ By fitting mechanical steam purifiers,
- ★ Avoiding rapid change in steaming rate,
- ★ Maintaining low water levels in boilers,
- ★ Efficient softening and filtration of the boiler-feed water.



b) FOAMING:

It is the production of persistent foam, bubbles in boilers, which do not break easily.

- It is due to presence of oils and alkalis in boiler water.
- Oils, alkalis react to form soaps which lower the surface tension of water and increase the foaming.

Foaming can be avoided by

- Addition of antifoaming agents like castor oil.
- By removing foaming agent like oil and alkalis in boiler water.
- The oils can be removed by adding compounds like sodium aluminates and aluminum sulphate.

Disadvantages of priming and foaming:-

- The actual height of the water in boiler is not judged,
- Wastage of heat,
- Efficiency f the boiler is lowered and
- corrosion of the machineries.

2.Boiler Corrosion:

The decay (or) disintegration of boiler material either due to chemical (or) electrochemical reaction with its environment is called boiler corrosion.

Disadvantages of boiler corrosion are:

1. Shortening of boiler life,
2. Leakages of boiler life,
3. Increased cost of repairs.

Main sources for boiler corrosion are

A. Dissolved oxygen

B. Dissolved carbon dioxide

C. Acids from dissolved salts

A. Dissolved oxygen: Water usually contains about 8ml of dissolved oxygen per lit. at RT.

- It attacks boilers at high temperature.
  - $4Fe + 2H_2O + O \rightarrow 4Fe[OH]_2\downarrow$
  - $4Fe[OH]_2\downarrow + O_2 \rightarrow 2[Fe_2O_32H_2O]\downarrow$

(Ferrous hydroxide) (Rust)

Removal of dissolved oxygen:

By adding sodium sulphite , hydrazine and sodium sulphide

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

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$$

$$Na_2S + 2O_2 \rightarrow Na_2SO_4$$

B. Disolved carbon dioxide: The disolved CO_2 in water produces carbonic acid, which has slow corrosive effect.

This is also produced inside the boiler, if water contains bicarbonates.

$$H_2O + CO_2 \rightarrow H_2CO_3$$

$$Mg(HCO_3)_2 \rightarrow MgCO_3 + H_2CO_3$$

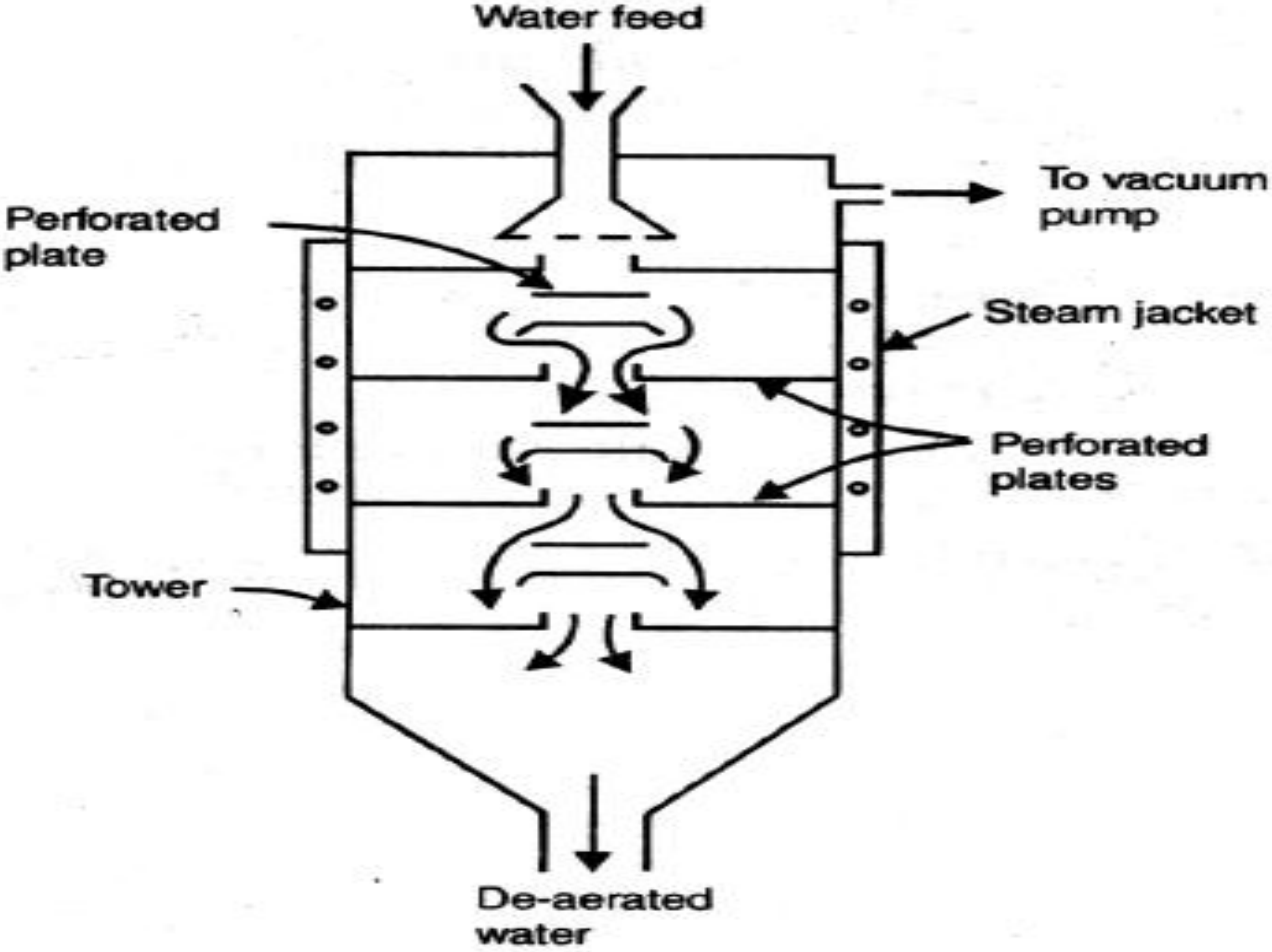
Removal of dissolved CO_2:

a. By adding ammonia:

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

b. By mechanical de-aeration:

Spraying water over preheated plates stacked in a tower.


Water feed
To vacuum pump
Perforated plate
Steam jacket
Perforated plates
Tower
De-aerated water

C. Acids from dissolved salts:

- Mineral acids are generated by the hydrolysis of disolved acidic salts.
- The liberated acid reacts with Fe of boiler to form $Fe(OH)_2$ subsequently get converted into rust .
- Small amount of $MgCl_2$ will cause corrosion of Fe to a large extent.

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

$$2HCl + Fe \rightarrow FeCl_2 + H_2$$

$$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2HCl$$

$$Fe(OH)_2 + O_2 \rightarrow Fe_2O_3 .2H_2O$$

Prevention of Acid corrosion :

- HCl can be removed by adding alkalis
- By addition of inhibitors
- By frequent blow down operation
- By softening of boiler water .

3. Caustic Embrittlement:

- Caustic embrittlement is a phenomenon in which the boiler material becomes brittle due to accumulation of caustic substances.
- The boilers feed water contains carbonates and bi – carbonates of alkali metals.
- Na_2CO_3 used for softening of the water decomposes to give NaOH and CO_2.

$$\mathbf{Na_2CO_3 + H_2o \rightarrow 2NaOH + CO_2}$$

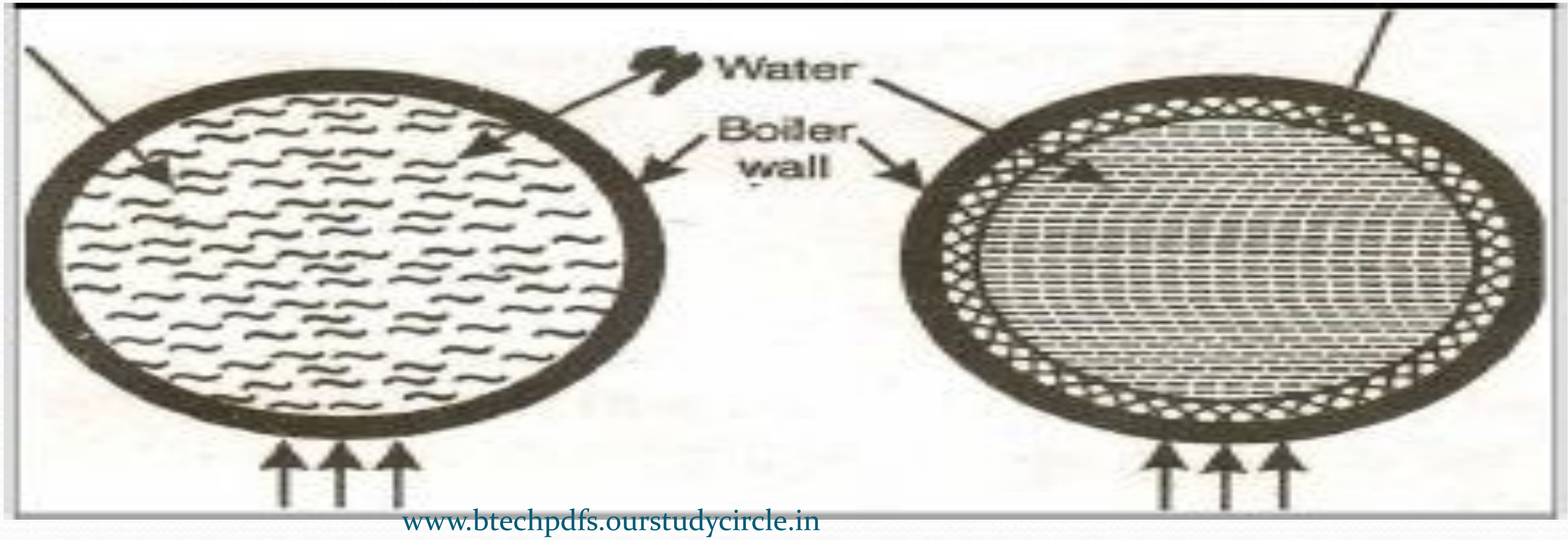
- The NaOH concentration increases by evaporation and attacks the surround area there by Fe dissolves as sodium ferrate.
- This causes embrittlement of boiler parts causing even failure of the boiler.

Prevention methods:-

- By using sodium phosphate as softening reagent instead of Na_2CO_3 for boiler water.
- By adding Na_2SO_4 to boiler water which blocks the hair cracks in the boiler.
- By adding tannin or lignin to boiler water which blocks the hair cracks in the boiler there by preventing formation of concentration cells.

4. SLUDGE & SCALE FORMATION

- In boilers, water evaporates continuously and concentration of dissolved salts increases. When it reaches saturation point they will be precipitated on the inner walls of the boilers.
- If the precipitation takes place in the form of loose and slimy, it is called **sludge.**
- If the precipitation takes place in the form of hard, adhering on the inner walls of the boilers, it is called **scale.**



Difference between Sludges and Scales

Sludges	Scales
1. Sludges are soft loose and slimy precipitate.	1. Scales are hard deposits.
2. They are non-adherent deposits and can be easily removed.	2. They sticks very firmly to the inner surface of boiler and are very difficult to remove.
3. Formed by substances like $CaCl_2$, $MgCl_2$,$MgSO_4$, $MgCO_3$ etc.	3. Formed by substance like $CaSO_4$, $Mg(OH)_2$ etc.
4. Formed at comparatively colder portion of the boiler.	4. Formed generally at heated portions of the boiler.
5. They decrease the efficiency of boiler but are less dangerous.	5. Decrease the efficiency of boiler and chances of explosions are also there.
6. Can be removed by blow-down operation.	6. Cannot be removed by blow-down operation.

a) SLUDGE:

- It is formed at colder portions of the boilers.
- It is formed by substances, which have greater solubility in hot water than cold water($MgCO_3$, $MgCl_2$, $MgSO_4$, $CaCl_2$).
- It can easily scrapped off with a wire brush.

Disadvantages:

- Sludges are poor conductors of heat.
- Disturbs the working of boilers.

Prevention of Sludge Formation:

- By using well-softened water.
- By frequently blow-down operation(nothing but the removal concentrated water through an out let at the bottom of the boiler).

b) Scales

Scales may be formed inside the boiler due to:

A).Decomposition of Ca $(HCO_3)_2$:-

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

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

B).Deposits of $CaSO_4$:-

The solubility of $CaSO_4$ decreases with increasing the temperature. So it is soluble in cold water and insoluble in hot water. Hence it get precipitated in hotter region.

C). Hydrolysis of $MgCl_2$:-

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

D).Presence of silica:-

Even if small quantity of SiO_2 is present, it may deposits as $CaSiO_3$ (or) $MgSiO_3$. These deposits adhere very firmly on inner side of boiler surface.

- In low pressure boilers CaCO3 causes scale formation, but high pressure boilers CaCO3 is soluble

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

Disadvantages of scale formation:

- Wastage of fuel,
- Lowering of boiler safety,
- Decrease in efficiency,
- Danger of explosion

Removal of scales: removed by chemical and mechanical method.

- If scales are loosely sticking, removed with help of wire brush.
- By frequently blow-down operation.
- If the scales are brittle, it can be removed by giving thermal shocks.
- If the scales are hard, they can be removed with chemicals.

Treatment (or) Softening of water for industry:

- **Treatment of boiler Feed water:-**

  Water used in boiler should be free from impurities. Otherwise cause operational troubles.

- The removal of hardness is done by following methods.

  I. **Internal Treatment of water.**

  II. **External Treatment of water**

I. Internal Treatment

- In this method, raw water is treated inside the boiler.

- Addition of suitable chemicals to reduce scale and sludge formation and to convert the scale forming chemicals into sludge which can be removed by blow down process.

- Some of the internal treatment methods used for the removal of scale formation in boilers are.

A) **Phosphate conditioning**

B) **Carbonate conditioning**

C) **Calgon conditioning**

A) Phosphate conditioning

- It is generally applicable to high pressure boilers.
- Scale formation is avoided by adding sodium phosphate, which reacts with magnesium and calcium salts forming non-sticky and easily removable sludge of calcium and magnesium phosphate and easily removed by blow down operation.

$$3MCl_2 + 2Na_3PO_4 \rightarrow M_3(PO_4)_2\downarrow + 6NaCl$$

[Where M = Ca^{2+}, Mg^{2+}]

$$3MSO_4 + 2Na_3PO_4 \rightarrow M_3(PO_4)_2\downarrow + 6NaSO_4$$

B) Carbonate conditioning

- In low pressure boilers, scale formation can be avoided by adding sodium carbonate to boiler water.
- When salts like $CaSO_4$ can be converted into $CaCO_3$. $CaCO_3$ can be removed by blow down process.

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

C) Calgon conditioning:

- It involves in adding Sodium hexa meta phosphate (calgon) to boiler water to prevent the scale and sludge formation.
- Calgon converts the scale forming impurity like CaSO4 into soluble complex compound.

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

Calgon

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

Insoluble soluble insoluble

II. EXTERNAL TREATMENT:

- The removal of hardness causing salts from water before it *feed* into the boiler is external treatment
- *This treatment is given outside the boiler, to reduce the concentration of hardness producing ions.*

A. Lime –soda process,

B. Ion exchange process.

A. Lime –soda process:

- In this method soluble Ca & Mg salts in water are converted into insoluble compounds.
- Lime ($Ca(OH)_2$) and soda (Na_2CO_3) are quantitavely mixed with hard water with constant stirring either in cold (or) hot condition.
- The precipitates formed settle down at the bottom of the tank which can be removed by titration.

Reactions in L-S process:

i. **Temporary hardness causing salts:**

- $Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + H_2O$(1L)
- $Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + Mg(OH)_2\downarrow + 2H_2O$(2L)

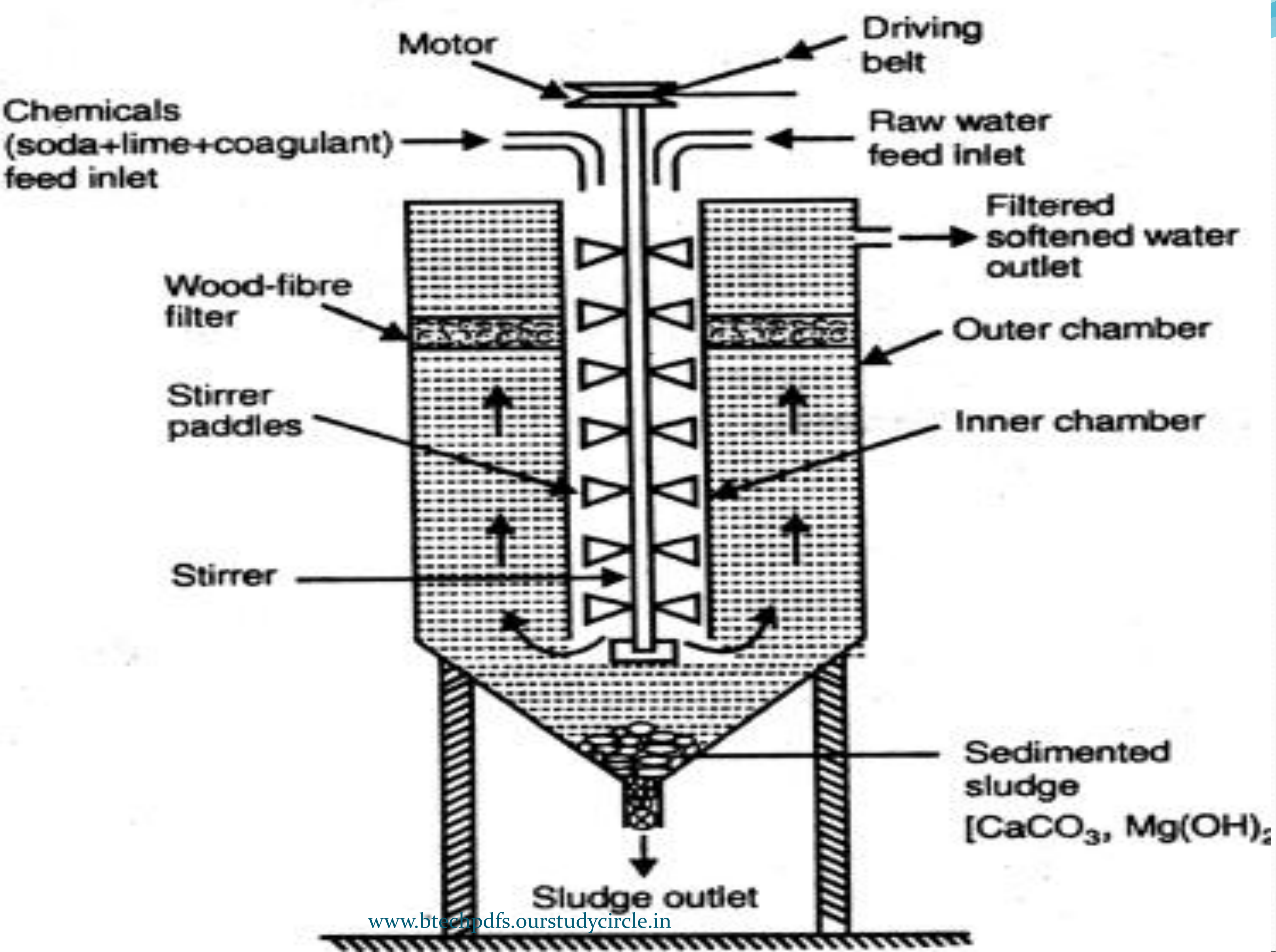
ii. **Permanent hardness causing salts:**

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

  $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2NaCl$\{L+S\}
- $CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_4$(S)
- $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2NaCl$(S)
- $CO_2 + Ca(OH)_2 \rightarrow CaCO_3\downarrow + H_2O$(L)

COLD LIME SODA PROCESS:

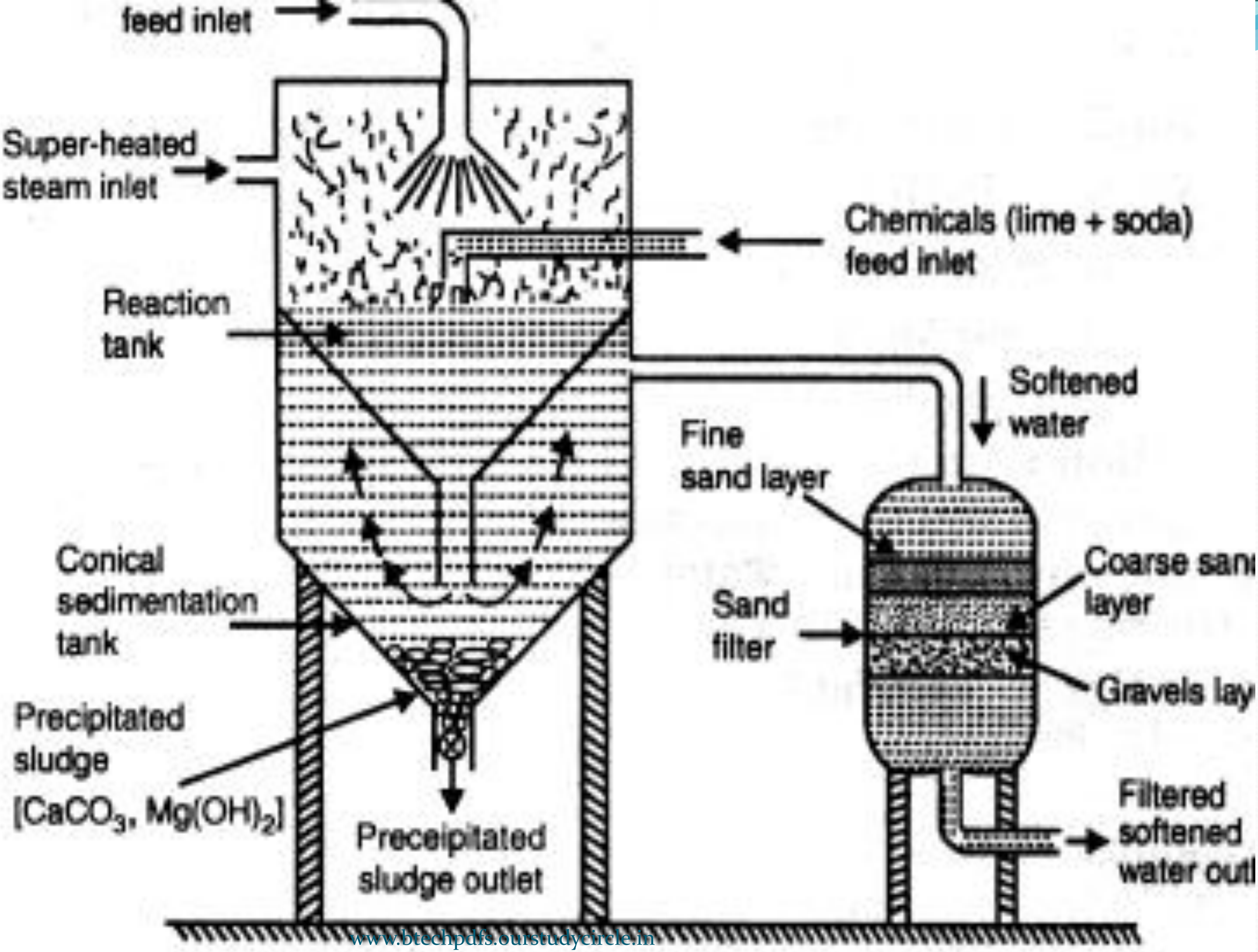
- It involves treating water with softening chemicals at room temperature.
- There are two chambers shown in apparatus.
- Raw water, lime and soda are continuously poured in tank through inlet pipes. Mechanical stirrer is used for mixing.
- Precipitates and sludge formed settle down not easily .
- Coagulants are needed like alum ,Aluminum sulphate, sodium aluminates etc.
- Cold L-S process provides water containing residual hardness off 50-60 ppm.


Motor
Driving belt
Chemicals (soda+lime+coagulant) feed inlet
Raw water feed inlet
Filtered softened water outlet
Wood-fibre filter
Outer chamber
Stirrer paddles
Inner chamber
Stirrer
Sedimented sludge
[$CaCO_3$, $Mg(OH)_2$
Sludge outlet

HOT LIME SODA PROCESS:

- It involves treating water with softening chemicals at a temperature of 80-150^{o}C .
- Hot-lime soda apparatus contain three parts.

1. A reaction tank in which water, chemicals &steam are thoroughly mixed.
2. A conical sedimentation vessel in which sludge settle down.
3. A sand filter, for removal of sludge forms the softened water


feed inlet
Super-heated steam inlet
Chemicals (lime + soda) feed inlet
Reaction tank
Softened water
Fine sand layer
Conical sedimentation tank
Coarse san
layer
Sand filter
Gravels lay
Precipitated sludge
[$CaCO_3$, $Mg(OH)_2$]
Preceipitated sludge outlet
Filtered softened water outl

Advantages of this process are

- Precipitation is rapid and it completes in 15 minutes.
- The residual hardness (15-30ppm) is far less than the cold process.
- Precipitate and sludge settle down rapidly. Hence coagulate is not needed.
- Lime and soda required in small quantity.
- Much of the dissolved gases driven out of the water.

B. ION EXCHANGE PROCESS

- It is also called **de-ionization** or **demineralization**.
- Ion exchange resins are in soluble, long chain, cross-linked polymers with a micro porous structure.

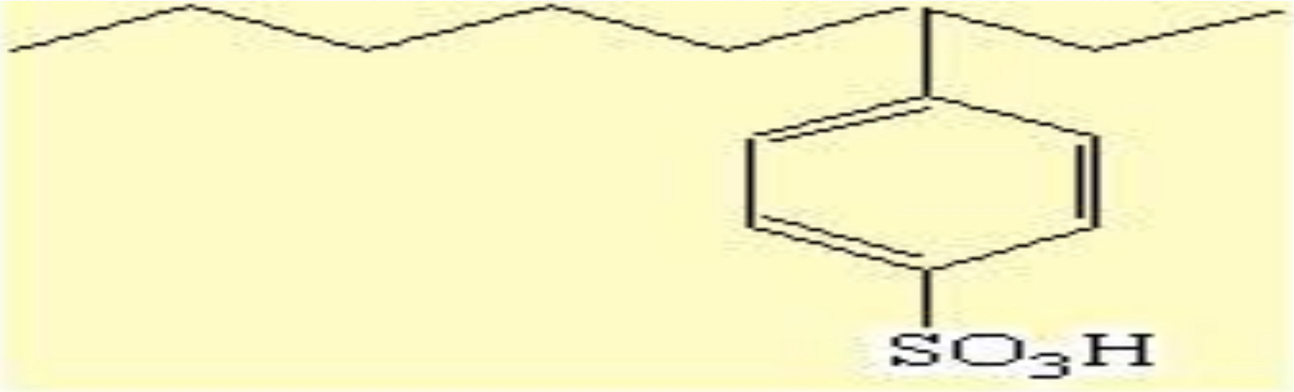
1. Resins containing acid groups (COOH, SO_3H) are capable of exchanging their H+ ions with other cations. This is called **Cation exchange resin**.

   Ex: RCOOH, RSO3H

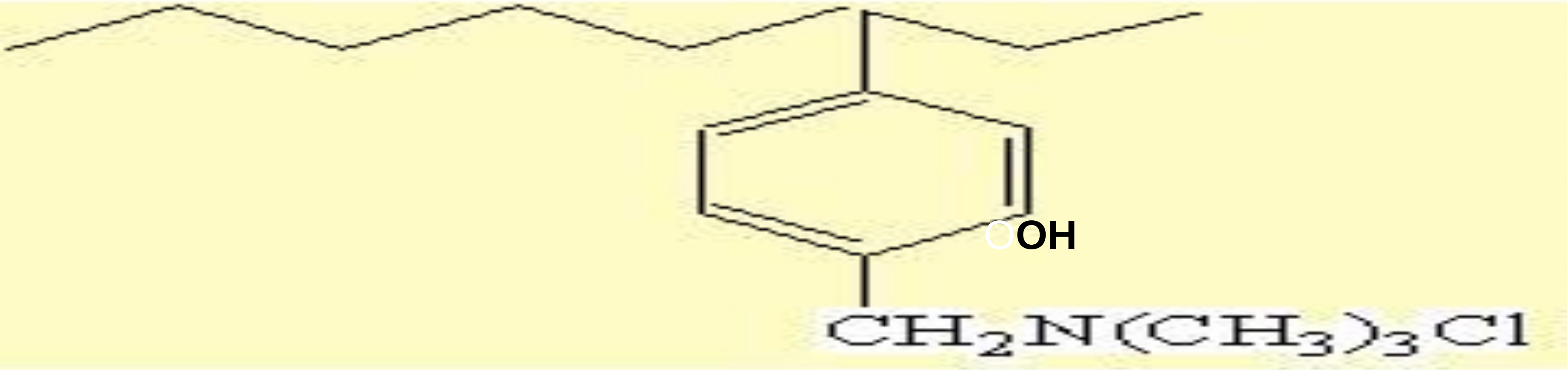
2. Resins containing basic groups (OH^-, NH_2^-) are capable of exchanging their anions with other anions. This is called **Anion exchange resin**.

   Ex: $R\text{-}CH2NMe_2OH$

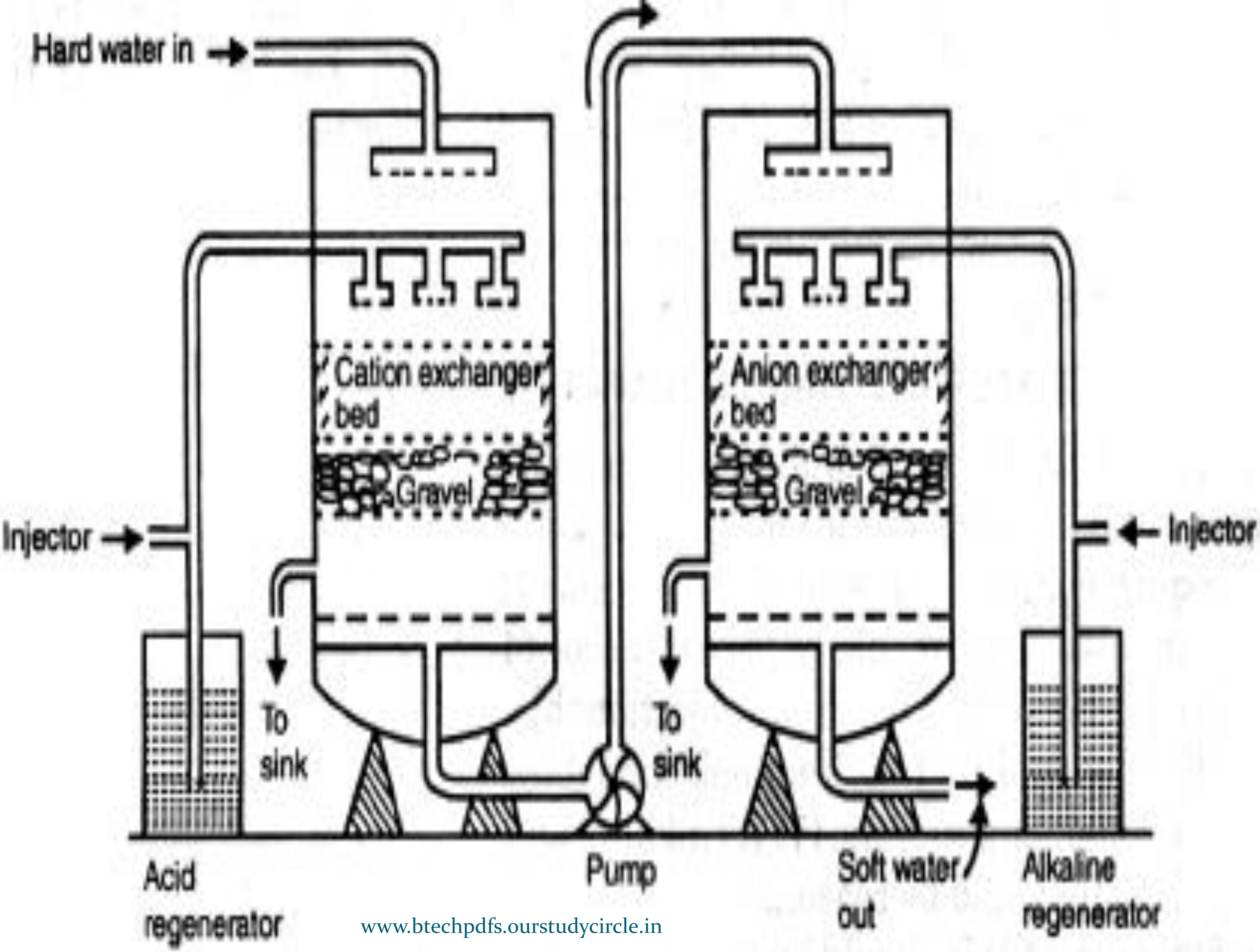
Examples of resins:



Cation exchange



Anion exchange


Hard water in
Cation exchanger bed
Gravel
Injector
To sink
Acid regenerator
Pump
Anion exchanger bed
Gravel
Injector
To sink
Soft water out
Alkaline regenerator

Ion exchange process:

- The hard water is pass 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 thus:

$$2RH + Ca^{+2} \rightarrow R2Ca + 2H^{+}$$

$$2RH + Mg^{+2} \rightarrow R2Mg + 2H^{+}$$

- 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 thus:

$$ROH + Cl^{-} \rightarrow RCl + OH^{-}$$

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

- H^+ & OH^- ions get combined to produced water molecule.

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

- Thus water coming from the exchanger is free from cations as well as anions.

Regeneration : Exhausted cation resin regenerated by dil. HCl , anion by dil.NaOH.

$$R2Ca + 2\,H^+ \rightarrow 2RH + Ca^{+2} \text{ (washed)}$$

$$R2SO4 + 2OH^- \rightarrow 2ROH^- + SO_4^{-2}\text{(washed)}$$

Desalination

The process of removal of dissolved salts (NaCl, KCl) present in water is known as desalination.

- Water is divided into three categories on the basis of salinity:

(a) Sea water: The salinity is greater than 35000 mg/L.

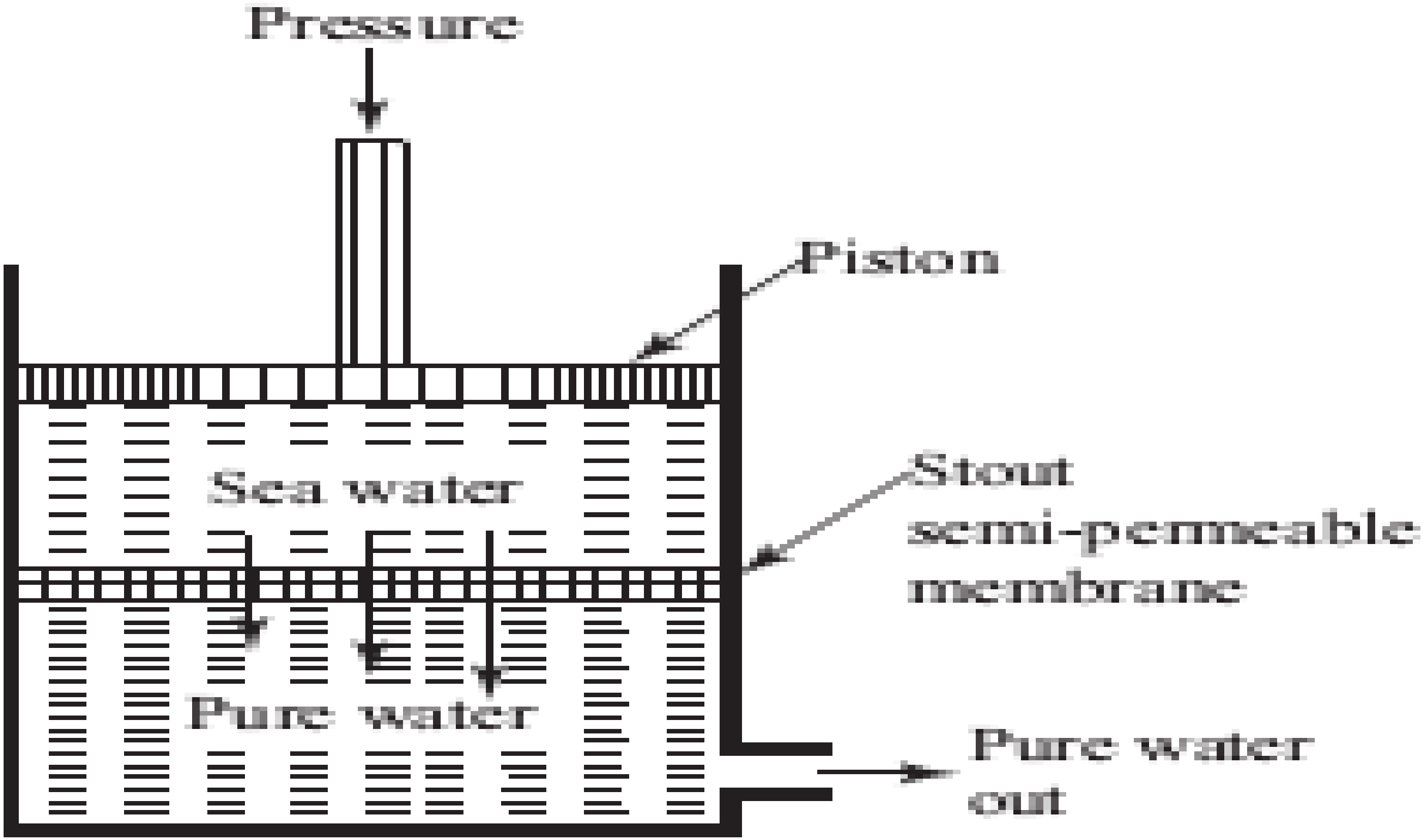
(b) Brakish water: The salinity is in the range of 1000–35000 mg/L. It has peculiar salty taste.

- Important desalination methods are:
  - **Reverse osmosis,**
  - **Electrodialyis.**

Reverse Osmosis Process

- When two solutions of unequal concentration are separated by a semi permeable membrane, flow of solvent takes from dilute solution to concentrated solution. This is called osmosis.
- During osmosis solvent develops a pressure on membrane which is called osmotic pressure.
- If pressure higher than osmotic pressure is applied from the higher concentrated side, so that the path of the solvent reversal which is called reverse osmosis.

- This method is applicable mainly for the desalination of sea water. Ionic, non-ionic, Colloidal and organic matter can be removed from the water sample



Reverse osmosis cell

Advantages of the process

- The process removes ionic as well as non-ionic dissolved salts easily.
- It is effective in removing colloidal impurities in water.
- The process is economical and convenient. The process can be carried out at a room temperature.
- It is suitable for converting sea water into drinking water

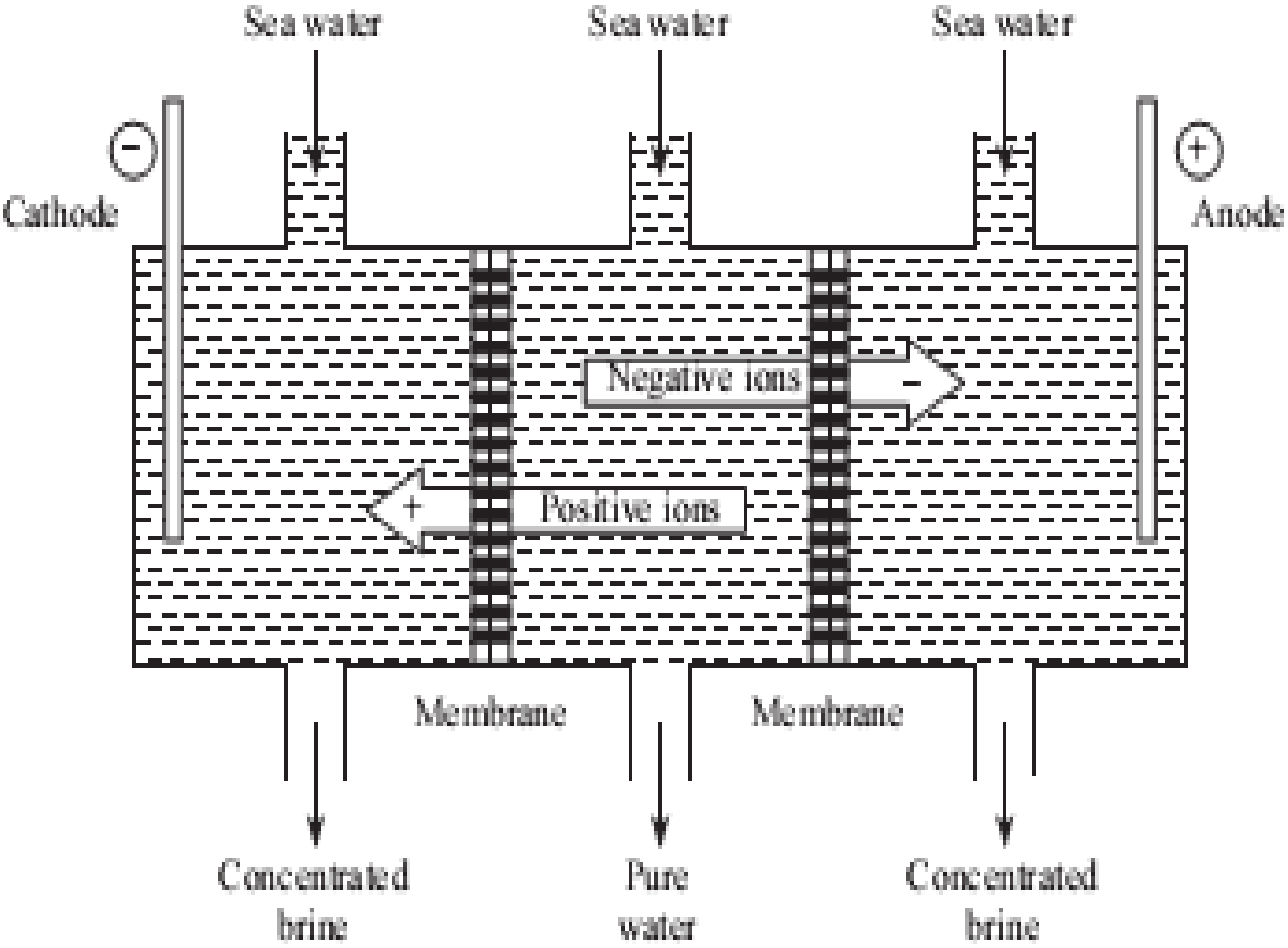
Disadvantages:

- The life time of membrane is quite high ,which is an average more than a year.
- The maintenance cost is only replacement of membrane.

Electrodialysis

- Dialysis is a process in which diffusion of smaller particles takes place through a semi-permeable membrane.
- By this process, crystalloids are removed from colloids. The process has been successfully applied for the purification of sea water. Sea water is called brackish water (salty water). It has 3.5% salt. Dialysis removes salt from sea water (brine) through a membrane.
- **Principle:**

  In electro dialysis, ion-selective membrane is used, which permits the passage of only one kind of ions having specific charge, i.e., cation selective membrane allows the passage of cations only but not anions and vice versa.



Line diagram of electrodialysis

Potable/Domestic/Municipal Water

The water supplied by municipality should be fit for human consumption. It should satisfy the following requirements:

- It should be colorless, odourless, and pleasant to taste.
- Turbidity should not exceed 10 ppm. TDS should not exceed 500 ppm.
- It should not be very alkaline (pH 8.0).
- It should be free from dissolved gases.(H2S,CO2)
- It should be free from objectionable minerals such as Pb, As, Cs, Mn

Water Treatment Plant Stages

Depending on the type of treatment plant and the quality of raw water, treatment generally proceeds in the following sequence of stages:

1. Screening
2. Sedimentation
3. Coagulation
4. Filtration
5. Disinfection(chlorination & ozonization)

- As required, other steps will be added, depending on the chemistry of the treated water.

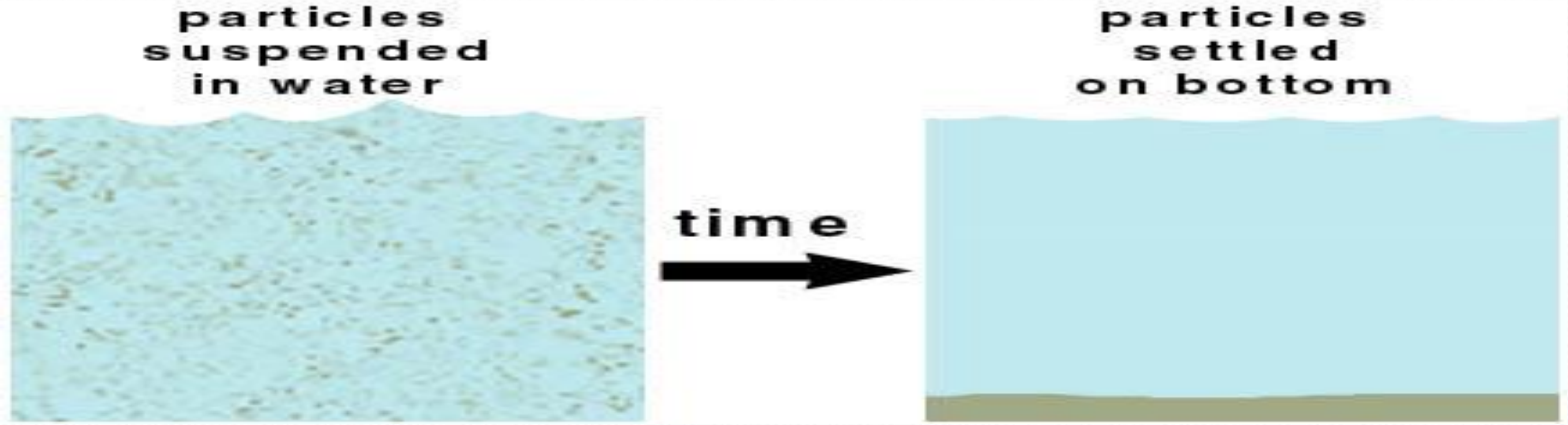
Treatment of municipal water involves the following:

- 1. **Screening:** Water is allowed to pass through the mesh screens whereby large floating matters are removed

- **2. Sedimentation:** Water is allowed to stand undisturbed for 2–5 h in big setting tanks. Suspended particles settle down due to gravity and clear water raises which can be drawn out with the help of the pumps.

Disadvantages

- It requires long big tanks. It takes a long time.
- It removes 70–75% suspended matter.
- If water contains clay and colloidal impurities, coagulants are added before sedimentation.



- 3. **Coagulation:** Colloidal particles from the water are removed by adding coagulants such as alum ($Al_2(SO_4)_3$, $NaAlO_2$). Smaller particles gather together to form bigger particles. They can be easily removed by filtration. Some bacteria and colour are also removed.

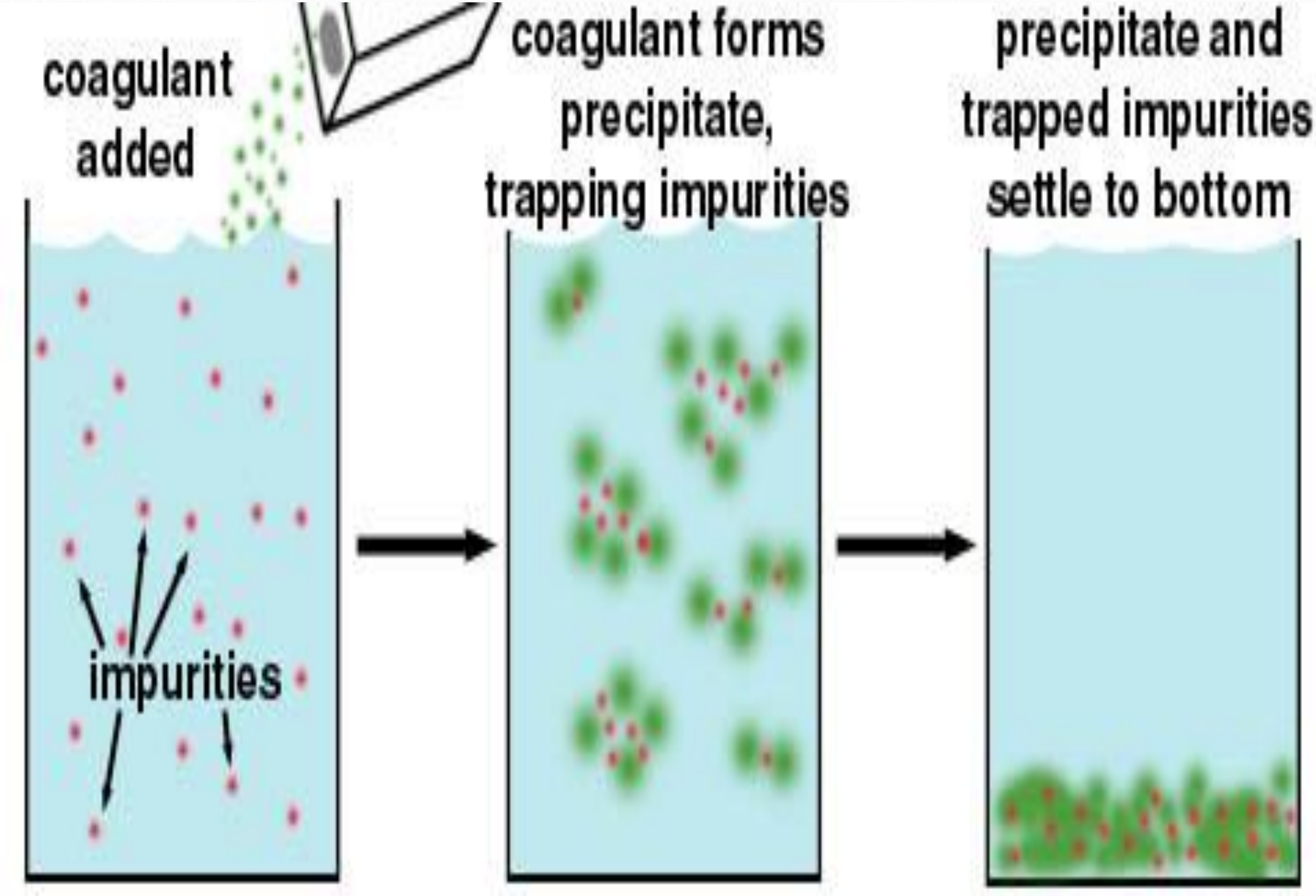
$$Al_2(SO_4)_3 + 3\,Ca(HCO_3)_2 \rightarrow 2\,Al(OH)_3\downarrow + 3CaSO_4 + 6\,CO_2$$

$$NaAlO_2 + 2\,H_2O \rightarrow Al(OH)_3\downarrow + NaOH$$

$$FeSO_4 + Mg(HCO_3)_2 \rightarrow Fe(OH)_2 + MgCO_3 + CO_2 + H_2O$$

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4\,Fe(OH)_3$$

Coagulation



- ## 4. Filtration:

Colloidal matter, bacteria, micro-organism are removed. Water is passed through a large area sand bed. The filter may be pressure filter or gravity filter.

- ## 5. Sterilization/disinfection:

Water after passing through sedimentation, coagulation, and filtration still contains a small percentage of pathogenic micro-organisms such as bacteria. Its removal can be achieved by sterilization

- The chemicals used for killing bacteria are called disinfectants. Water can be sterilized by the following methods:

(a)Boiling: Water is boiled for 10–15 min, where most of the pathogenic bacteria are killed.

(b)By adding bleaching powder. Bleaching powder in calculated amount is added to water and allowedto stand for several hours.

$$CaOCl_2 + H_2O \rightarrow Ca(OH)_2 + Cl_2$$

$$Cl_2 + H_2O \rightarrow HCl + HOCl$$

$$HOCl + \text{Germs} \rightarrow \text{germs are killed}$$

Disadvantages:

Bleaching powder introduces Ca^{2+} hardness in water and adds lime residue.

Excess of it gives bad smell and bad taste. Excess chlorine is irritating to mucous membrane.

(c)By chlorination

$$Cl_2 + H_2O \rightarrow HCl + HOCl$$

$$\text{Bacteria} + HOCl \rightarrow \text{killed bacteria}$$

The quantity of chlorine to be added is important. The disinfection will not complete if chlorine is insufficient. If excess chlorine is added, it causes irritation, bad taste, and odour.

De-chlorination

Over chlorinated water can be de chlorinated by passing it through a bed of activated carbon. Excess chlorine can also be removed by adding SO2 (or) NaSO3.

$$SO_2 + Cl_2 + 2H_2O \rightarrow H_2SO_4 + 2HCl$$

$$Na_2SO_3 + Cl_2 + H_2O \rightarrow Na_2SO_4 + 2 HCl$$

(d) By using chloramine (NH_2Cl): It is obtained by mixing chlorine and NH_3 in 2:1 ratio. It has better bactericidal action than chlorine. It is more stable and not producing any irritating odour.

$$NH_3 + Cl_2 \rightarrow HCl + NH_2Cl$$

$$NH_2Cl + H_2O \rightarrow NH_3 + HOCl$$

(e) Disinfection by ozone: O_3 is prepared by passing silent electric discharge through cold, dry O_2. It is highly unstable.

$$O_3 \rightarrow O_2 + (o)$$

O_3 is an excellent, harmless disinfectant. It is highly unstable and decomposes to give nacent oxygen (o). (o). is a powerful oxidizing agent. It oxidizes organic matter in water and also kills bacteria

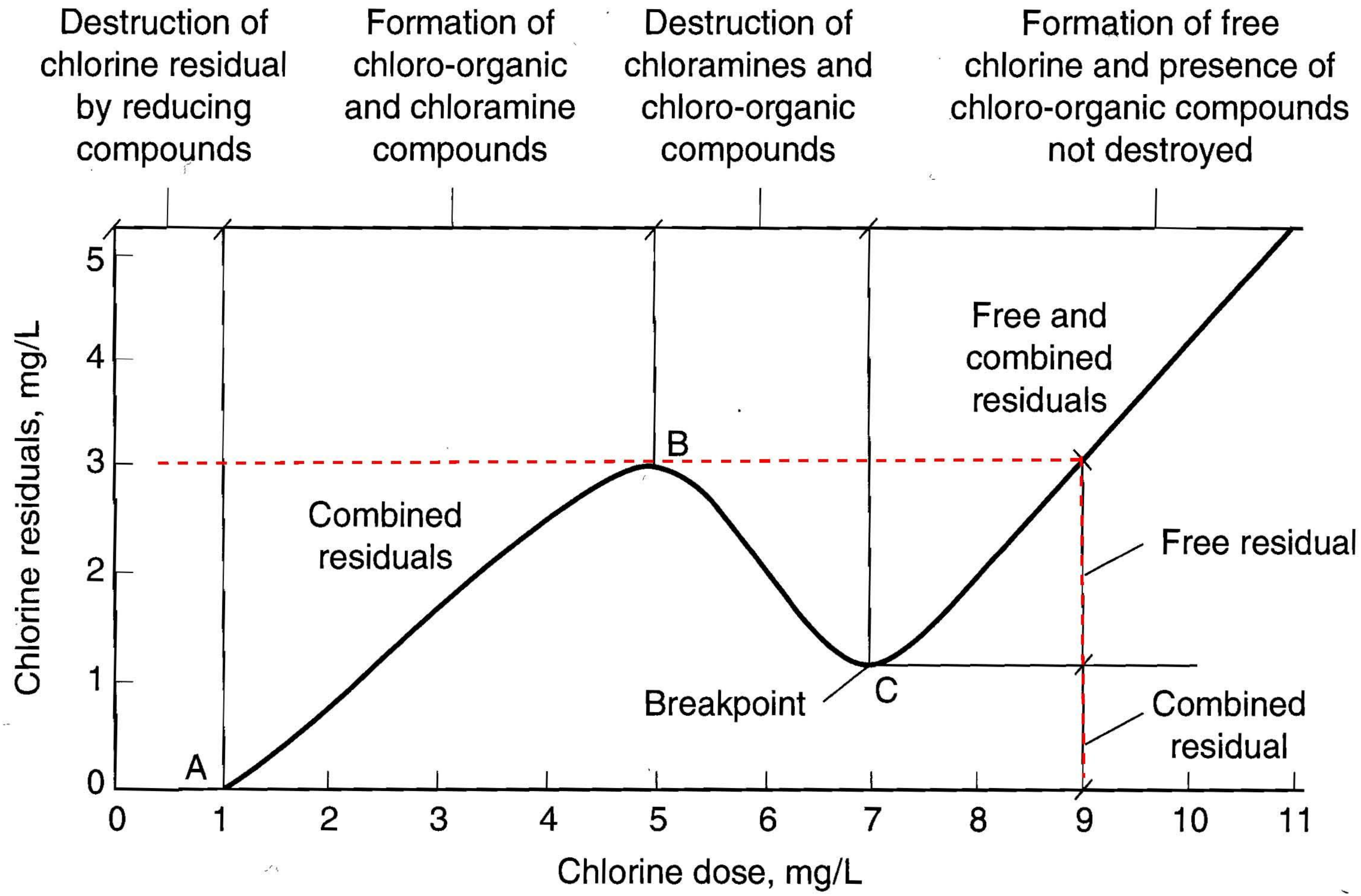
Break-point Chlorination (Free residual chlorination):

It involves in addition of sufficient amount of chlorine to oxidize

a) **Organic matter**
b) **Reducing substances**
c) **Free ammonia**

The dosage of applied chlorine and the free Chlorine can be depicted graphically in which appearance of following four stages occurs:

Break point chlorination



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

- First (between points 1 and 2), the water reacts with reducing compounds in the water, such as hydrogen sulfide. These compounds use up the chlorine, producing no chlorine residual.
- Next, between points 2 and 3, the chlorine reacts with organics and ammonia naturally found in the water. Some combined chlorine residual is formed - chloramines.
- Note that if chloramines were to be used as the disinfecting agent, more ammonia would be added to the water to react with the chlorine. The process would be stopped at point 3.
- Using chloramines as the disinfecting agent results in little tri halo methane production but causes taste and odor problems since chloramines typically give a "swimming pool" odor to water.

- In contrast, if hypo chlorous acid is to be used as the chlorine residual, then chlorine *will* be added past point 3. Between points 3 and 4, the chlorine will break down most of the chloramines in the water, actually lowering the chlorine residual.

- Finally, the water reaches the breakpoint, shown at point 4. 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. When more chlorine is added past the breakpoint, the chlorine reacts with water and forms hypo chlorous acid in direct proportion to the amount of chlorine added. This process, known as **breakpoint chlorination**, is the most common form of chlorination, in which enough chlorine is added to the water to bring it past the breakpoint and to create some free chlorine residual.

Methodology and working of mineral water plant for drinking purpose: