Water

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Introduction

1). Like air, water is one of the few basic materials which is of prime importance for the preservation of life on this earth.

2). All are aware of the uses of water for drinking, cooking, cooking, bathing & for farming etc.

3). But few know the importance of water as an engineering material.

4). As an engineering material water is used for producing steam, in boilers to generate hydro-electric power, furnishing steam for engines, for construction of concrete structures for manufacturing purposes & as a solvent in chemical process.

Sources of Water:

The Main Sources Of Water Are:

1). Rain water

2). River water

3). Spring or well water

4). Sea water

Types of impurities in water:

The impurities present in water are classified as:

1). Dissolved impurities: dissolved impurities may organic or inorganic.

Inorganic impurities: the carbonates, bicarbonates, sulphates, chlorides of calcium, magnesium, iron potassium and aluminium.

Organic impurities: Organic water products, amino acids, proteins, etc. Gases: O_2, CO_2, Oxides of nitrogen and sulphur, H_2S etc.

2). **Suspended impurities:** It is of two types:

1. Inorganic- sand & clay;
2. Organic- vegetable and animal matter.

3) **Biological Impurities:** Micro-organisms like pathogenic bacteria, fungi, algae, etc.

DISADVANTAGES OF HARDWATER/ CAUSES OF HARDNESS:

The following are the disadvantages when hard water is used for various purpose:

(i) DOMESTIC USE:

(a) Washing and Bathing: Hard water does not form lather easily with soap, so soap is wasted

(b) Drinking: Hard water causes bad effects on our digestive system. Sometimes, stone formation takes place in kidneys

(c) Cooking: The boiling point of water is increased due to the presence of salts. Hence, more fuel and time are required for cooking.

(ii) INDUSTRIAL USE:

(a) Textile Industry: Hard water causes wastage of soap. Precipitates of calcium and magnesium soap adhere to the fabrics and cause problem such difference in color shades, dull shades, patches, etc.

(b) Paper Industry: Calcium and Magnesium salts in water may affect the quality of paper.

(c) Sugar Industry: Water containing sulphates, carbonates, nitrates affects the crystallisation of sugar.

(d) Pharmaceutical Industry: Hard water may form some undesirable products while preparation of pharmaceutical products.

(iii) STEAM GENERATION IN BOILERS: For steam generation, boilers are employed. If hard water is used in boilers, It may lead to the following troubles-

(a) Boiler Corrosion
(b) Scale and Sludge formation.
(c) Priming and Foaming
(d) Caustic embrittlement Pharmaceutical industry

HARDNESS OF WATER (OR) HARDWATER AND SOFT WATER:

Hard Water: The water which does not produce lather (or) very little lather with soap is called Hard Water.

Soft Water: Soft water readily produces a lot of lather when mixed with little soap.

The Hardness of water is caused by the presence of dissolved salts such as Bicarbonates, Sulphates, Chlorides and Nitrates of bivalent metal ions like Ca^{+2} & Mg^{+2}.

Soap is sodium/ potassium salt of higher fatty acids like stearic, oleic and palmetic acids. When soap is mixed with soft water lather is produced due to stearic acid and sodium stearate.

Na – Stearate + H_2O → NaOH + Stearic Acid [$C_{17}H_{35}COOH$]

Stearic Acid + Na-Stearate → Formation of lather.

When soap comes in contact with HARD WATER, Sodium stearate will react with dissolved calcium and magnesium salts and produce calcium stearate or magnesium stearate which is white precipitate.

$2Na–\ Stearate + Ca^{+2} \rightarrow Ca–\ Stearate\downarrow + 2Na^{+}$

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

(Soap) (Soluble) (Insoluble) (Soluble)

$[2C_{17}H_{35}COONa] + Mg^{+2} \rightarrow [(C_{17}H_{35}COO)_2Mg]\downarrow + 2Na^{+}$

(Soluble) (Soluble) (Insoluble) (Soluble)

TYPES OF HARDNESS

The hardness of water is of two types-

(1) Temporary hardness (or) Carbonate hardness

(2) Permanent hardness (or) Non-Carbonate hardness

(1) Temporary Hardness: Temporary hardness is caused by two dissolved bicarbonate salts $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$. The hardness is called "Temporary Hardness" because it can be removed easily by means of boiling.

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

$$Mg(HCO_3)_2 + \text{Heating} \rightarrow Mg(OH)_2\downarrow + 2CO_2\uparrow$$

(2) Permanent Hardness: Permanent hardness of water is due to the dissolved chlorides, sulphates and nitrates of calcium and magnesium. These salts are $CaCl_2$, $CaSO_4$, $Ca(NO_3)_2$, $MgCl_2$, $MgSO_4$, $Mg(NO_3)_2$. These hardness cannot be removed easily by boiling. Hence it is called "Permanent Hardness". Only chemical treatment can remove this hardness.

Total Hardness Of Water = Temporary Hardness + Permanent Hardness

DEGREE OF HARDNESS:

- The Concentration of hardness as well as non-hardness constituting ions are, usually expressed in the term of "Equivalent amount of $CaCO_3$"
- Since this mode permits the multiplication and division concentration, when required.
- The choice of $CaCO_3$ in particular is due to its molecular weight (m.wt.) is "100" (Equivalent wt. = 50), and
- Moreover, it is insoluble salt that can be precipitated in water treatment.

Therefore, 100 parts by weight of $CaCO_3$ hardness must be equivalent to-

- 162 parts by weight of $Ca(HCO_3)_2$ hardness
- 146 parts by weight of $Mg(HCO_3)_2$ hardness
- 136 parts by weight of $CaSO_4$ hardness
- 111 parts by weight of $CaCl_2$ hardness
- 164 parts by weight of $Ca(NO_3)_2$ hardness
- 120 parts by weight of $MgSO_4$ hardness
- 146 parts by weight of $MgCl_2$ hardness
- 148 parts by weight of $Mg(NO_3)_2$ hardness

Salt	Molar Mass	Chemical Equivalent	Multiplication Factor
$Ca(HCO_3)_2$	162	81	100/ 162
$Mg(HCO_3)_2$	142	73	100/ 142
$CaSO_4$	136	68	100/ 136
$FeCl_2$	127	63.5	100/ 127
$CaCl_2$	111	55.5	100/ 111
$MgSO_4$	120	60	100/ 120
$MgCl_2$	95	47.5	100/ 95
$CaCO_3$	100	50	100/ 100
$MgCO_3$	84	42	100/ 84
CO_2	44	22	100/ 44
$Ca(NO_3)_2$	164	82	100/164
$Mg(NO_3)_2$	148	74	100/ 148
HCO_3^-	61	61	100/ 122
OH^-	17	17	100/ 34
CO_3^{2-}	60	30	100/ 60

Salt	Molar Mass	Chemical Equivalent	Multiplication Factor
$NaAlO_2$	82	82	100/ 164
$Al_2(SO_4)_3$	342	57	100/ 114
$FeSO_4.7H_2O$	278	139	100/ 278
H^+	1	1	100/ 2
HCl	36.5	36.5	100/ 73

The method of calculating degree of hardness is given by the following formula

- **Hardness causing salt in terms of equivalent of $CaCO_3$= (Amount (Mass) of the hardness causing salt x 100)/ Molecular weight of hardness causing salt**

UNITS OF HARDNESS:

The 5 different units in which the hardness of water is expressed as given below-

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

i.e., 1 PPM = 1 part of $CaCO_3$ equivalent hardness in 10^6 parts of water.

(2) Milli grams Per Litre (mg/litre): mg/L is the number of milligrams of $CaCO_3$ equivalent hardness present per litre of water.

i.e., 1 mg/L = 1 mg of $CaCO_3$ equivalent hardness in 1L of water.

But 1 L water weighs = 1 kg of water

1 kg = 1000 gms = 1000 x 1000 mg = 10^6 mg

∴ 1 mg/L = 1mg of $CaCO_3$ equivalent per 10^6 mg of water

= 1 part of $CaCO_3$ equivalent per 10^6 parts of water

∴ 1 mg/L = 1 ppm

(3) Degree Of Clarke (^oCl): It is number of grains (1/7000 lb) of $CaCO_3$ equivalent hardness per gallon (10 lb) of water.

(or) It is defined as the number of parts of $CaCO_3$ equivalent hardness per 70,000 parts of water.

$\therefore$ 1 ^oCl = 1 grain of $CaCO_3$ eq. hardness per gallon of water.

(or) 1 ^oCl = 1 part of $CaCO_3$ eq. hardness per 70,000 parts of water

$\therefore$ 1 ppm = 0.07 ^oCl

(4) Degree Of French (^oFr): It is the number of parts of $CaCO_3$ equivalent hardness per 10^5 parts of water.

1 ^oFr = 1 part of $CaCO_3$ equivalent hardness per 10^5 parts of water

$\therefore$ 0.1 ^oFr = 1 ppm

<u>Note:</u> The hardness of water can be converted into all the four units by making use of the following interconversion formula-

1 ppm = 1mg/L = 0.07^oCl = 0.1^oFr

1 ^oCl = 1.43^oFr = 14.3 ppm = 14.3 mg/L

(5) Milliequivalent per Litre (meq/L): It is the number of milliequivalent of hardness present per litre of water.

1 meq/L= 1 meq of $CaCO_3$ per litre of water

= 10^{-3} x 50 g of $CaCO_3$ eq. of hardness per litre of water

= 50 mg of $CaCO_3$ eq. of hardness per litre of water

= 50 mg/L of $CaCO_3$ eq.

= 50 ppm

$\therefore$ 1 meq/L= 50 ppm

PROBLEM:

(1) A sample of water gives an analysis 13.6 mg/L of $CaSO_4$, 7.3 mg/L of $Mg(HCO_3)_2$. Calculate the total hardness and permanent hardness.

Sol:

Salt	Quantity (mg/L)	M. Wt.	Multiplication Factor	Eq. of $CaCO_3$	Hardness
$CaSO_4$	13.6	136	100/ 136	13.6 x (100/ 136)= 10	P
$Mg(HCO_3)_2$	7.3	146	100/ 146	7.3 x (100/ 146)= 5	T

Total hardness= Temporary hardness + Permanent Hardness = 5 + 10 = 15 mg/L = 15 ppm

Permanent hardness = 10 ppm

Temporary hardness= 5 ppm

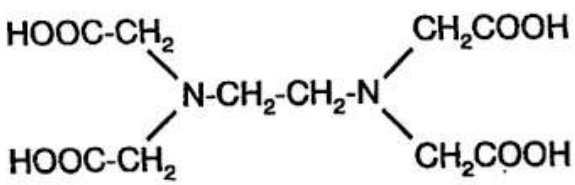
DETERMINATION OF HARDNESS OF WATER BY EDTA METHOD:-

1. This is a Complexometric titration method where Ethylenediamine tetraacetic acid (EDTA) is used.
2. EDTA forms complexes with different metal ions at different pH.
3. Calcium & Magnesium ions form complexes with EDTA at pH 9- 10.

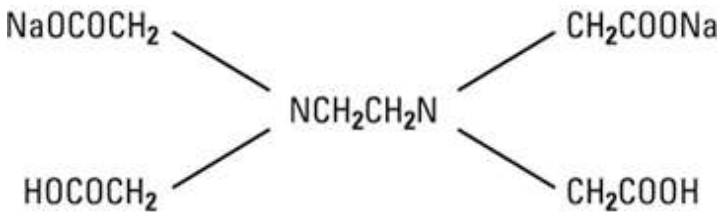
To maintain the pH 9- 10 NH_4Cl, NH_4OH buffer solution is used.

4. The disodium salt of EDTA is used for complexation.

5. An alcoholic solution of Eriochrome Black-T (EBT) is used as an indicator.



EDTA



EDTA disodium salt

Metal-EDTA complex

BASIC PRINCIPLE:

When hard water comes in contact with EDTA, at pH 9- 10, the Ca^{+2} & Mg^{+2} forms stable, colourless complex with EDTA.

Ca^{+2} + EDTA + pH 9-10 → Ca-EDTA

Mg^{+2} + EDTA + pH 9-10 → Mg-EDTA

Working:-

To the hard water sample, the alcoholic blue coloured EBT indicator is added along with the NH_4Cl + NH_4OH buffer (pH 9-10) solution.

EBT forms an unstable wine-red complex with Ca^{+2} & Mg^{+2}.

(Ca^{+2} + Mg^{+2}) + EBT + Buffer (pH 9-10) → (Ca-EBT + Mg-EBT) complex
(Hard water) (Indicator) (Unstable **wine-red** complex)

This wine-red coloured [Ca-EBT & Mg-EBT] complex is then titrated against EDTA; when EDTA replaces EBT from Ca-EBT & Mg-EBT complex and forms stable colourless [Ca-EDTA] & [Mg-EDTA] complex releasing the blue coloured indicator EBT into H_2O.

[Ca-EBT + Mg-EBT] complex + EDTA → EBT + [Ca-EDTA + Mg-EDTA] complex
(Unstable **wine-red** complex) (**Blue**) (Stable colourless complex)

Hence the colour change at the end point is wine-red to blue colour.

The titration is carried out in the following steps

1. PREPARATION OF STANDARD HARD WATER: Dissolve 1gm of pure, dry $CaCO_3$ in minimum quantity of dilute HCl and evaporate the solution to dryness on a water-bath. Dissolve the residue in distilled water to make 1 litre in a standard flask and shake well.

Molarity of standard hard water solution =

$$\frac{\text{wt. of } CaCO_3}{\text{M.wt. of } CaCO_3} = \frac{1}{100} = 0.01M$$

(2) PREPARATION OF EDTA SOLUTION:

Dissolve 4 gms of pure EDTA-disodium salt crystals along with 0.1 gm of $MgCl_2$ in one litre of distilled water.

(3) PREPARATION OF INDICATOR (EBT):

Dissolve 0.5 gms of Erichrome Black-T in 100 ml of alcohol.

(4) PREPARATION OF BUFFER SOLUTION: Add 67.5 gm of NH_4Cl to 570 ml of concentrated ammonia solution and dilute with distilled water to one litre

(5) STANDARDISATION OF EDTA SOLUTION: Pipette out 20 ml of standard hard water solution into a conical flask. Add 2- 3 ml of buffer (pH 9- 10) solution and 2- 3 drops of EBT indicator. Titrate the wine-red coloured complex with EDTA taken in a burette after rinsing it with EDTA solution till the wine red colour changes to clear blue.

Note the burette reading and let the volume be "x"ml. Repeat the titration to get concurrent values.

(6) TITRATION OF SAMPLE HARD WATER (Total) :

Pipette out 20 ml of the water sample into a 250ml conical flask, add 2- 3 ml of buffer (pH 9-10) solution and 2- 3 drops of EBT indicator. Titrate the wine-red coloured solution with EDTA taken in the burette till a clear blue coloured end point is obtained.

Let the volume of EDTA be “y” ml. Repeat the titration to get concurrent values

(7) TITRATION FOR PERMANENT HARDNESS:

Pipette out 100 ml of hard water sample in a beaker and boil till the volume reduces to 20 ml. All the bicarbonates of Ca^{++} and Mg^{++} decomposes to $CaCO_3$ and $Mg(OH)_2$. Cool the solution and filter the water into a flask, wash the beaker and precipitate with distilled water and add the washing to conical flask. Add 2- 3 ml of buffer (pH 9- 10) solution and 2- 3 drops of EBT indicator and titrate with EDTA solution taken in the burette till a clear blue colour end point is obtained.

Note the burette reading. Let the volume be “z” ml.

CALCULATIONS:

Molarity of standard hard water solution = 0.01 M.

(Calculated in the preparation of standard hard water)

Molarity of EDTA solution (M2): $\frac{V_1 M_1}{n_1} = \frac{V_2 M_2}{n_2}$

n_1 & n_2 are no. of moles of Ca^{+2} and EDTA = 1 each

i.e., $n_1=1$, $n_2=1$

V_1 = volume of standard hard water

M_1= Molarity of standard hard water

V_2= volume of EDTA

M_2= molarity of EDTA

$$M_2 = \frac{V_1 M_1}{V_2} = \frac{20 \text{ X } 0.01}{\text{x (titre value)}}$$

Molarity of sample hard water (M_3):

$$\frac{V_2 M_2}{n_2} = \frac{V_3 M_3}{n_3}$$

V_2= volume of EDTA

M_2= molarity of EDTA

V_3= volume of sample hard water

M_3= Molarity of sample hard water

$$M_3 = \frac{V_2 M_2}{V_3} = \frac{M_2 \text{ x y (titre value)}}{20} = \frac{\text{y x 0.01}}{\text{x}}$$

Total Hardness Of Water

= M_3 x 100 gms/1 litre

=M_3 X 100 X 1000mg/L or ppm= (y/ x) X 1000ppm

Permanent Hardness Of Water:

$$\frac{V_2M_2}{n_2} = \frac{V_4M_4}{n_4} \qquad M_4 = \frac{V_2M_2}{V_4} = \frac{zM_2}{20} = \frac{z}{x} \times 0.01$$

V_2= volume of EDTA

M_2= molarity of EDTA

V_4 = volume of water sample containing permanent hardness (100 ml)

M_4= Molarity of water sample containing permanent hardness

Permanent Hardness Of The Water Sample

= M_4 x 100 x 1000 ppm

= z/ x X 1000ppm

Temporary Hardness Of The Water Sample

= (Total Hardness – Permanent Hardness)

= (M_3 x 100 x1000 – M_4 x 100 x1000) ppm

= (M_3 – M_4) x 100 x1000 ppm

$$= \frac{(y-z)}{x} \times 1000 \text{ ppm}$$

Problem:

1 gm of $CaCO_3$ was dissolved in HCl and the solution was made upto 1 Lit with distilled water. 50 ml of the above solution required 30 ml of EDTA solution for titration. 50 ml of hard water sample required 40 ml of the same solution of EDTA for titration. 50 ml of the hard water after boiling, filtering, etc. required 30 ml of the same EDTA solution for titration. Calculate the temporary hardness of the water.

Soln:

Molarity of $CaCO_3$ (SHW) solution (M_1)= 1/100= 0.01 M

Molarity of EDTA solution (M_2) = V_1 M_1/ V_2

V_1= volume of $CaCO_3$ solution = 50 ml

M_1= Molarity of $CaCO_3$ solution = 0.01 M

V_2= volume of EDTA = 30 ml

M_2= 50 x 0.01/ 30 = 0.016 M

Molarity of Hard Water Sample Sol.(M_3)= V_2M_2/ V_3

V_2= volume of EDTA = 40 ml

M_2= Molarity of EDTA = 0.016 M

V_3= volume of hard water sample= 50 ml

M_3= 40 x 0.016/ 50 = 0.0128 M

Total Hardness of water

= 0.0128 x 100 x 1000

= 1280 ppm

Permanent hardness of water: $= \frac{V_4 M_4}{n_4} = \frac{V_2 M_2}{n_2}$

$M_4 = V_2M_2/ V_4$

n_4=1; V_2= volume of EDTA = 30 ml

n_2=1; M_2= molarity of EDTA = 0.016

V_4= volume of permanent hardness containing water = 50

M_4 = 30 x 0.016/ 50= 0.0096 M

Permanent hardness of water

= 0.0096 x 100 x 1000 = 960 ppm

Temporary hardness

= Total hardness – Permanent hardness

= 1280 – 960 = 320 ppm

BOILER TROUBLES:

Water finds a great use in various industries for generation of steam in boilers. When water is continuously evaporated to generate steam, the concentration of the dissolved salts increase progressively causing bad effects for steam boilers. The following are the boiler troubles that arise:

(1) Priming and foaming
(2) Caustic embrittlement
(3) Boiler corrosion
(4) Scale and sludge formation

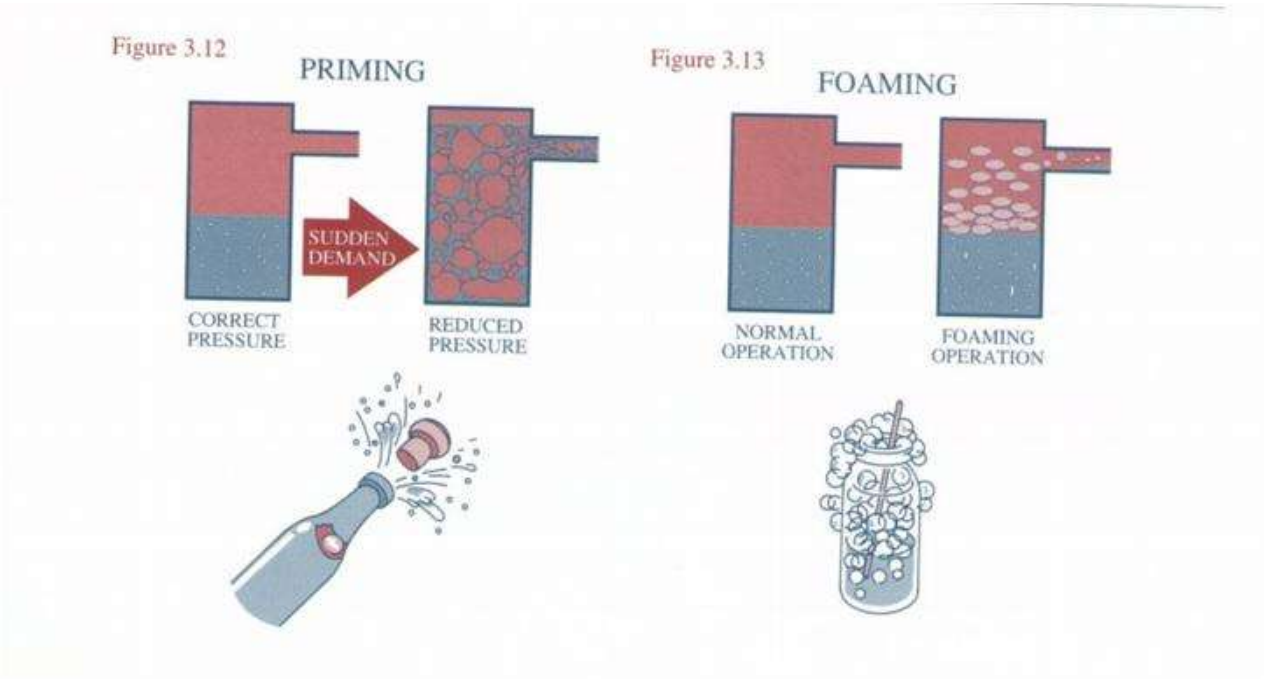
PRIMING & FOAMING:

Priming: When a boiler is steaming rapidly, some particles of the liquid water are carried along with the steam. This process of “WET STEAM” formation is called ‘PRIMING’. Priming is caused by:

(1) Presence of large amount of dissolved solids
(2) High steam velocities
(3) Sudden boiling
(4) Improper boiler design
(5) Sudden increase in steam production rate

It can be avoided by: (<u>Preventions</u>)

(1) Maintaining low water level
(2) Using softened water
(3) Fitting mechanical steam purifiers
(4) Using a well-designed boiler
(5) Avoiding rapid change in steam rate
(6) Blow-down of the boiler



FOAMING:

Foaming is phenomenon of formation of foam or bubbles on the surface of water inside the boiler with the result that the foam may pass along with the steam.

Causes: The presence of large quantity of suspended impurities and oils lowers the surface tension producing foam.

Preventions: Foaming can be avoided by-

(1) Adding anti foaming chemicals like castor oil
(2) Removing oil from boiler water by adding compounds like "$NaAlO_2$"
(3) Blow down of the boiler can prevent the foaming

Disadvantages Of Priming & Foaming:

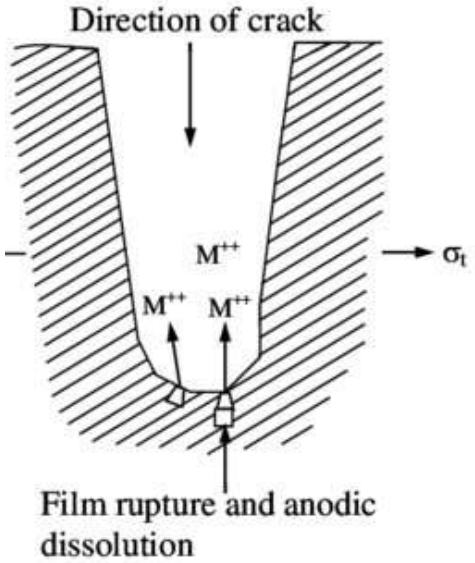
Priming & Foaming may cause the following boiler troubles:-

(1) The actual height of the water in boiler is not judged

(2) Wastage of heat with the result that it becomes difficult to keep up steam pressure and efficiency of the boiler is lowered

CAUSTIC EMBRITTLEMENT:

Caustic embrittlement is a term used for the appearance of cracks inside the boiler particularly at those places which are under stress such as rivetted joints due to the high concentration of alkali leading to the failure of the boiler. The cracks have appearance of brittle fracture. Hence, the failure is called “Caustic Embrittlement”



Reasons for the formation of Caustic Embrittlement:

The boiler feed water containing carbonates and bicarbonates of alkali metals, sodium hydroxide (NaOH) and a small quantity of silica or sodium silicate; it is purified by Lime-Soda Process.

During the softening process by lime soda process, free Na_2CO_3 is usually present in small portion in the soft water which decomposes to give NaOH and CO_2 at high pressure of the boilers.

$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2$

The precipitation of NaOH makes the boiler water "Caustic"

The NaOH containing water flows into the small pits and minute haircracks present on the inner walls of the boiler.

As the water evaporates, the concentration of caustic soda (NaOH) increases progressively, creating a "Concentration Cell"

Thus, dissolving the iron of the boiler as Sodium Ferrate.

$Fe + 2NaOH \rightarrow Na_2FeO_2 + H_2$

The cracking of the boiler occurs particularly at stressed parts like bends, joints, rivets, etc. causing the failure of the boiler.

The iron at plane surfaces surrounded by dilute NaOH becomes Cathodic; while the Iron at bends, rivets and joints is surrounded by highly concentrated NaOH becomes Anodic which consequently decayed or corroded

(Anodic site) Conc NaoH || dil NaoH (Cathodic site)

Iron at Joints &bends Iron at Plane surface

<u>Prevention Of Caustic Embrittlement:</u>

(1) By adding Na_2SO_4 , tannin, etc. to the boiler water which blocks hair cracks. There by preventing infiltration of caustic soda solution

(2) By using sodium phosphate as the softening agent instead of sodium carbonate

DISADVANTAGES OF CAUSTIC EMBRITLLEMENT:

The cracking or weakening of the boiler metal causes failure of the boiler

(3) BOILER CORROSION: The decay of boiler material by chemical/ electro- chemical attack by its environment is called "Boiler Corrosion". Reasons for boiler corrosion are: (a) Dissolved oxygen (b) Dissolved CO_2 (c) Acids from dissolved salts.

(a) <u>Dissolved Oxygen:</u> Water usually contains about 8 mg/L of dissolved oxygen at room temperature. Dissolved O_2 at high temperature attacks boiler material.

$2Fe + 2H_2O + O_2 \rightarrow 2Fe(OH)_2\downarrow$ (ferrous hydroxide)

$4Fe(OH)_2\downarrow + O_2 \rightarrow 2[Fe_2O_3.2H_2O]\downarrow$ (ferric oxide)

<u>Removal of dissolved O_2 :</u>

By adding calculated quantity of sodium sulphate (or) hydrazine (or) sodium sulphide

$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$

Sodium Sulphite

$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$

Hydrazine

$Na_2S + 2O_2 \rightarrow Na_2SO_4$

(b) Dissolved CO_2:

Dissolved CO_2 has slow corrosive effect on the materials of boiler plate. Source of CO_2 into water is the boiler feed water which contains bicarbonates. Under the high temperature and pressure, maintained in the boiler the bicarbonates decompose to produce CO_2.

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

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

The disadvantage of the CO_2 is slow corrosive effect on boiler plates by producing carbonic acid

$CO_2 + H_2O \rightarrow H_2CO_3$

Removal of CO_2:

By the addition of calculated quantity of ammonia.

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

(c) Acids from dissolved salts:

Water containing dissolved Mg-salts liberate acids on hydrolysis

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

Disadvantages of the acid production is that the acids react with Iron of the boiler plate in a chain reaction to produce decay of the metal.

$Fe + 2HCl \rightarrow FeCl_2 + H_2$

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

$Fe(OH)_2 + H_2O + 1/2O_2 \rightarrow Fe_2O_3 .3H_2O$ (ferric oxide)

Consequently even a small amount of $MgCl_2$ can cause corrosion to a large extent.

<u>Preventions:</u>

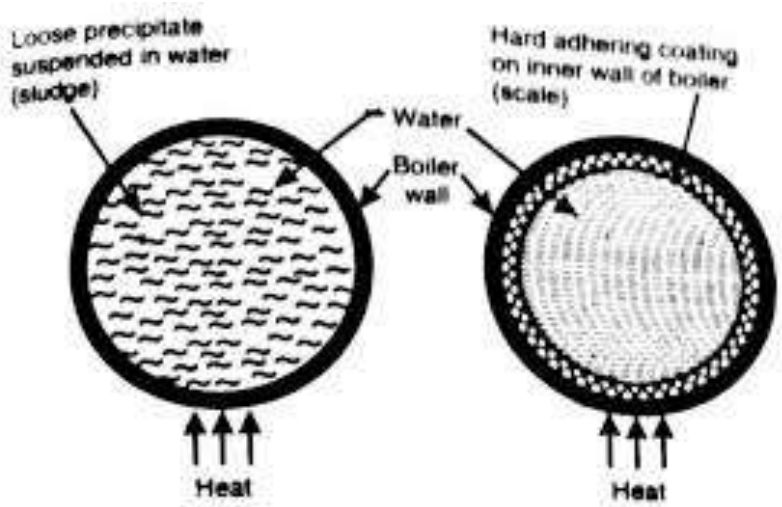
(1) Softening of boiler water to remove $MgCl_2$ from the water
(2) Addition of corrosion inhibitors like sodium silicates, sodium phosphate & sodium chromate
(3) By frequent blow-down operation i.e., removal of water, concentrated with dissolved salts and feeding the boiler with fresh soft water.
(4) Sludges and Scales formation: In boiler, water evaporates continuously and the concentration reaches saturation point, they form precipitates (scale or sludge) on the inner wall of the boiler

SLUDGE: "Sludge is a soft, loose and slimy precipitate formed within the boiler". Sludge are formed by substances which have greater solubility in hot water than in cold water. Salts like $MgCO_3$, $MgSO_4$, $MgCl_2$, $CaCl_2$ etc., are responsible for sludge formation in boilers.

Disadvantages:

(a) Sludge is a bad conductor of heat, hence it wastes a portion of heat generated.

(b) Excessive sludge formation reduces the efficiency of the boiler.



Prevention:

(a) Frequent blow-down operation should be carried out.

(b) Use well-softened water.

SCALES: "Scales are the hard, adhering ppt formed on the inner wall of the boiler". Very difficult to remove once they are deposited on Inner wall of the boiler.

They formed due to decomposition of Calcium bicarbonate, Calcium sulphate etc..,

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

Boiler scale on water side

REMOVAL OF SCALES:

(1) Frequent blow-down operation can remove the scales which are loosely adhering.
(2) By chemical treatment eg: $CaCO_3$ scale removed by washing with 5-10% of HCl.
(3) By giving thermal shocks.

Prevention: Use soft water.

SOFTENING OF WATER:

The removal of hardness causing salts from water is called “Softening of water”.

The 3 Industrial methods employed for softening of water are:

(1) Lime-Soda Process

(2) Zeolite (or) Permutite Process

(3) Ion-Exchange (or) Demineralization process

(1) LIME-SODA PROCESS:

This process is based on converting the soluble calcium and magnesium salts into Insoluble calcium carbonate and magnesium hydroxide precipitates by addition of calculated amount of lime ($Ca(OH)_2$) and Soda (Na_2CO_3). The precipitate are removed by filtration. Any free dissolved CO_2 and acids are also removed by this process. The various chemical reactions involved in this process are:

(a) For Calcium and Magnesium bicarbonates, only lime is required

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

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

(b) For $MgSO_4$ & $MgCl_2$, both lime & soda are required

(iii) $MgSO_4 + Na_2CO_3 + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + CaCO_3\downarrow + Na_2SO_4$

(iv) $MgCl_2 + Na_2CO_3 + Ca(OH)_2 \rightarrow Mg(OH_2)\downarrow + CaCO_3 + 2NaCl$

(c) For $CaSO_4$ & $CaCl_2$, only Soda is required

(v) $CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_4$

(vi) $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2NaCl$

(d) Other Reactions: Free acids, CO2 , H2S dissolved iron and aluminium salts etc are also removed in this process

$2HCl + Na_2CO_3 \rightarrow 2NaCl + H_2O + CO_2\uparrow$

$H_2SO_4 + Na_2CO_3 \rightarrow Na_2SO_4 + H_2O + CO_2\uparrow$

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

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

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

$Al_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Al(OH)_3\downarrow + 3CaSO_4 + H_2O$

Constituent	Reaction	Requirement
Ca^{+2} (Permanent)	(i) $CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_4$ (ii) $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2NaCl$	S
Mg^{+2} (Permanent)	(iii) $MgSO_4 + Na_2CO_3 + Ca(OH)_2 \rightarrow Mg(OH)_2 \downarrow + CaCO_3\downarrow + Na_2SO_4$ (iv) $MgCl_2 + Na_2CO_3 + Ca(OH)_2 \rightarrow Mg(OH_2) \downarrow + CaCO_3 + 2NaCl$	L + S
$HCO3^-$	(v) $2NaHCO_3 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O + Na_2CO_3$	L - S
$Ca(HCO_3)_2$ (Temporary)	(vi) $Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O$	L
$Mg(HCO_3)_2$ (Temporary)	(vii) $Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + Mg(OH)_2\downarrow + 2H_2O$	2L
CO_2	(viii) $CO_2 + Ca(OH)_2 \rightarrow CaCO_3\downarrow + H_2O$	L
H^+	(ix) $2HCl + Ca(OH)_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl + H_2O$	L + S
Coagulants $FeSO_4$	(x) $FeSO_4 + Ca(OH)_2 \rightarrow Fe(OH)_2 + CaSO_4$ $2Fe(OH)_2 + H_2O + O_2 \rightarrow 2Fe(OH)_3$ $CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$	L + S
$Al_2(SO_4)_3$	(xi) $Al_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Al(OH)_3\downarrow + 3CaSO_4 + H_2O$ $3CaSO_4 + 3Na_2CO_3 \rightarrow 3CaCO_3 + 3Na_2SO_4$	L + S
$NaAlO_2$	(xii) $NaAlO_2 + H_2O \rightarrow Al(OH)_3 + NaOH$	-L

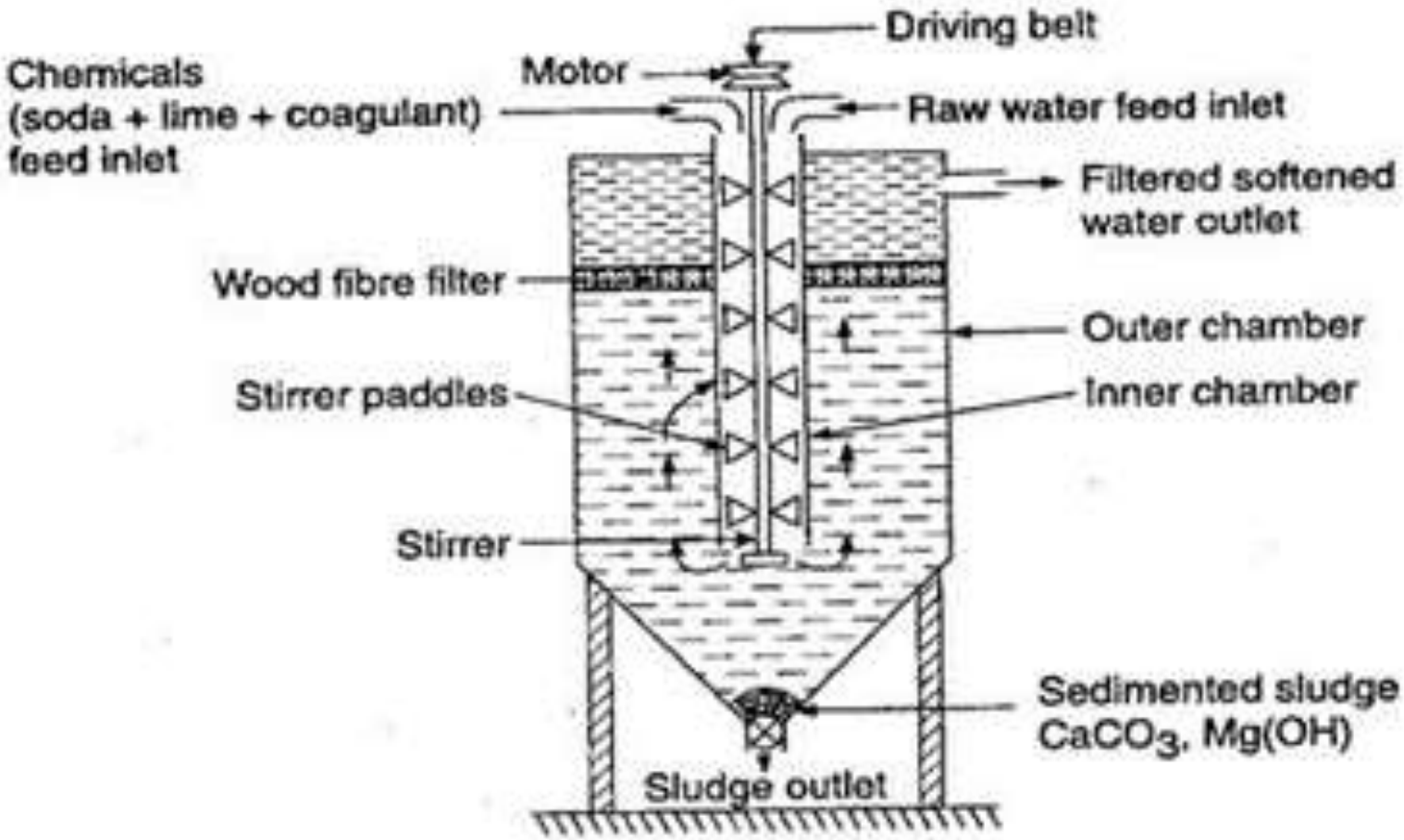
Calculation:

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

(a) Amount of lime required for softening = 74/100 (Temp Ca^{2+} + 2 x Temp. Mg^{2+} + Perm. (Mg^{+2} + Fe^{+2} + Al^{3+}) + CO_2 + H^+ (HCl/H_2SO_4) + HCO_3 - all in terms of $CaCO_3$ equivalent)

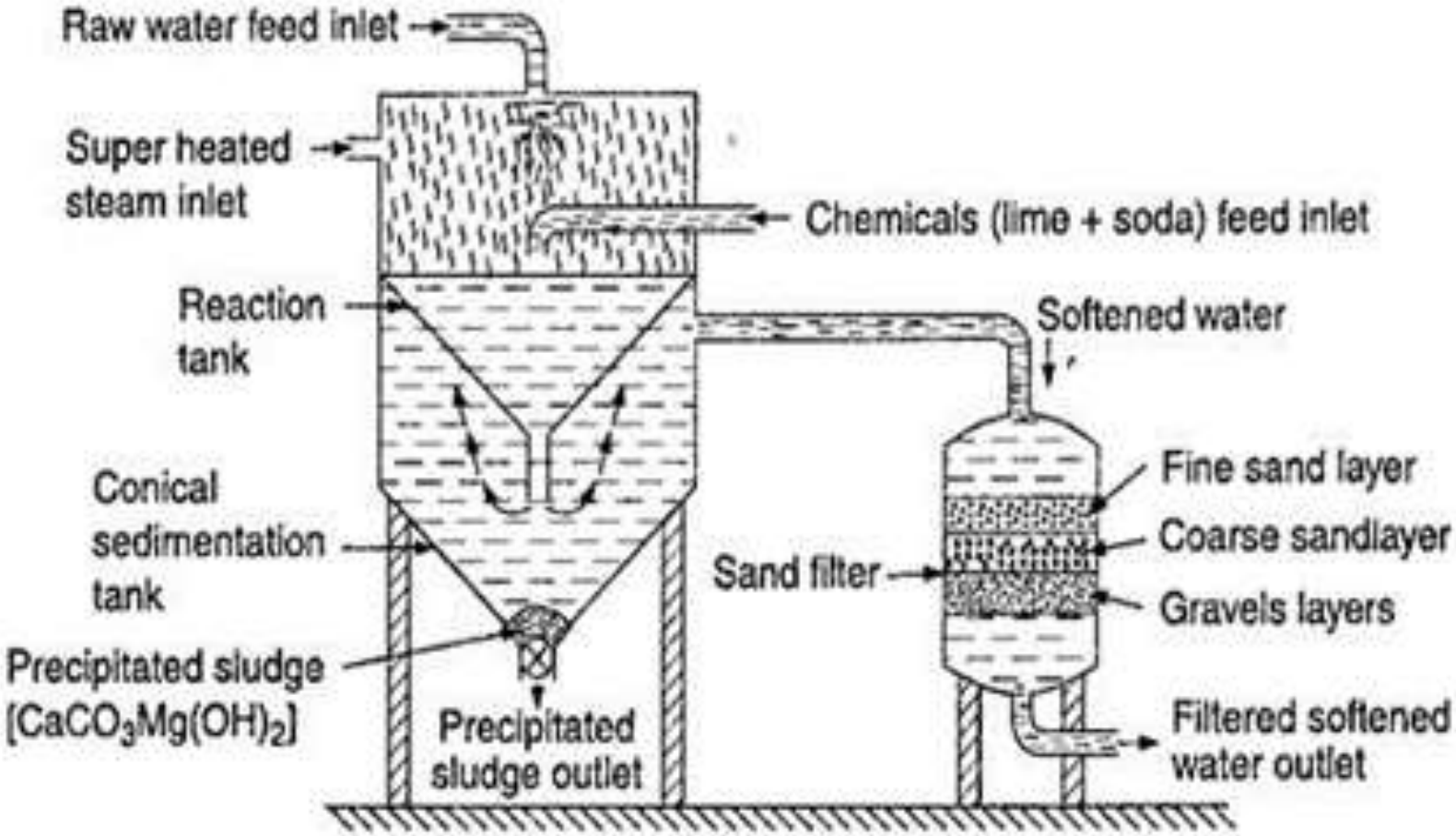
(b) Amount of soda required for softening = 106/100 (Perm. (Ca^{2+} + Mg^{2+} + Fe^{+2} + Al^{3+}) + H^+ (HCl/H_2SO_4) + HCO_3 - all in terms of $CaCO_3$ eq.)

COLD-LIME-SODA PROCESS:



- In this method the lime & soda are mixed with hard water at room temperature with constant stirring.
- Generally the precipitates formed by this process are finely divided and in order to settle the precipitates, coagulants like alum, ferrous sulphate, etc. are added.
- The hard water to be softened is mixed with calculated quantity of chemicals (Lime + Soda + Coagulant) from the top into the inner chamber on vigorous stirring. The chemical reactions takes place and the hardness producing salts get converted into insoluble precipitates.
- The sludge is removed from the bottom of the outer chamber while the softened water passes through a wood fibre filter to ensure the complete removal of any residual sludge particles.
- The clear softened water is withdrawn from the top of the outer chamber.
- The softened water from this process contains a residual hardness of 50-60ppm

HOT-LIME-SODA PROCESS:



- This process is similar to the cold lime-soda process, but no coagulant is needed.
- Here the process is carried at a temperature of 80° to 150^oC. Since the reaction carried out at high temperature.

  (a) The reaction takes place faster

  (b) The sludge settles rapidly

  (c) Viscosity of soft water is lower, hence filtered easily

  (d) The dissolved gases such as CO_2, air, etc. driven out of the water

  (e) The residual hardness is low, compared to cold lime- soda process.

Hot lime soda process consists of three parts-

- "REACTION TANK" in which complete mixing of water, chemicals and steam takes place and water gets softened.
- "Conical Sedimentation Vessel" where the sludge settle down.
- "SAND FILTER" where sludge is completely removed.

The softened water from this process contains a residual hardness of 15-30 ppm.

ADVANTAGES OF LIME-SODA PROCESS:

I. This process is economical.
II. Mineral content of the water is reduced.
III. The process increases the pH value of water, which reduces the content of pathogenic bacteria.
IV. Manganese and Iron salts are also removed by this process.
V. The process improves the corrosion resistance of the water.

DISADVANTAGES OF LIME-SODA PROCESS:

1) Due to residual hardness, water is not useful for high pressure boilers.
2) Large amount of sludge is formed which create disposal problem.

PROBLEMS:

1) Calculate the quantities of Lime & Soda required to soften 5000 litres of water containing the following salts: $MgCl_2$ = 15.5 ppm; $Ca(HCO_3)_2$ = 32.5 ppm, $CaSO_4$ = 22.4 ppm; $Mg(HCO_3)_2$ = 14.6 ppm; NaCl = 50 ppm

Soln: Calculation of Calcium Carbonate Equivalents:

Impurity mg/L	M. Wt.	CaCO3 eq.	Requirement
$MgCl_2$ = 15.5	95	15.5 x 100 ÷ 95= 16.31	L + S
$Ca(HCO_3)_2$ = 32.5	162	32.5 x 100 ÷ 162= 20.06	L
$CaSO_4$ = 22.4	136	22.4 x 100 ÷ 136= 16.47	S
$Mg(HCO_3)_2$ = 14.6	146	14.6 x 100 ÷ 146= 10	2L
NaCl = 50	-		

Lime = 74/100 (Temp Ca^{2+} + 2 x Temp. Mg^{2+} + Perm. (Mg^{+2} + Fe^{+2} + Al^{3+}) + CO_2 + H^+ (HCl/H_2SO_4) + HCO_3 - all in terms of $CaCO_3$ equivalent) x (Vol of water/ 1000) x (100/ %P)

Lime required for litre of water:

= 74/100 ($Ca(HCO_3)_2$ + 2 x $Mg(HCO_3)_2$ + $MgCl_2$) as $CaCO_3$ eq.

= 74/100 (20.06 + 2x10 + 16.31)

= 74/100 x 56.37

= 41.71 mg

Lime req'd for 5000 litres of water

= 41.71 x 5000 ÷ 1000 = 208.55 g= 0.208 kg

Soda = 106/100 (Perm. (Ca^{2+} + Mg^{2+} + Fe^{+2} + Al^{3+}) + H^+ (HCl/H_2SO_4) + HCO_3 - all in terms of $CaCO_3$ eq.) x (Vol of water/ 1000) x (100/ %P)

Soda req'd for litre of water

= 106/100 [$MgCl_2$ + $CaSO_4$] as $CaCO_3$ eq.

= 106/100 [16.31 + 16.47]

= 106/100 [32.78]

= 34.74 mg

Soda req'd for 5000 litres of water:

= 34.74 x 5000 ÷ 1000 = 173.70 gm= 0.173 kg

Zeolite or Permutit Process:

Zeolite is "Hydrated sodium alumino silicate". Its general formula is: $Na_2O.Al_2O_3.xSiO_2.yH_2O$; x= 2-10 y= 2- 6. Eg: Natrolite: $Na_2O.Al_2O_3.3SiO_2.2H_2O$. Natural zeolites are generally non-porous.

The artificial zeolite is called Permutit. These are prepared by heating together with chain clay, feldspar and soda ash. These are porous and have greater softening capacity than natural zeolite.

Working:

They exchange Na^+ ions with the hardness, producing ions (Ca^{2+}, Mg^{2+}, etc.) in water.

Sodium Zeolite is denoted as Na_2Ze.

PROCESS: In this process hard water is passed through a bed of zeolite at ordinary temperature. The hard water percolates (filtered), Ca^{+2}, Mg^{2+} present in hard water are exchanged with Na^+ ions. The following reactions taking place:

$MgCl_2 + Na_2Ze \rightarrow MgZe + 2NaCl$

$MgSO_4 + Na_2Ze \rightarrow MgZe + Na_2SO_4$

$CaCl_2 + Na_2Ze \rightarrow CaZe + 2NaCl$

$CaSO_4 + Na_2Ze \rightarrow CaZe + Na_2SO_4$

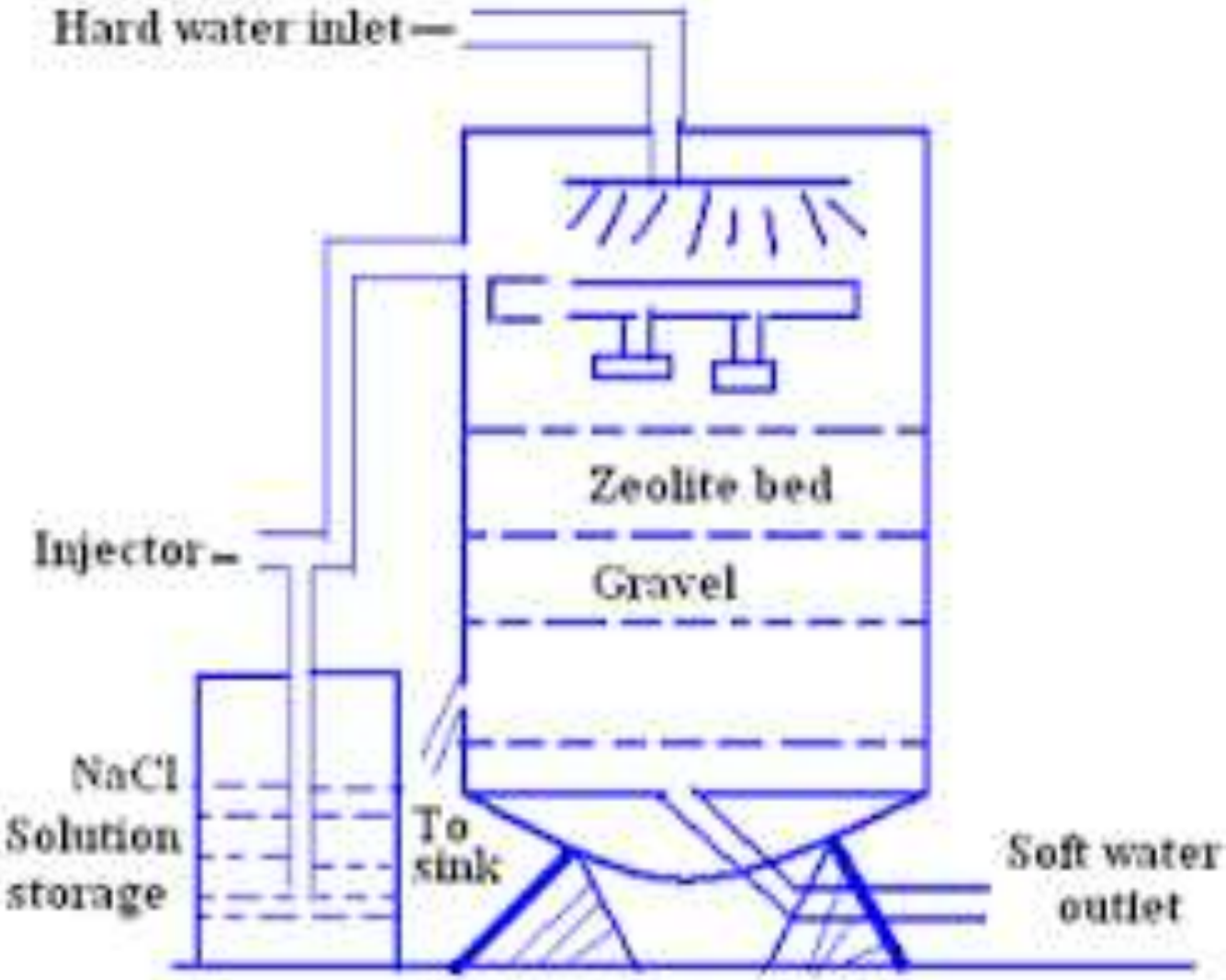
$Mg(HCO_3)_2 + Na_2Ze \rightarrow MgZe + 2NaHCO_3$

$Ca(HCO_3)2 + Na_2Ze \rightarrow CaZe + 2NaHCO_3$

Regeneration Of Zeolite: On continuous passing of hard water through sodium zeolite bed it is converted to calcium and magnesium zeolite which is known as 'Exhausted Bed'. Hence, it must be regenerated. This can be done by washing zeolite bed with 10% sodium chloride solution.

$CaZe + 2NaCl \rightarrow Na_2Ze + CaCl_2$

$MgZe + 2NaCl \rightarrow Na_2Ze + MgCl_2$


Hard water inlet
Zeolite bed
Injector
Gravel
NaCl
Solution
storage
To
sink
Soft water
outlet

ADVANTAGES:

1) The equipment is small and easy to handle.
2) It requires less time for softening.
3) Water obtained from this process contains a residual hardness upto 10 ppm.
4) Easy to regenerate.
5) No sludge is formed in this process.

DISADVANTAGES:

1) Highly turbid water cannot be treated by this process.
2) The process exchanges only Ca^{+2} & Mg^{2+} ions by sodium ions and hence the softened water contains more sodium salts.
3) All the acidic ions like $HCO3^{-}$, $CO3^{2-}$, etc. are not removed by this process.
4) Sodium bicarbonate decomposes in the boiler releasing CO_2 which leads to corrosion.
5) While Na_2CO_3 is hydrolysed to NaOH which creates caustic embrittlement of boiler.

Problem-1:

The hardness of 10,000 Lit of hard water was completely removed by passing it through a zeolite softner. The zeolite softner required 5000Lit of NaCl solution containing 1170mg/Lit. Determine the hardness of water sample.

Solution: 5000L of NaCl solution= 5000 x 1170mg/Lit

= 5850000mg

$$= 5850000 \times \frac{50}{58.5} \text{ mg } CaCO_3 \text{ eq.}$$

= 5000000mg

Hardness of 10000Lit water= 5000000mg

Thus, hardness for 1Lit= 5000000/ 10000 = 500mg $CaCO_3$ eq

Hence, Hardness = 500ppm

Problem-2:

An exhausted zeolite softner was regenerated by passing 75Lit of NaCl solution having strength 75g/Lit. If hardness of water is 300ppm, then calculate the total volume that can be softened by the zeolite.

Solution: Amount of NaCl in 75Lit= 75 x 75 = 5625gm of NaCl

Quantity of NaCl= $5625 \times \frac{100}{117}$ = 4807.69gm= 4.81×10^6mg $CaCO_3$ eq.

Hardness= 300ppm

So, 4.81×10^6 ppm is present in $\frac{4.81 \times 10^6}{300}$ Lit of water

= 1.6×10^4 Lit

Thus, Zeolite can soften 1.6×10^4 Lit of water

ION EXCHANGE PROCESS/ DEMINERALISATION PROCESS:

Ion exchange resins are insoluble, cross-linked, long chain organic polymers.

The functional groups attached to the chains can exchange hardness producing cations and anions present in the water.

PROCESS: The process involves the following steps:

1) The first chamber is packed with cation exchange resin (RH^+). When the hard water is passed through a bed of cation exchange resin it exchanges H^+ with Ca^{+2}, Mg^{+2}, K^+, Na^+ etc. of hard water.

$2RH^+ + Mg^{+2}Cl_2 \rightarrow R_2Mg^{2+} + 2H^+Cl$

$2RH^+ + Ca^{2+}Cl_2 \rightarrow R_2Ca^{2+} + 2H^+Cl$

Thus, the hardness producing cations (Ca^{2+}, Mg^{2+} etc) are removed

1) The second chamber is packed with anion exchange resin. The water coming out of the first chamber contains H^+, Cl^-, SO_4^{2-} and HCO_3^- ions.

It is now passed through anion exchange resin bed which can exchange OH^- ions with anions like Cl^-, SO_4^{2-} and HCO_3^-

$R\text{-}OH + Cl^- \rightarrow RCl + OH^-$

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

Thus, hardness producing anions like Cl^-, SO_4^{2-} and HCO_3^- are removed.

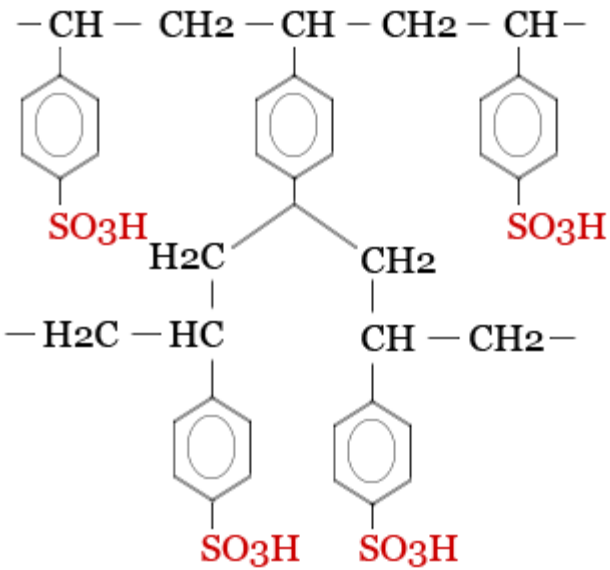
3) Thus, H^+ ions produced from first chamber combine with OH^- ions produced from second chamber to form water.

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

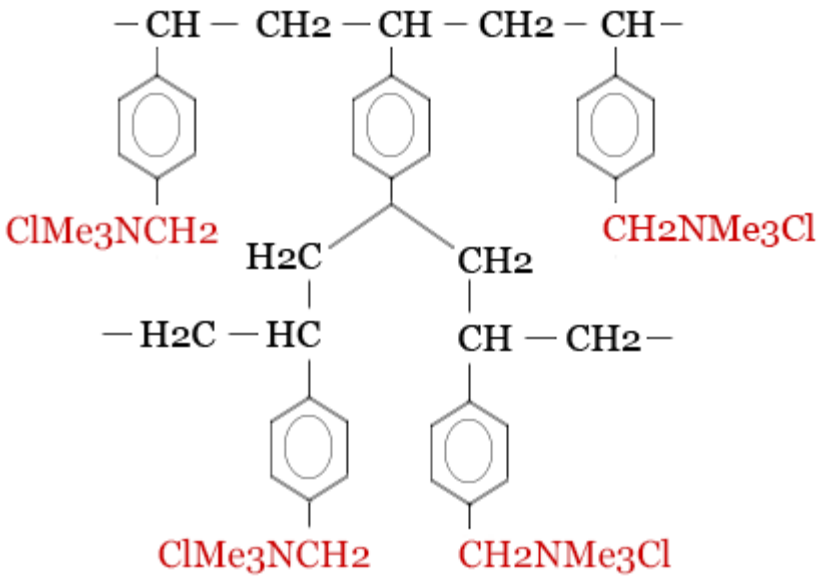
Hence, the water produced from ion-exchange process is completely free from all cations and anions of salts.

Ion Exchange Resin

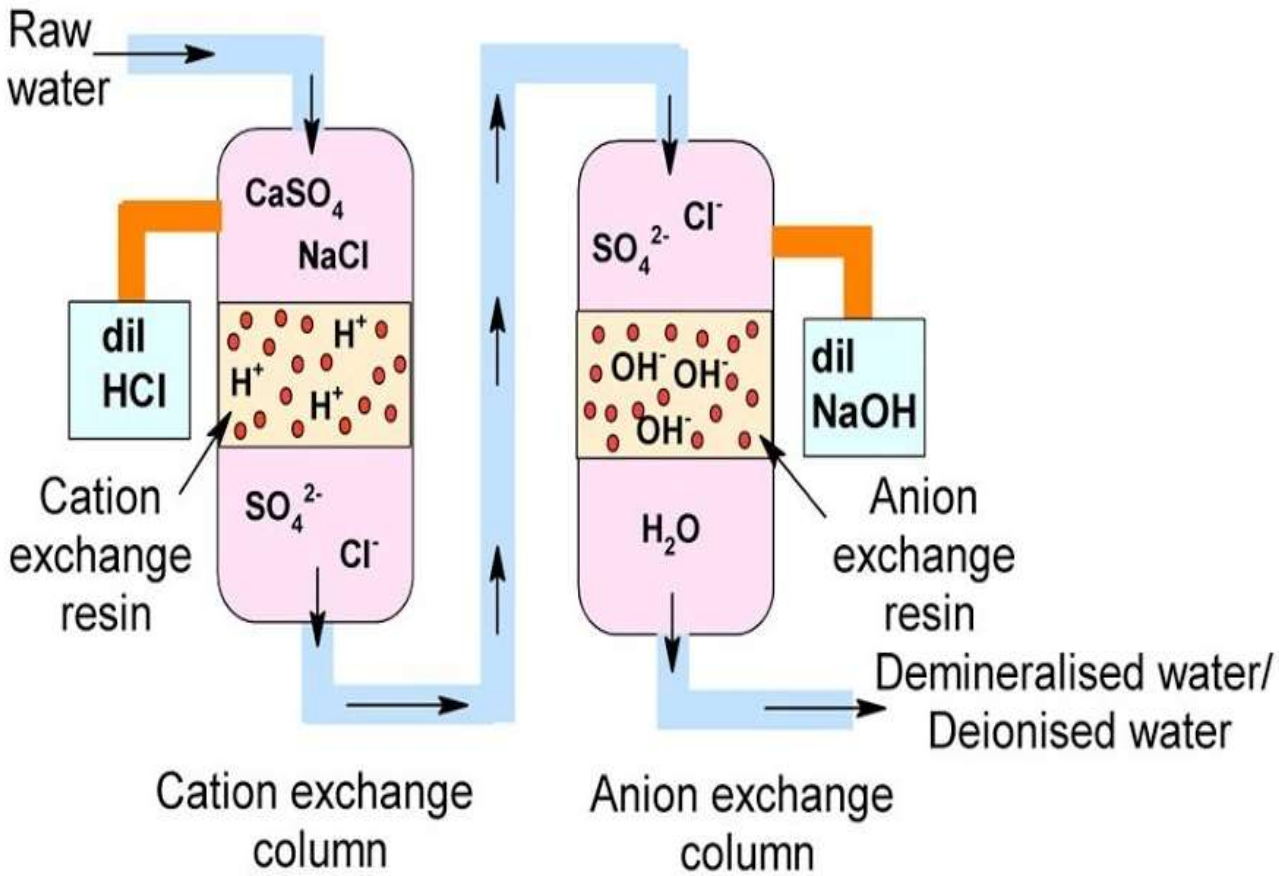
Cation exchange resin



Anion exchange resin



DEMINERALISATION PROCESS/ ION-EXCHANGE PROCESS



REGENERATION OF RESINS:

The resin bed gets exhausted, when used for a long period and can be regenerated:

(a) The exhausted cation exchange resin can be regenerated by passing dil. HCl (H^+)

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

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

(b) The exhausted anion exchange resin can be regenerated by passing dil. NaOH (OH^-)

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

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

ADVANTAGES:

1) The softened water by this method is completely free from all salts and fit for use in boilers.

2) It produces very low hardness nearly 2 ppm.

3) Highly acidic or alkaline water can be treated by this process.

DISADVANTAGES:

1) The equipment is costly.

2) More expensive chemicals are required for regeneration.

3) Turbid water cannot be treated by this method.

Numerical

After treating 10^4 litres of water by ion-exchange, the cationic resin required 200 litres of 0.1N HCl and the anionic resin required 200 litres of 0.1N NaOH solutions for regeneration. Find the hardness of water.

Solution: Hardness of 10^4 litres of water= 200lit of 0.1N HCl

= 200 x 0.1 Lit x 1 N $CaCO_3$ eq.

= 20 lit of 1N $CaCO_3$ eq.

= 20 x 50 g of $CaCO_3$ eq.

= 1000 g of $CaCO_3$ eq.

So, Hardness in 1lit water= 1000/ 10^4 g of $CaCO_3$ eq.

= 100 mg of $CaCO_3$ eq.

Thus, hardness of water sample= 100ppm

DESALINATION OF BRACKISH WATER:

Water containing high concentrations of dissolved solids with a peculiar salty or brackish taste is called ‘brackish water’.

Sea water is an example of brackish water containing about 3.5% of dissolved salts. This water cannot be used for domestic and industrial applications unless the dissolved salts are removed by desalination.

Commonly used methods are: 1) Electrodialysis 2) Reverse Osmosis

Electrodialysis:

Electrodialysis is based on the principle that the ions present in saline water migrate towards their respective electrodes through ion selective membranes under the influence of applied e.m.f.

The unit consists of a chamber with two electrodes, the cathode and anode.

The chamber is divided to 3-compartments with the help of thin, rigid, ion-selective membranes which are permeable to either cation or anion.

The anode is placed near anion selective membrane while the cathode placed near cation selective membrane.

The anion selective membrane is containing positively charged functional groups such as R_4N^+ and is permeable to anions only.

The cation selective membrane consists of negatively charged functional groups such as RSO_3^- and is permeable to cations only.

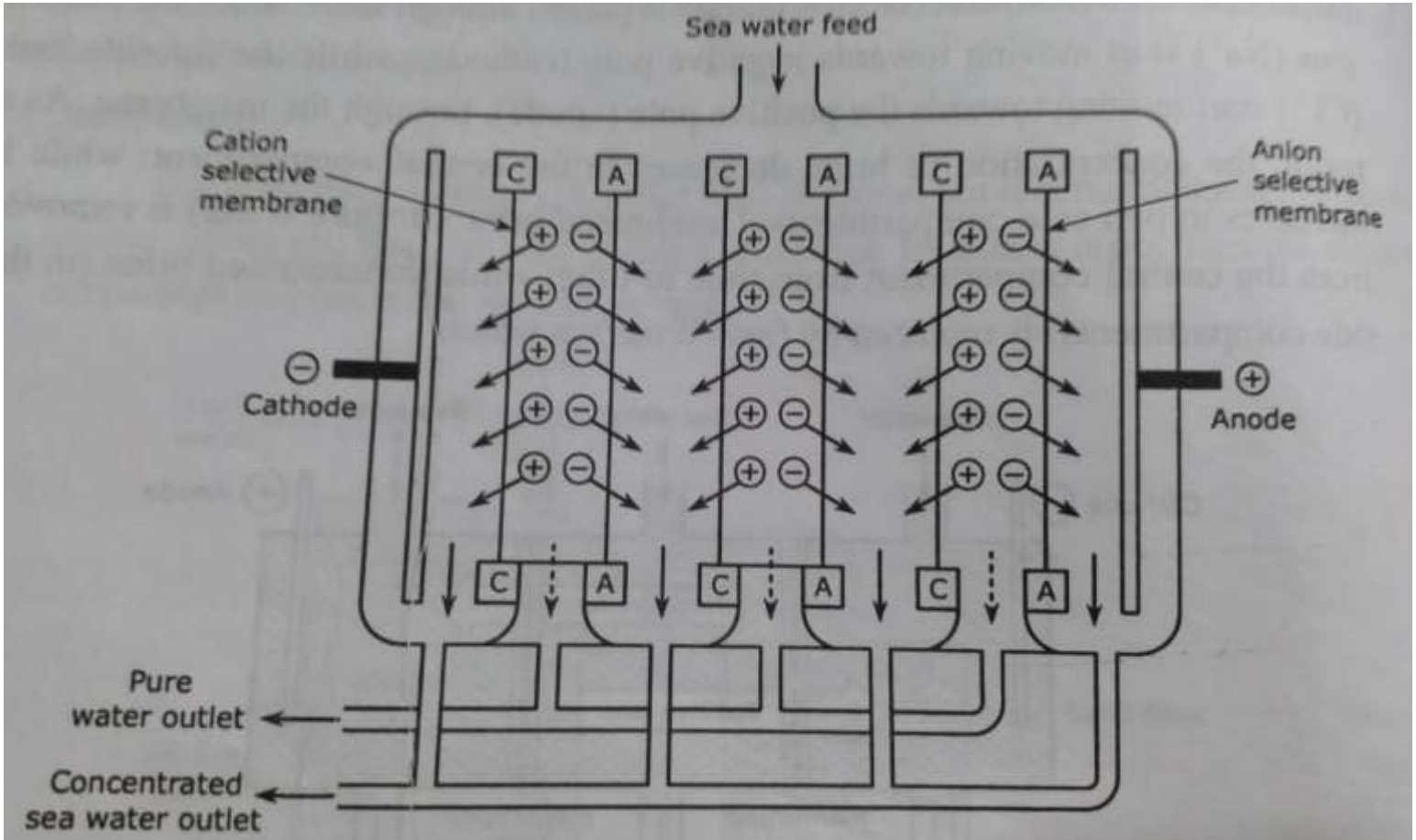


Fig. 1.13 : Electrodialysis cell

Under the influence of applied e.m.f. across the electrodes the cations move towards cathode through the membrane and the anions move towards anode through the membrane.

The net result is depletion of ions in the central compartment, while it increases in the cathodic and anodic compartments.

Desalinated water is periodically drawn from the central compartment while concentrated brackish water is replaced with fresh sample.

ADVANTAGES OF ELECTRODIALYSIS:

The unit is compact.

The process is economical as for as capital cost and operational expenses are concerned.

REVERSE OSMOSIS:

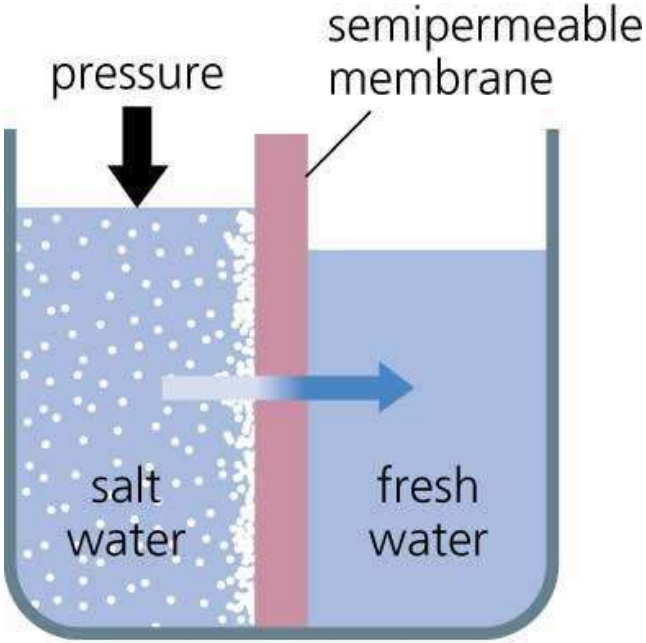
When two solutions of unequal concentration are separated by a semi-permeable membrane which does not permit the passage of dissolved solute particles, i.e., molecules and ions, flow of solvent takes place from the dilute solution to concentrated solution this is called as “OSMOSIS”.

If a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated side the solvent is forced to move from higher concentration to lower concentrated side across. Thus, solvent flow is reversed hence this method is called “Reverse Osmosis”

Thus, in reverse osmosis pure water is separated from the contaminated water. This membrane filtration is also called “Super Filtration” or “Hyper-Filtration”.

METHOD OF PURIFICATION:

The reverse osmosis cell consists of a chamber fitted with a semi-permeable membrane, above which sea water/ impure water is taken and a pressure of 15 to 40 kg/cm^2 is applied on the sea water/ impure water. The pure water is forced through the semi permeable membrane which is made of very thin films of cellulose acetate. However superior membrane made of Polymethacrylate and Polyamide polymers have come to use.



ADVANTAGES:

Both ionic and non-ionic colloidal and high molecule weight organic matter is removed from the water sample

Cost of purification of water is less and maintenance cost is less.

This water can be used for high pressure boilers.

BOD and COD

BOD (Biological Oxygen Demand)

- It is a measure of amount of oxygen required for the biological oxidation of organic matter under aerobic conditions at 20°C for a period of 5 days.

Organic matter + O_2 $\xrightarrow{\text{Micro-organisms}}$ $CO_2 + H_2O$

- BOD is the direct measurement of extent of pollution in waste water & industrial effluent.
- Only applicable for bio-degradable pollutants.
- Higher the BOD, higher will be the level of pollutants in water.
- **Drinking water should have BOD less than 1 ppm.**

Principle

- Dissolved oxygen content of diluted waste-water is determined at the beginning of the reaction by Winkler's method or by DO meter.
- Same sample of water is kept for incubation in the presence of micro-organisms for 5 days at 20°C and decrease in the dissolved oxygen content is determined by Winkler's method or by DO meter.

$$BOD = [(DO)_{Blank} - (DO)_{Incubated}] \times \text{Dilution Factor}$$

$(DO)_{Blank}$ = Dissolved oxygen of diluted sample in the beginning of the reaction

$(DO)_{Incubated}$ = Dissolved oxygen of diluted sample after incubation for 5 days at 20 ^{0} C.

$$\text{Dilution Factor} = \frac{\text{Volume of sample after dilution}}{\text{Volume of sample before dilution}}$$

Significance of BOD

1. BOD gives the extent of bio-degradable pollutants in wastewater sample
2. It also helps in pollution control in water
3. It also express self-purification capacity of any water body.

BOD Meter

COD (Chemical Oxygen Demand)

- It is a measure of amount of oxygen required for the chemical oxidation of organic matter when refluxed in acidified potassium dichromate in the presence of Ag_2SO_4 or $HgSO_4$ catalyst for 3 hours.

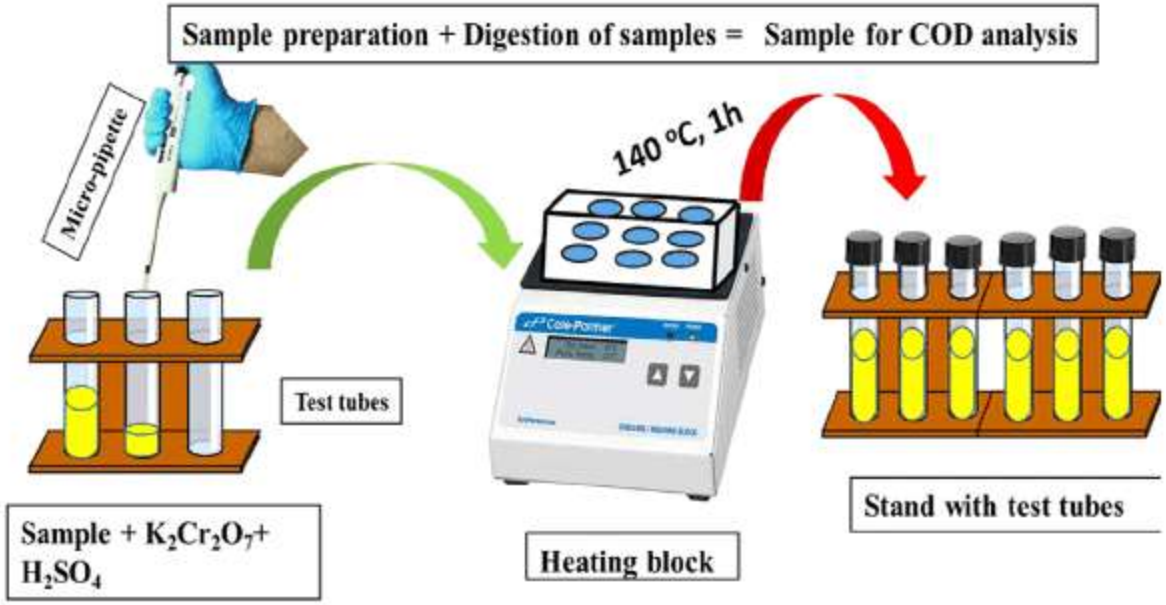
$$\underset{\text{(Organic matter)}}{\mathbf{CxHyOz}} + \underset{\text{[O]}}{\mathbf{(X + Y/4 - Z/2)\ O_2}} \longrightarrow \mathbf{X\ CO_2 + (Y/2)\ H_2O}$$

- COD is the direct measurement of extent of pollution in waste water & industrial effluent.
- Applicable for both bio-degradable and non bio-degradable pollutants.
- Higher the COD, higher will be the level of pollutants in water.
- **Drinking water should have COD less than 1 ppm.**

Principle

- A known volume of waste water sample (say 250 ml) is refluxed with a known excess of standard potassium dichromate (1 N) and dilute/conc. sulfuric acid mixture in the presence of silver sulphate catalyst for about 3 hours.
- This oxidases organic matter to CO_2, NH_3 and H_2O.
- The unreacted potassium dichromate is titrated against Ferrous ammonium sulphate (Mohr's salt) with ferroin indicator till blue colour changes to wine red, the reading is **(Vt).**
- This gives the amount of potassium dichromate consumed (in terms of equivalent oxygen) required for degradation of organic pollutants.
- Blank titration is performed initially with known volume of distilled water sample and added acidified standard potassium dichromate titrated against Ferrous ammonium sulphate (Mohr's salt) with ferroin indicator till blue colour changes to wine red, the reading is **(Vb)** (zero minute reading)

COD Meter


Sample preparation + Digestion of samples = Sample for COD analysis
Micro-pipette
140 °C, 1h
Test tubes
Sample + $K_2Cr_2O_7$+ H_2SO_4
Heating block
Stand with test tubes

Principle

$$COD = \frac{(Vb - Vt) \times N_{FAS} \times 8 \times 1000}{Y} \quad mg/L \text{ or } ppm$$

Vb = Volume of FAS required for blank titration

Vt = Volume of FAS required for reaction mass after time

Y = Volume of waste water sample taken

Significance of COD

1. COD gives the extent of pollution caused by bio-degradable and non bio-degradable pollutants in wastewater sample

2. It helps in rapid determination of pollutants level in water compared to BOD

3. It is taken as a basis for calculation of efficiency and designing of water treatment plants.

Comparison between BOD and COD

BOD	COD
It measures oxygen demand of bio-degradable organic pollutants only	It measures oxygen demand of bio-degradable and non biodegradable organic pollutants
Less stable measurement technique as micro-organisms are susceptible to variables such as pH and temperature	More stable measurement technique as no micro-organisms are used and potassium dichromate oxidizes any type of organic pollutants in water
Slow process, takes 5 days	Fast process , takes 3 hours
BOD values are generally less than COD values	COD values are generally greater than BOD values

Formulae

1. BOD = [$(DO)_{Blank}$ – $(DO)_{Incubated}$] x Dilution Factor

$(DO)_{Blank}$ = Dissolved oxygen of diluted sample in the beginning of the reaction

$(DO)_{Incubated}$ = Dissolved oxygen of diluted sample after incubation for 5 days at 20 ^{0} C.

$$\text{Dilution Factor} = \frac{\text{Volume of sample after dilution}}{\text{Volume of sample before dilution}}$$

2.

$$COD = \frac{(Vb - Vt) \times N_{FAS} \times 8 \times 1000}{Y} \quad \text{mg/L or ppm}$$

Vb = Volume of FAS required for blank titration

Vt = Volume of FAS required for reaction mass after time

Y = Volume of waste water sample taken

Problem 1.20.58 : *Two BOD bottles contained each of 5 ml of sewage sample and water diluted with distilled water to 300 ml. One 100 ml portion of the blaenk consumed 6.4 ml of 0.05 N thiosulphate in the Winkler's method for the determination of dissolved oxygen while 100 ml of the second bottle incubated at 20 ℃ for the five days required 1.6 ml of the same thiosulphate solution. Calculate the BOD content of the sample.*

Solution : Difference in the volume of thiosulphate solution required for blank and the sample solution.

= 6.4 – 1.6 = 4.8 ml of 0.05 N thiosulphate solution

Since 1 litre of 1 N thiosulphate solution = 8 g oxygen

4.8 ml of 0.05 thiosulphate solutio n = [(8 * 4.8 * 0.05)/1000] * 100/300

$= 3.4 \times 10^{-4}$ g oxygen for 5 ml of sewage sample

Oxygen required for 1000 ml of sewage sample = 0.128 g

BOD for sample = 1285 mg/lit

...Ans.

A 50 ml of sample contains 840 ppm dissolved oxygen. After 5 days the dissolved oxygen value becomes 230 ppm after the sample has been diluted to 80 ml. Calculate the BOD of the sample.

Problem 1.20.60 : *A 10 ml of sample of waste water was refluxed with 20 ml of potassium dichromate solution and after refluxing the excess unreacted dichromate required 26.2 ml of 0.1 M FAS solution. A blank of 10 ml of distilled water on refluxing with 20 ml of dichromate solution required 36 ml of 0.1 M FAS solution. Calculate the COD value of the wastewater.*

Solution :

Difference in the volumes of the FAS required for the blank and sample solution = 36 – 26.2 = 9.8 ml

Since 1 litre of 1 M FAS = 8 g of oxygen

9.8 ml of 0.1 M FAS = 8 * 9.8 * 0.1/1000

= $7.84 * 10^{-3}$ of oxygen for 10 ml of sample

Oxygen required for 1000 ml of waste water = 0.784 g

COD for waste water sample = 784 mg/lit **...Ans.**

A 25 ml of sewage water sample was refluxed with 10 ml of 0.25 N $K_2Cr_2O_7$ solution of dil. H_2SO_4, Ag_2SO_4 & $HgSO_4$. The unreacted dichromate required 6.5 ml of 0.1 N ferrous ammonium sulphate. 10 ml of the same $K_2Cr_2O_7$ solution and 25 ml of distilled water under the same conditions as the sample required 27 ml of 0.1 N FAS. Calculate the COD of sewage sample.

WATER FOR DOMESTIC USE & TREATMENT OF WATER FOR MUNICIPAL SUPPLY:

The following are the specification of water drinking purpose:

This water should be clear, colourless and odourless.

The water must be free from pathogenic bacteria and dissolved gases like H2S.

The optimum hardness of water must be 125 ppm and

pH must be 7.0 to 8.5

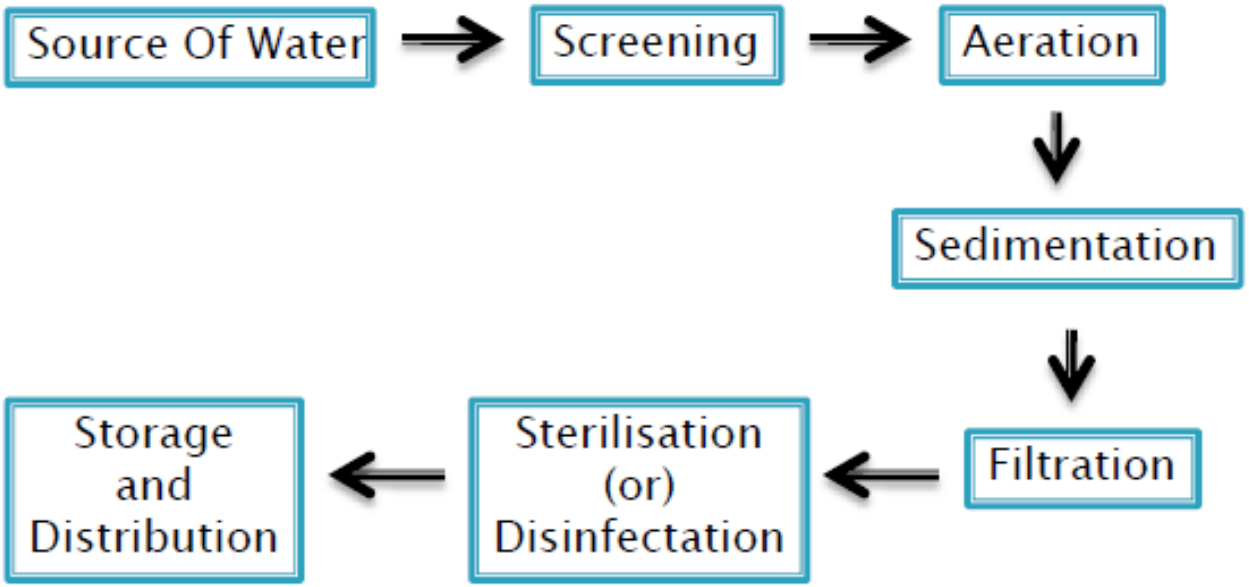
The turbidity in drinking water should not exceed 25ppm

The recommended maximum concentration of total dissolved solids in potable water must not exceed 500ppm

TREATMENT OF WATER FOR MUNICIPAL SUPPLY:

The treatment of water for drinking purposes mainly includes the removal of suspended impurities, colloidal impurities and harmful pathogenic bacteria.

Various stages involved in purification of water for Municipal Supply:



1) SCREENING: The process of removing floating matter from water is known as “Screening”. In this process, water is passed through a screen (mesh/ sieve). The floating matter is arrested by the screen and the water is free from the floating matter.

2) AERATION: The water is then subjected to aeration which
i) Helps in exchange of gases between water and air.
ii) Increases the oxygen content of water
iii) Removes the impurities like ‘Fe’ and ‘Mn’ by precipitating as their hydroxides.

3) SEDIMENTATION:
i) Plain Sedimentation: The process of removing big sized suspended solid particles from water is called ‘Plain Sedimentation’. In this process, water is stored in big tanks for several hours. 70% of the solid particles settle down due to the force of gravity.

ii) Sedimentation By Coagulation:
This is the process of removing fine suspended and colloidal impurities by adding coagulants like alum, ferrous sulpate and sodium aluminate.
When coagulant is added to water, “Floc Formation” takes place due to hydroxide formation which can gather tiny particles together to form bigger particles and settle down quickly.

4) FILTRATION: This process of passing a liquid containing suspended impurities through a suitable porous materials so as to effectively remove suspended impurities and some micro-organisms is called “Filtration”.
It is mechanical process. When water flows through a filter bed, many suspended particles are unable to pass through the gaps and settle in the bed.

5) DISINFECTION OR STERILISATION: The process of killing pathogenic bacteria and other micro-organisms is called ‘Disinfection or Sterilisation’. The water which is free from pathogenic bacteria and safe for drinking is called Potable water. The chemicals used for killing bacteria are called ‘DISINFECTANTS’.

a) By adding Bleaching Powder: Water is mixed with required amount of bleaching powder, and the mixture is allowed o stand for several hours

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

$Cl_2 + H_2O \rightarrow HOCl + HCl$

(Hypo Chlorous Acid)

Germs + HOCl → Germs are killed

The disinfection action of bleaching powder is due to available chlorine in it. It forms hypochlorous acid which act as a powerful germicide (disinfectant).

b) CHLORINATION: Chlorine is mixed with water in a chlorinator, which is a high tower having a number of baffle plates. Water and required quantity of concentrated chlorine solution are introduced from its top during their passage through the tower. They get thoroughly mixed and then sterilised water is taken out from the bottom.

ADVANTAGES:

i) Storage required less space

ii) Effective and economical

iii) Stable and does not deteriorate

iv) Produces no salts

v) Ideal disinfectant

DISADVANTAGES:

i) Excess of chlorine causes unpleasant taste and odour.

ii) More effective at below pH 6.5 and less effective at higher pH values.

c) OZONATION: Ozone (O_3) is an excellent, disinfectant which can be prepared by passing silent electric discharge through pure and dry oxygen. Ozone is highly unstable and breaks down, liberating nascent oxygen.

$3O_2 \rightarrow 2O_3$

$O_3 \rightarrow O_2 + (O)$ Nascent Oxygen

This nascent oxygen kills bacteria as well as oxidizes the organic matter present in water.

ADVANTAGES:

Removes colour, odour and taste

DISADVANTAGES:

The method is costly.

Sewage treatment/ Activated sludge process

16 WASTE WATER TREATMENT

The main objectives of waste water treatment are :

(*i*) To make sewage inoffensive so that it causes no odour,

(*ii*) To prevent the destruction of aquatic life in rivers, canals, etc. into which waste water is generally discharged.

(*iii*) To reduce or eliminate danger to the public health by possible contamination of water supplies.

Artificial treatment methods are generally used for waste water treatment. The main features of this method are :

(*a*) To reduce the solid contents of the waste water,

(*b*) To remove all nuisance-causing elements, and

(*c*) To change the character of the waste water so that it safely be discharged in river, sea or applied on land.

The following steps are generally employed in the artificial sewage treatment :

(A) Preliminary Process

The preliminary processes cause removal of large and coarse solids and inorganic matter suspended in waste water. The waste water is passed through mesh screens to remove gravels, coarse solids, silt, etc. Moreover, for the removal of large suspended floating matter, the waste water is passed through bar screens.

(B) Settling Process

The suspended inorganic and organic solids from the waste water are largely removed by settling process. In settling process, continuous flow type sedimentation tanks are employed. Sometimes, prior to sedimentation, chemical treatment is given to waste water. This helps in more rapid and complete removal of suspended matter. Alum, ferrous sulphate etc. are chemicals which are used for chemical treatment. These chemicals can produce large gelatinous flocs, which entrap finely divided organic matter and settle rapidly.

$$Al_2(SO)_3 + 6\,H_2O \longrightarrow 2\,Al(OH)_3 \downarrow + 3\,H_2SO_4 \qquad (\text{at pH} \geq 5)$$

It is important to note that chemical coagulants have the ability to remove colloidal materials.

(C) Biological Treatment Process

It is essentially a aeration process in which aerobic chemical oxidation takes place. In this process, aerobic conditions are maintained all the times by filtering waste water through specially designed sprinkling filters. During this process, the carbon of the organic matter is converted into CO_2 ; the nitrogen into NH_3 and finally into nitrites and nitrates. The dissolved bases, present in the waste water, then form nitrite and nitrate of ammonium, and calcium nitrate etc.

Thus :

$$\underset{\text{Urea}}{NH_2CONH_2} \xrightarrow[\text{Aerobic}]{\text{Oxidation}} CO_2 + 2\,NH_3$$

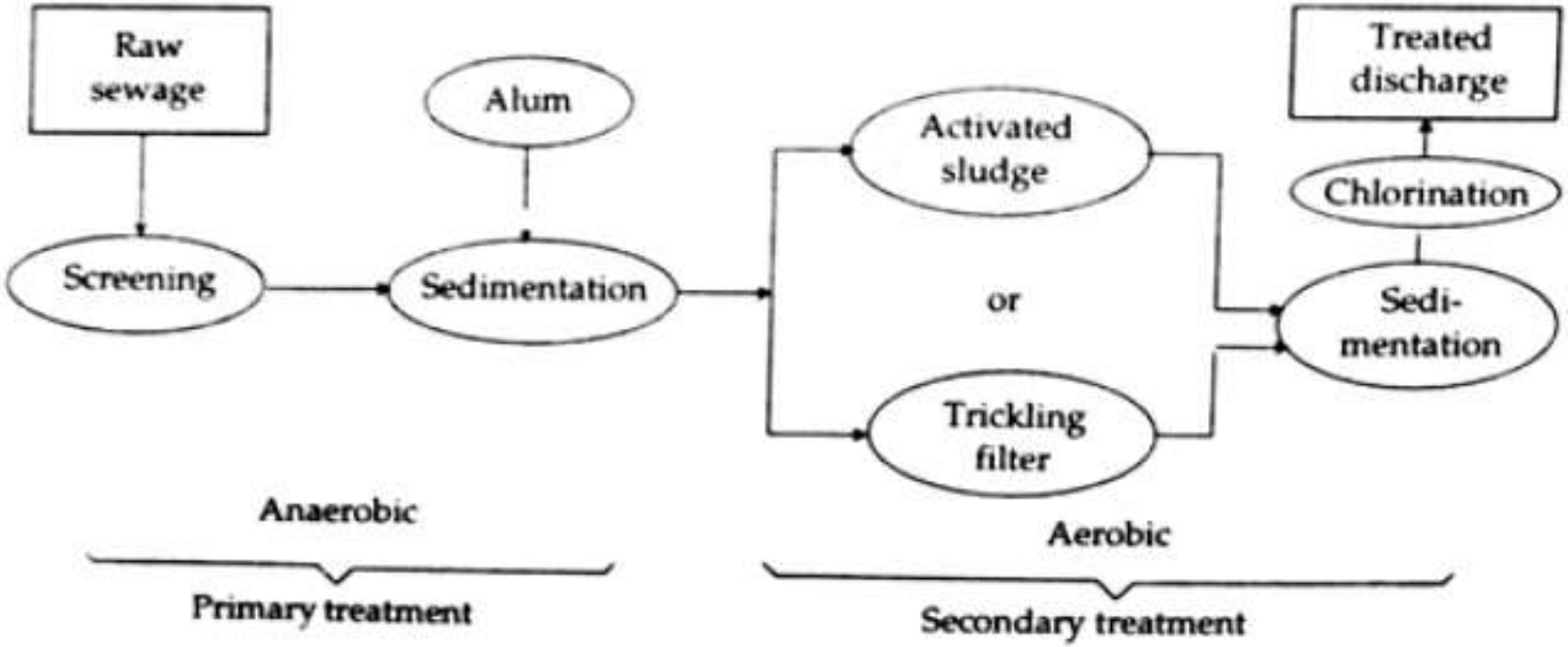
$$NH_3 \xrightarrow{\text{Oxidation}} HNO_3, HNO_2, \text{etc.}$$

In the bottom of bed, the underdrain system is provided to collect effluent. Rotating arm distributions are used for delivering waste water to the filters. As the micro organism present in the waste water grow on surface of aggregates, using the organic material of sewage as food. Aerobic conditions are maintained and purified water is removed from the bottom. About 90% of BOD is removed by normal trickling filters.

Activated Sludge Process

This process is based on the principle that if enough oxygen or air is passed through waste water containing aerobes, slow but complete aerobic oxidation occurs. This oxidation process can be quickened, if this aeration is carried out in the presence of a part of sludge from the previous oxidation process. This sludge is known as *activated sludge* since it contains organic matters inhabited by numerous bacterias, etc.

The activated sludge process consists in mixing the sedimented waste water with proper quantity of activate sludge. This mixture is then sent to the aeration tank, in which the mixed liquor is simultaneously aerated and agitated for 4 to 6 hours. Oxidation of the suspended organic matter takes place during this aeration process. The affluent, after aeration is sent to sedimentation tank. In this tank, sludge is deposited and clean and non-putrefying liquid (*i.e.*, a liquid which is free from bacteria) is drawn off. For seeding fresh batch of sewage, a part of the settled sludge is sent back while the remainder is disposed off by either dumping in sea or spreading uniformly over soil, followed by ploughing in or digestion process.

In this digestion process, the sludge is kept in the absence of air for a prolonged period of about 30 days in a closed tank. The sludge under these conditions suffers anaerobic decomposition yielding gases like methane, hydrogen sulphide, ammonium sulphide and phosphine.

The waste water treatment process is schematically summarized below in Fig. 24.