UNIT -1

WATER AND ITS TREATMENT

Hard Water: The water which does not give lather with soap is called hard water. This is due to presence of

certain salts like Ca^{+2}, Mg^{+2} and other heavy metals dissolved in water

$2C_{17}H_{35}COONa + CaCl_2/MgCl_2 \rightarrow (C_{17}H_{35}COO)_2 Ca/Mg + 2NaCl$

soap (soluble) salts (soluble) insoluble scum

CAUSES OF HARDNESS

Hardness of water is due to the presence of Bicarbonates, Chlorides, Sulphates and Nitrates of Calcium and Magnesium. These soluble salts get mixed with natural water due to the following reasons:

When natural water containing CO_2 flows over the rocks of the limestone ($CaCO_3$) and Dolamite

($CaCO_3$ & $MgCO_3$), they get converted into soluble bicarbonates. Thus, water gets hardness.

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

Insoluble Soluble

When natural water flows over the rocks containing chlorides and sulphates and Nitrates of Calcium

and magnesium, these salts dissolve in water. Thus water gets hardness.

DISADVANTAGES OF HARDNESS

In Domestic use:

Washing: Hard water, when used for washing purposes, does not producing lather freely with soap. As a result cleaning quality of soap is decreased and a lot of it is wasted.

Bathing: Hard water does not lather freely with soap solution, but produces sticky scum on the bath- tub and body. Thus, the cleaning qualityof soap is depressed and a lot of it is wasted.

Cooking: The boiling point of water is increased because of presence of salts. Hence more fuel and time are required for cooking.

Drinking: Hard water causes bad effects on our digestive system. Moreover, the possibility of forming calcium oxalate crystals in urinary tracks is increased.

Industrial Use:

Textile Industry: Hard water causes wastage of soap. Precipitates of calcium and magnesium soaps adhere to the fabrics and cause problem.

Sugar Industry: The water which containing sulphates, nitrates, alkali carbonates are used in sugar refining, cause difficulties in the crystallization of sugar.

Dyeing Industry: The dissolved salts in hard water may reacts with costly dyes forming precipitates.

Paper Industry: Calcium, magnesium, Iron salts in water may affect the quality of paper.

Pharmaceutical Industry: Hard water may cause some undesirable products while preparation of pharmaceutical products.

Steam generation in Boilers:

For steam generation, boilers are almost invariably employed. If the hard water is fed directly to the boilers, there arise many troubles such as: Scales & sludges formation, Corrosion, Priming & Foaming and Caustic embrittlement.

TYPES OF HARDNESS

Hardness of water is mainly two types:

Temporary Hardness 2. Permanent Hardness

Temporary Hardness: Temporary Hardness mainly caused by the presence of dissolved bicarbonates of Calcium, Magnesium ($Ca(HCO_3)_2$, $Mg(HCO_3)_2$). Temporary Hardness can be largely removed by boiling of water.

$Ca(HCO_3)_2$ by heating $CaCO_3\downarrow + H_2O + CO_2$ Calcium bicarbonate

$Mg(HCO_3)_2$ by heating $Mg(OH)_2\downarrow + 2CO_2$ Magnesium bicarbonate

Permanent Hardness: It is due to the presence of dissolved Chlorides, Nitrates and Sulphates of Calcium, Magnesium, Iron and other metals. Permanent hardness responsible salts are $CaCl_2$, $MgCl_2$, $CaSO_4$, $MgSO_4$, $FeSO_4$, $Al_2(SO_4)_3$. Permanent Hardness cannot be removed by boiling but it can be removed by the use of ***chemical agents***.

EXPRESSION AND UNITS OF HARDNESS

The expression of hardness producing salts usually expressed in terms of an equivalent amount of $CaCO_3$. Calcium Carbonate is chosen as a standard because:

Its molecular weight (100) and equivalent weight (50) is a whole number, so the calculations in water analysis can be simplified.

It is the most insoluble salt that can be precipitated in water treatment.

The conversion of the hardness causing salts into $CaCO_3$ equivalents can be achieved by using the following formula:

$$\boxed{\text{Degree of Hardness} = \frac{\text{The weight of hardness causing salts}}{\text{Molecular weight of hardness causing salts}} \times 100 \text{ (Molecular weight of } CaCO_3\text{)}}$$

Units of Hardness:

Parts per Million (ppm): The number of parts of calcium carbonate equivalent hardness presents in 10^6 parts of water.

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

Milligrams per litre (mg/l): The number of milligrams of calcium carbonate equivalent hardness presents in litre of water.

1 mg/L = 1 mg of $CaCO_3$ eq hardness in 1 litre of water. But one litre of water weights =1 kg =1000g = 1000 x 1000 mg = 10^6 mg = 1 ppm.

Clark's degree (°Cl): The number of parts of calcium carbonate equivalent hardness presents in 70,000 or (7×10^4) parts of water.

1° Clarke = 1 part of $CaCO_3$ eq hardness per 70,000 parts of water.

Degree French (°Fr): The number of parts of calcium carbonate equivalent hardness presents in 10^5 parts of water.

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

Relationship between various units of hardness:

1 ppm = 1 mg/L = 0.1° Fr = 0.07° Cl

1 mg/L = 1 ppm = 0.1° Fr = 0.07° Cl

1 ° Cl = 1.433° Fr = 14.3 ppm = 14.3 mg/L

1 ° Fr = 10 ppm = 10 mg/L = 0.7° Cl

Problem-1: A sample of water is found to contains following dissolving salts in milligrams per litre $Mg(HCO_3)_2$ = 73, $CaCl_2$ = 111, $Ca(HCO_3)_2$ = 81, $MgSO_4$ = 40 and $MgCl_2$ = 95. Calculate temporary and permanent hardness and total hardness.

Solution:

Name of the hardness causing salts	Amount of the hardness causing salts(mg/Lit)	Molecular weight of hardness causing salts	Amounts equivalent to $CaCO_3$ (mg/Lit)
$Mg(HCO_3)_2$	73	146	73×100/146 = 50
$CaCl_2$	111	111	111×100/111 = 100
$Ca(HCO_3)_2$	81	162	81×100/162 = 50
$MgSO_4$	40	120	40×100/120 = 33.3
$MgCl_2$	95	95	95×100/95 = 100

Temporary hardness = $Mg(HCO_3)_2$ + $Ca(HCO_3)_2$

= 50 + 50 = 100mgs/Lit.

Permanent hardness = $CaCl_2$ + $MgSO_4$ + $MgCl_2$

= 100 + 33.3 + 100 = 233.3mgs/Lit.

Total hardness = Temporary hardness + Permanent hardness

= 100 + 233.3 = 333.3mgs/Lit.

Problem-2: A sample of water is found to contains following dissolving salts in milligrams per litre $Mg(HCO_3)_2$ = 16.8, $MgCl_2$ = 12.0, $MgSO_4$ = 29.6 and NaCl = 5.0. Calculate temporary and permanent hardness of water.

Solution:

Name of the hardness causing salts	Amount of the hardness causing salts(mg/Lit)	Molecular weight of hardness causing salts	Amounts equivalent to $CaCO_3$ (mg/Lit)
$Mg(HCO_3)_2$	16.8	146	16.8×100/146 = 11.50
$MgCl_2$	12.0	95	12.0×100/95 = 12.63
$MgSO_4$	29.6	120	29.6×100/120 = 24.66
NaCl	5.0	NaCl does not contribute any hardness to water hence it is ignored.	

Temporary hardness = $Mg(HCO_3)_2$ = 11.50mgs/Lit.

Permanent hardness = $MgCl_2$ + $MgSO_4$ = 12.63 + 24.66 = 37.29mgs/Lit.

Problem-3: A sample of water is found to contains following analytical data in milligrams per litre $Mg(HCO_3)_2$ = 14.6, $MgCl_2$ = 9.5, $MgSO_4$ = 6.0 and $Ca(HCO_3)_2$ = 16.2. Calculate temporary and permanent hardness of water in parts per million, Degree Clarke's and Degree French.

Solution:

Name of the hardness causing salts	Amount of the hardness causing salts(mg/Lit)	Molecular weight of hardness causing salts	Amounts equivalent to $CaCO_3$ (mg/Lit)
$Mg(HCO_3)_2$	14.6	146	14.6×100/146 = 10
$MgCl_2$	9.5	95	9.5×100/95 = 10
$MgSO_4$	6.0	120	6.0×100/120 = 5
$Ca(HCO_3)_2$	16.2	162	16.2×100/162 =10

Temporary hardness [$Mg(HCO_3)_2$ + $Ca(HCO_3)_2$] = 10 + 10 = 20mg/Lit

= 20ppm

= 20×0.07°Cl = 1.4°Cl

= 20×0.1°Fr = 2°Fr

Permanent hardness [$MgCl_2$ + $MgSO_4$] = 10 + 5 = 15mg/Lit

= 15ppm

= 15×0.07°Cl = 1.05°Cl

= 15×0.1°Fr = 1.5°Fr

Problem-4: Calculate the amount of temporary and permanent hardness of a water sample in Degree Clarke's, Degree French and Milligrams per Litre which contains following impurities.

$Ca(HCO_3)_2$ = 121.5 ppm, $Mg(HCO_3)_2$= 116.8 ppm, $MgCl_2$ = 79.6 ppm and $CaSO_4$ = 102 ppm.

Solution:

Name of the hardness causing salts	Amount of the hardness causing salts(ppm)	Molecular weight of hardness causing salts	Amounts equivalent to $CaCO_3$ (ppm)
$Ca(HCO_3)_2$	121.5	162	121.5×100/162 = 75
$Mg(HCO_3)_2$	116.8	146	116.8×100/146 = 80

$MgCl_2$	79.6	95	79.6×100/95 = 3.37
$CaSO_4$	102	136	102×100/136 = 75

Temporary hardness [$Mg(HCO_3)_2$ + $Ca(HCO_3)_2$] = 75 + 80 = 155 ppm

= 155×0.07°Cl = 10.85°Cl

= 155×0.1°Fr = 15.5°Fr

= 155×1mg/Lit = 155 mg/Lit Permanent hardness [$MgCl_2$ + $CaSO_4$] = 10 + 5 = 15mg/Lit

= 15ppm

= 15×0.07°Cl = 1.05°Cl

= 15×0.1°Fr = 1.5°Fr

DETERMINATION OF HARDNESS BY COMPLEXOMETRIC METHOD / EDTA METHOD

Principle: The determination of hardness is carried out by titrating water sample with Sodium salt of Ethylene Diamine Tetra Acetic Acid (EDTA)

using Eriochrome Black-T as an indicator and keeping the pH of the water at 9.0 - 10.0. The end point is the change in colour from wine - red to blue, when the EDTA solution complexes the calcium and magnesium salt completely.

(Ca^{2+} or Mg^{2+}) + EBT → [Ca – EBT] (or) [Mg – EBT]

Hardness-salts indicator unstable complex (wine red)

[Ca – EBT] (or) [Mg – EBT] + EDTA → [Ca – EDTA] (or) [Mg – EDTA] + EBT

Unstable complex (wine red) stable complex (colourless) blue

Chemicals Required:

Preparation of standard hard water (0.01M): Dissolve 1g of pure, dry $CaCO_3$ in minimum quantity of dil.HCl and then evaporate the solution to dryness on a water bath. Dissolve the residue in distilled water to make 1 Litre solution. Each ml of this solution thus contains 1mg of $CaCO_3$ equalent hardness.

Preparation of EDTA solution: Dissolve 4 g of pure EDTA crystals + 0.lg $MgCl_2$ in 1 Litre of distilled water.

Preparation of Indicator (EBT): Dissolve 0.5 g of Eriochrome Black–T in 100mL alcohol.

Preparation of Buffer solution: Add 67.5g of NH_4Cl to 570 ml of Con. Ammonia solution and then dilute with distilled water to 1 Litre.

Various steps involved in this method:

Standardization of EDTA solution: Rinse and fill the burette with EDTA solution. Pipette out 20 ml of standard hard water (M_1) in a conical flask. Add 4ml of buffer solution and 2 drops of EBT indicator. Titrate with EDTA solution till wine-red colour changes to clear blue. Let volume used by

'X' ml.

$M_1 V_1 = M_2 V_2$

Where, M_1 = Molarity of Standard Hard water (0.01M), V_1 = Volume of Standard Hard water (20 ml), M_2 = Molarity of EDTA,

V_2 = Volume of EDTA **(Xml)**.

Determination of Total Hardness: Rinse and fill the burette with EDTA solution. Pipette out 20 ml of sample water (V_3) in a conical flask. Add 4 ml of buffer solution and 2 drops indicator. Titrate with EDTA solution till wine-red colour changes to clear blue. Let volume used by **'Y' ml**.

$M_2 V_2 = M_3 V_3$

Where, M_2 = Molarity of EDTA,

V_2 = Volume of EDTA **(Yml)**. M_3 = Molarity of sample water,

V_3 = Volume of Sample water (20 ml).

Total Hardness = M_3 × Molecular weight of $CaCO_3$ (100) × One Litre (1000ml)

= $M_3 \times 10^5$ ppm

Determination of Permanent Hardness: Take 100 ml of sample water in 250 ml beaker. Boil it to remove temporary hardness to about half of its volume and cool to room temperature, filter through filter paper to remove insoluble salts. Make up the volume to the original 100ml by adding distilled water. Now Pipette out 20 ml of this solution (V_4) in a conical flask. Add 4 ml of buffer solution and 2 drops indicator. Titrate with EDTA solution till wine-red colour changes to clear blue. Let volume used by **'Z' ml**.

$M_2 V_2 = M_4 V_4$

Where, M_2 = Molarity of EDTA,

V_2= Volume of EDTA (**Z ml)**.

M_4 = Molarity of Permanent hard water,

V_4 = Volume of Permanent hard water (20 ml)

Permanent Hardness = M_4 × Molecular weight of $CaCO_3$ (100) × One Litre (1000ml)

= $M_4 \times 10^5$ ppm

Determination of Temporary Hardness:

Temporary Hardness = Total Hardness - Permanent Hardness

Problem-1: 50 ml of standard hard water containing 1 gram of pure $CaCO_3$ per liter consumed 20 ml of EDTA. 50 ml of hard water consumed 25 ml of same EDTA solution EBT indicator. Calculate the total hardness of water sample in ppm.

Solution:

Strength of standard hard water sample ($CaCO_3$ solution) M_1=

$$\frac{\text{Weight of } CaCO_3}{\text{Mol. wt of } CaCO_3} \times \frac{1000}{1000}$$

$$= \frac{1\text{ gm}}{100} \times \frac{1000}{1000} = 0.01\text{ M}$$

Strength of EDTA solution M_2 $= \frac{V_1 M_1}{V_2} = \frac{50 \times 0.01}{20} = 0.025$ M

V_1 = Volume of standard hard water (50 ml), M_1 = Strength of standard hard water (0.01M) V_2 = Volume of EDTA solution (20 ml), M_2 =Strength of EDTA solution =?

Calculation of Total hardness M_3 $= \frac{V_2 M_2}{V_3} = \frac{25 \times 0.025}{50} = 0.0125$ M

V_2 = Volume of EDTA solution (25 ml), M_2 =Strength of EDTA solution= 0.025M V_3 = Volume of sample hard water (50 ml), M_3 = Strength of sample hard water =?

Total Hardness = 0.0125×10^5 ppm

= 0.0125 × 100 (Mol. Wt of $CaCO_3$) × 1000 (ml)ppm

= 1250 ppm.

Problem-2: 0.28 grams of $CaCO_3$ were dissolved in HCl and the solution was made upto one litre with distilled water. 100 ml of the above solution required 28 ml of EDTA solution on titration. 100 ml of hard water sample consumed 33 ml of same EDTA solution EBT indicator. 100 ml of this water after boiling cooling and filtering required 10 ml of EDTA solution in titration. Calculate the permanent and temporary hardness of water sample in ppm.

Strength of standard hard water sample (CaCO3 solution) M = Weight of CaCO3 × 1000

Mol. wt of CaCO3 1000

= 0.28gm × 1000 = 0.0028 M

100 1000

Strength of EDTA solution M2 = V1 M1 = 100 × 0.0028 = 0.01 M

V2 28

V1 = Volume of standard hard water (100 ml), M1 = Strength of standard hard water (0.0028M) V2 = Volume of EDTA solution (28 ml), M2 = Strength of EDTA solution=?

Calculation of Total hardness M3 = V2 M2 = 33 × 0.01 = 0.0033 M

V3 100

V2 = Volume of EDTA solution (33 ml), M2 = Strength of EDTA solution (0.01M) V3 = Volume of sample hard water (100 ml), M3 = Strength of sample hard water =?

Total Hardness = 0.0033 × 10^5 ppm = 0.0033 × 100 (Mol. Wt of CaCO3) × 1000 (ml)ppm

= 330 ppm

Calculation of Permanent hardness M4 = V2 M2 = 10 × 0.01 = 0.001 M

V4 100

V2 = Volume of EDTA solution (10 ml), M2 = Strength of EDTA solution (0.01M) V4 = Volume of sample hard water after boiling cooling and filtering (100 ml)

M4 = Strength of sample hard water after boiling cooling and filtering =?

Permanent Hardness = 0.001 × 10^5 ppm

= 0.001 × 100 (Mol. Wt of CaCO3) × 1000 (ml)ppm

= 100 ppm

Calculation of Temporary hardness = Total hardness - Permanent hardness

POTABLE WATER AND ITS SPECIFICATIONS

= 330 – 100 = 230 ppm

Water free from contaminants or water that is safe for human consumption is called potable water.

The following are the **specifications of water drinking purpose.**

The water should be clear (colorless), odorless and pleasant taste.

The optimum *hardness* of water must be 125ppm.

The *pH* of potable water should be 7.0 to 8.0

The recommended maximum concentration of *total dissolved solids (TDS)* in potable water must not exceed 500 ppm.

The *turbidity* in drinking water should not exceed 10 ppm.

The water must be free from *heavy metals* like Lead, Arsenic, Chromium and Manganese.

The water must be *free from pathogenic bacteria*

The water must be *free from dissolved gases* like H_2S, CO_2 and NH_3.

STEPS INVOLVED IN THE TREATMENT OF POTABLE WATER

Treatment of water for drinking purposes mainly includes the removal of suspended impurities, colloidal impurities and harmful pathogenic bacteria. The following stages are involved in purification.

Screening: The water is passed through screens having larger number of holes; it retains floating impurities like wood pieces, leaves, heaver objectives etc.,

Coagulation: Coagulants like alum, sodium aluminates and Aluminum sulphate are added which produce gelatinous precipitates called flock. Flock attracts and helps accumulation of the colloidal particles resulting in setting of the colloidal particles.

Filtration: Filtration helps in removal of the colloidal and suspended impurities not removed by sedimentation. Usually sand filters are employed. In this filtration fine sand layer on the top supported by coarse sand layer, which is supported by gravel.

The colloidal impurities are retained by the fine sand layer resulting the very slow filtration of water. Periodically the top layers of the fine sand layer is scraped off, washed, dried and introduced into the filter bed for reuse.

Disinfection of water by sterilization: The process of destroying the harmful bacteria’s is known as sterilization or disinfection.

DISINFECTION OF POTABLE WATER

By Ozonization: Ozone is a powerful disinfectant and is readily absorbed by water. Ozone is highly unstable and breaks down to give nascent oxygen.

$O_3 \rightarrow O_2 + [O]$ nascent oxygen The nascent oxygen is a powerful oxidizing agent and kills the bacteria.

Disadvantages: This process is costly and cannot be used in large scale, due to unstable of ozone cannot be stored for long time.

By Chlorination: The process of adding chlorine to water is called chlorination. Chlorination can be done by the following methods.

By adding Chlorine gas: Chlorine gas is a very good disinfectant, which can be bubbled in the water. In this process calculated amount of chlorine gas is passed in order to destroy the pathogenic bacteria is called chlorination. Chlorine is also reacts with water and generates hypochlorous acid and nascent oxygen, which acts a powerful oxidizing agent and kills the bacteria.

$Cl_2 + H_2O \rightarrow HOCl$ (Hypochlorous acid) $+ HCl$ $HOCl \rightarrow HCl + [O]$ nascent oxygen

By adding Chloramine: When chlorine and ammonia are mixed in the ratio 2:1 a compound chloramine is formed.

$Cl_2 + NH_3 \rightarrow ClNH_2 + HCl$

Chloramine

$ClNH_2 + H_2O \rightarrow NH_3 + HOCl$ (Hypochlorous acid) $HOCl \rightarrow HCl + [O]$ nascent oxygen

Chloramine compounds decompose slowly to give nascent oxygen which will be act as good disinfectant than the Chlorine. Chloramine gives good taste to the treated water.

BREAK-POINT CHLORINATION

Break-point chlorination: The amount of chlorine required to kill bacteria and to remove organic matter is called break-point chlorination.

The water sample is treated with chlorine and estimated for the residual chlorine in water and ploted a graph as shown below which gives the break-point chlorination.

From graph it is clear that:

‘a’ gms of chlorine added oxidizes reducing impurities of water.

‘b’ gms of chlorine added forms chloramines and other chloro compounds.

‘c’ gms of chlorine added causes distruction of bacteria.

‘d’ gms of chlorine is residual chlorine.

‘c’ gms is the break point for addition of chlorine to water. This is called **break- point chlorination**.

Advantages of break-point chlorination:

It removes bad taste, colour, oxidizes completely organic compounds, ammonia and other reducingimpurities

It destroys completely (100%) all disease producing bacteria.

It prevents growth of any weeds in water.

DEFLOURIDATION:

Fluorine is most active element found in naturally occurring rocks.

Defluoridation is the removal of excess fluoride from water

Fluoride is precipitated using 500mg/l of alum,30mg/l of lime with small amount of bleaching powder 3 mg/l for disinfection

Steps involved in the Nalgonda technique:

Raw water → mixer → flocculation → sedimentation →filtration → disinfection

Step 1 :Addition of chemicals

Raw water is added with alum,lime and bleaching powder

Step 2:Mixing:

The water is thoroughly mixed with added chemicals for some time using mechanical stirrer

Step 3: Flocculation:

Flocculation involves subsequent gentle agitation before entry to sedimentation tank

Step 4:Sedimentation:

It removes settled floc,loaded with fluorides,turbidity,bateria and other impuritie

Step 5: Filteration:

The Treated water from sedimentation tank is filtered by gravity sand filter

Step 6:Disinfection:

The filtered water collected in the storage water tank is rechlorinated and distributed to consumers.

ADVANTAGES:

It is preferable due to low price

Ease of Handling

BOILER TROUBLES

A boiler is a closed vessel in which water under pressure is transformed into steam by the application of heat. The steam so generated is used in industries and generation of power. In modern pressure boilers and laboratories, the water required is used pure than the distilled water.

A boiler feed water should correspond with the following composition:

Its hardness should be below 0.2ppm.

Its caustic alkalinity (due to OH^-) should lie between 0.15ppm to 0.45ppm.

It's should be free from dissolved gases like O_2, CO_2, in order to prevent boiler corrosion.

Excess of impurities in the boiler feed water generally cause the following problems:

Sludge's and Scale formation 2. Caustic embrittlement

Boilers are employed for the steam generation in power plants, where water as continuously heated to produce steam. As more and more water is removed from water in the form of steam, the boiler water gets concentrated with dissolved salts progressively reaches the saturation point. At this point the dissolved salts are precipitated out and slowly settle on the inner walls of the boiler plate. The precipitation takes place in two ways.

SLUDGES

Sludge is a soft, loosy and slimy precipitate formed within the boiler. It is formed at comparatively colder portions of the boiler and collects in the area where flow rate is slow.

Ex: $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$.

Reasons for formation of sludges:

The dissolved salts whose solubility is more in hot water and less in cold water produce sludges.

Disadvantages of sludges:

Sludges are bad conductors of heat and results in the wastage of heat and fuel.

Excessive sludge formation leads to the settling of sludge in slow circulation areas such as pipe connections, plug openings, gauge–glass connections leading to the choking of the pipes.

Prevention of sludge formation:

By using soft water which is free from dissolved salts like $MgCO_3$, $MgCl_2$, $CaCl_2$ and $MgSO_4$ can be

prevent sludge formation.

By blow down operation carried out frequently can prevent sludge formation.

SCALES

Scales are hard, adhering precipitates formed on the inner walls of the boilers. Scales are stick very firmly on to the inner walls of the boiler. It is removed with chisel and hammer. Scales are formed by decomposition of calcium bicarbonate in low pressure boilers.

Reasons for formation of scales:

Decomposition of calcium bicarbonate: The calcium bicarbonate at high temperature decomposes to calcium carbonate which is insoluble salt, forms scale in low pressure boilers.

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

Hydrolysis of Magnesium salts: Magnesium salts gets hydrolyzed at high temperature forming $Mg(OH)_2$ precipitation which forms salt type scale.

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

Decomposition of calcium sulphate: The solubility of $CaSO_4$ in water decreases with the increase in temperature and forms precipitation on the surface of the boiler further which forms hard scale. This type of scales is formed in high-pressure boilers.

Presence of silica: Sio_2 present even in small quantities, deposits as Calcium silicates ($CaSiO_3$) or Magnesium silicates ($MgSiO_3$). The deposits form hard scale and are very difficult to remove.

Disadvantages of Scales:

Wastage of heat and fuels: Scales poor thermal conductivity so that rate of heat transformation is reduced.

Lowering of boiler safety is due to overheating of the boiler material becomes softer and weaker, which causes distortion of boiler.

Decrease in efficiency of the boiler due to scales deposited in the values and condensers of the boiler cause choking.

Danger of explosion which happens the formation of the scales, the boiler plate faces higher temperature outside and lesser temperature inside due to uneven expansion. The water comes suddenly contact with overheated portion and larger amount steam is formed immediately, this results in development of sudden high pressure which may cause explosion of the boiler.

Prevention of scales:

If the scale formation is soft it can be removed by a scrapper, wire brush.

By giving thermal shocks, by sudden heating and sudden cooling which makes scale brittle and removed by scrubbing with wire brush.

If scale is very hard that is formed by $CaCO_3$ can be removed by washing with 5-10% HCl and $CaSO_4$ can be removed with EDTA solution.

CAUSTIC EMBRITTLEMENT

The formation of brittle and in crystalline cracks in the boiler shell is called caustic embrittlement.

The main reason for this is the presence of alkali-metal carbonates and bicarbonates in feed water. In lime-soda process, it is likely that, some residual Na_2CO_3 is still present in the softened water. This Na_2CO_3 decomposes to give NaOH and CO_2, due to which the boiler water becomes "Caustic Soda".

$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2$

The H_2O evaporates, the concentration of NaOH increase progressively creating a concentration cell as given below thus dissolving the iron of the boiler as sodium ferrate (Na_2FeO_2).

(-)Anode: 'Fe' at bents | Conc.NaOH ‖ Dil.NaOH | 'Fe' at plane Surface: Cathode (+)

This causes embrittlement of boiler parts such as bends, joints, reverts etc, due to which the boiler gets fail. The iron at plane surfaces surrounded by dilute NaOH becomes cathodic while the iron at bends and joints surrounded by highly concentrated NaOH becomes anodic which consequently decayed or corroded.

Caustic embrittlement can be prevented:

By maintaining the pH value of water and neutralization of alkali.

Byusing Sodium Phosphate as softening reagents, in the external treatment of boilers.

Caustic embrittlement can also be prevented by adding Tannin or Lignin or Sodium sulphate which prevents the infiltration of caustic-soda solution blocking the hair-cracks.

INTERNAL TREATMENT OF WATER

Principal: In this process an ion is prohibited to exhibit its original character by converting it intoother more soluble salt. Suitable chemicals are added to the boiler water either: a) to precipitate the scale forming impurities in the form of sludges or b) to convert them into compounds, which will stay in dissolved form in water and thus do not cause any harm. Internal treatment can be done following types.

Calgon conditioning: Involves in adding calgon to boiler water. It prevents the scale and sludge formation by forming soluble complex compound with $CaSO_4$.

Calgon = Sodium hexa meta phosphate **=** $Na_2\,[Na_4\,(PO_3)_6]$

$Na_2\,[Na_4\,(PO_3)_6] \rightarrow 2Na^+ + [Na_4P_6O_{18}]^{-2}$ $2CaSO_4 + [Na_4P_6O_{18}]^{-2} \rightarrow [Ca_2\,P_6O_{18}]^{-2} + 2Na_2SO_4$

Phosphate conditioning: The addition of sodium phosphate in hard water reacts with the hardness causing agents and gives calcium and magnesium phosphates which are soft and non-adhere and can be removed easily by blow-down operation.

$3CaCl_2 + 2\ Na_3PO_4 \rightarrow Ca_3(PO_4)_2 + 6NaCl$

$3MgSO_4 + 2\ Na_3PO_4 \rightarrow Mg_3(PO_4)_2 + 3Na_2SO_4$

Genarally three types of Phosphates are employed.

Tri sodium Phosphate (Na_3PO_4): is too alkaline used for treat to too acidic water.

Di sodium Phosphate ($Na_2\ HPO_4$): is weakly alkaline used for treat to weakly acidic water.

Sodium dihydrogen Phosphate ($Na\ H_2PO_4$): is too acidic used for treat to too alkaline water.

Colloidal conditioning: The addition of organic substances such as Kerosene, tannin, agar-agar gel. These substances gets coated over the scale forming precipitates and gives a loose and non-sticky precipitates which an be removed by using blow-down operation.

ION EXCHANGE PROCESS/DE MINERALISATION/DE IONISATION

Ion exchange process is also known as demineralization process. Ion- Exchange resins are insoluble. Cross linked long chain organic polymers with a micro porous structure, and the “functional Groups” attached to the chains are responsible for the ion-exchanging properties. Resins with acidic functional group are capable of exchanging H^+ ions with other cations. Resins with basic functional groups are capable of exchanging OH^-ions with other anions.

Resins are classified as:

Cation Exchange Resins ii. Anion Exchange Resins.

Cation Exchange Resins: Cation exchange resins are styrene divinyl benzene co-polymers, which on sulphonation (or) carboxylation, which contains $–COOH$, $–SO_3H$ functional groups which responsible for exchanging their hydrogen ions with cations in water.

$2RH + Ca(HCO)_2 \rightarrow R_2Ca + H_2CO_3$

$2RH + Mg(HCO)_2 \rightarrow R_2Mg + H_2CO_3$

$2RH + CaCl_2 \rightarrow R_2Ca + 2HCl$

$2RH + MgCl_2 \rightarrow R_2Mg + 2HCl$

$2RH + MgSO_4 \rightarrow R_2Mg + H_2SO_4$

$2RH + CaSO_4 \rightarrow R_2Ca + H_2SO_4$ (RH = Cation exchange resin)

Anion Exchange Resins: Anion exchange resins are Phenol formaldehyde (or) amine formaldehyde copolymers, which contains amino or basic functional groups which responsible for exchanging their OH^- ions with anions in water.

$ROH + HCl \rightarrow RCl + H_2O$

$2ROH + H_2SO_4 \rightarrow R_2SO_4 + 2H_2O$

$ROH + H_2CO_3 \rightarrow RHCO_3 + H_2O$(ROH = anion exchange resin)

In ion-exchange process, hard water is allowed to pass through cation exchange resins, which remove Ca^{+2} and Mg^{+2} ions and exchange equivalent amount of H^+ ions. Anions exchange resins remove bicarbonates, chlorides and sulphates from water exchange equivalent amount of OH^- ions.

Thus by passing hard water through cation hardness is observed by the following reactions. H^+ and OH^-ions, thus released in water from respective cation and anion exchange columns, get combined to produce water molecules.

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

The water coming out from the exchanger is ion free from anions and cations. Thus water of zero hardness is obtained.

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

The water coming out from the exchanger is ion free from anions and cations. Thus water of zero hardness is obtained.

Regeneration: When cation exchanger losses capacity of producing H^+ ions and exchanger losses capacity of producing OH^- ions, they are said to be exhausted. The exhausted cation exchanger is regenerated by passing it through dilute sulphuric acid.

$R_2Ca + 2HCl \rightarrow 2RH + CaCl_2$ $R_2Mg + 2H_2SO_4 \rightarrow 2RH + MgSO_4$

The exhausted anion exchanger is regenerated by passing a dilute solution of NaOH.

$R_2SO_4 + NaOH \rightarrow 2ROH + Na_2SO_4$

$RCl + NaOH \rightarrow ROH + NaCl$ $RHCO_3 + NaOH \rightarrow ROH + NaHCO_3$

Merits of Ion-exchange process:

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

It produces water of very low hardness (2ppm)

So it is very good for treating water for use in high-pressure boilers.

Demerits of Ion-exchange process:

The equipment is costly and more expensive chemicals are needed.

If water contains turbidity, the output of the process is reduced. The turbidity must be below 10ppm; else it has to be removed by coagulation and filtration.

DESALINATION OF WATER -REVERSE OSMOSIS

The process of removing common salt (Sodium Chloride) from the water is known as **desalination.**

The water containing dissolved salts with a salty or brackish taste is called **brackish water**. Depending upon the quantityof dissolved solids, water is graded as:

Fresh Water: Contains less than 1000 ppm of dissolved solids.

Brackish Water: Contains more than 1000 ppm to less than 35000 ppm of dissolved solids.

Sea Water: Contains more than 35000 ppm of dissolved solids.

Sea water and brackish water can be made available as drinking water through desalination process. Desalination is carried out either by reverse osmosis or electro dialysis.

Reverse Osmosis:

Reverse Osmosis is a process in which pressure greater than the osmotic pressure is applied on the high concentration side of the membrane, the flow of solvent move from concentrated side to dilute side across the membrane.

Osmosis is the phenomenon by virtue of which flow of solvent takes place from a region of low concentration to high concentration when two solutions of different concentrations are separated by a semi-permeable membrane.

Method:

In this process pure water is separated from salt water. 15-40 kg/cm^2 pressure is applied for separating the water from its contaminants. The membranes used are cellulose acetate, polymethyl acrylate and polyamide polymers. The process is also known as **super or hyper filtration**.

Advantages:

It is simple and reliable process & Capital and operating expenses are low.

The life of the semi-permeable membrane is about two years and it can be easily replaced within a few minutes, thereby nearly uninterrupted water supply can be provided.

It removes colloidal silica which is not removed by demineralization.

It removes ionic and non ionic impurities