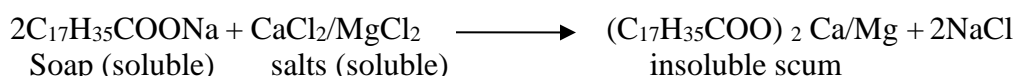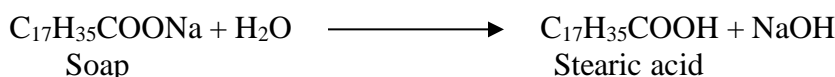# Water Technology

Introduction:
- Water is a natural gift on the earth, water is essential for humans, animals and plants.
- As engineering material, water is used for producing steam in boilers to produce hydro electric power. For refrigeration, air conditioning and as a solvent in chemical process.
- Water is a very good solvent and even called as the universal solvent.
- It is widely used in drinking, bathing, sanitary, washing, irrigation, fire-fights and also production of industrial materials.
- The distribution of water on the Earth's surface is extremely uneven.

Hardness of water:
- The water that has certain salts like Ca^{+2}, Mg^{+2} and other heavy metals dissolved in it is caused hard water.

- **Hard Water:** The water which does not give lather with soap is called hard water.

$$2C_{17}H_{35}COONa + CaCl_2/MgCl_2 \longrightarrow (C_{17}H_{35}COO)_2 Ca/Mg + 2NaCl$$
Soap (soluble)   salts (soluble)   insoluble scum

- **Soft Water:** The water which gives more lather with soap is called soft water.

$$C_{17}H_{35}COONa + H_2O \longrightarrow C_{17}H_{35}COOH + NaOH$$
Soap   Stearic acid

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 Dolomite ($CaMg(CO_3)_2$), they get converted into soluble bicarbonates. Thus, water gets hardness.

$$CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2$$
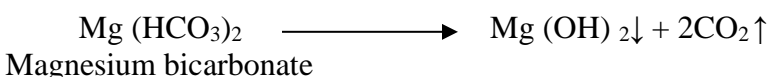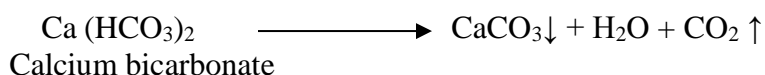Insoluble   Soluble
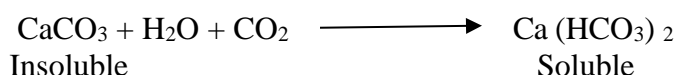
- When natural water flows over the rocks containing chlorides and sulphates and Nitrates of Calcium and magnesium, these salts dissolve in water. Thus water gets hardness.

Types of hardness:

Hardness of water is mainly two types:
   1. Temporary Hardness 2. Permanent Hardness

1. 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.

$$Ca(HCO_3)_2 \longrightarrow CaCO_3\downarrow + H_2O + CO_2 \uparrow$$
Calcium bicarbonate

$$Mg(HCO_3)_2 \longrightarrow Mg(OH)_2\downarrow + 2CO_2\uparrow$$
Magnesium bicarbonate

2. Permanent Hardness: It is due to the presence of dissolved Chlorides and Sulphates of Calcium & Magnesium salts ($CaCl_2$, $MgCl_2$, $CaSO_4$, and $MgSO_4$). Permanent Hardness cannot be removed by boiling but it can be removed by the other methods.

Expression and Units of Hardness:

- Hardness of water is measured in terms of an equivalent $CaCO_3$.
- Calcium Carbonate is chosen as a standard because:
    - i. Its molecular weight (100) and equivalent weight (50) is a whole number.
  So the calculations in water analysis can be simplified.
    - ii. 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:

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

Units of Hardness:

1. Parts per Million (ppm): The number of parts of equivalent $CaCO_3$ presents in 10^6 parts of water.
Ex: 1ppm hardness = 1 part of equivalent $CaCO_3$ in 10^6 parts of water.
OR
10^6 parts of water has 1 part of equivalent $CaCO_3$.

2. Milligrams per litre (mg/l): The number of milligrams of equivalent $CaCO_3$ presents in litre of water.
Ex: 1 mg/L haedness = 1 mg of equivalent $CaCO_3$ in 1 litre of water.
OR
1 litre of water has 1 mg of equivalent $CaCO_3$.

3. Degree Clark's (°Cl): The number of grains of equivalent $CaCO_3$ presents in one gallon of water.

4. Degree French (°Fr): The number of parts of equivalent $CaCO_3$ presents in 10^5 parts of water.

Relationship between various units of hardness:

1 ppm = 1 mg/L = 0.1° Fr = 0.07° Cl
OR
1 ° Cl = 1.43° Fr = 14.3 ppm = 14.3 mg/L

Problem-1: 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	$16.8 \times 100/146 = 11.50$
$MgCl_2$	12.0	95	$12.0 \times 100/95 = 12.63$
$MgSO_4$	29.6	120	$29.6 \times 100/120 = 24.66$
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-2: 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	$14.6 \times 100/146 = 10$
$MgCl_2$	9.5	95	$9.5 \times 100/95 = 10$
$MgSO_4$	6.0	120	$6.0 \times 100/120 = 5$
$Ca(HCO_3)_2$	16.2	162	$16.2 \times 100/162 = 10$

Temporary hardness [Mg $(HCO_3)_2$ + Ca $(HCO_3)_2$] = 10 + 10 = 20mg/Lit
$$= 20ppm$$
$$= 20 \times 0.07°Cl = 1.4°Cl$$
$$= 20 \times 0.1°Fr = 2°Fr$$

Permanent hardness [$MgCl_2$ + $MgSO_4$] = 10 + 5 = 15mg/Lit
$$= 15ppm$$
$$= 15 \times 0.07°Cl = 1.05°Cl$$
$$= 15 \times 0.1°Fr = 1.5°Fr$$

Estimation of Hardness of water by Complexometric method or EDTA method:

- In this method, water sample is titrated against the standard solution of EDTA using Eriochrome Black- T which act as a indicator in the presence of basic buffer solution (pH = 9 to 10).
- At the end point, wine red colour changes to blue colour.
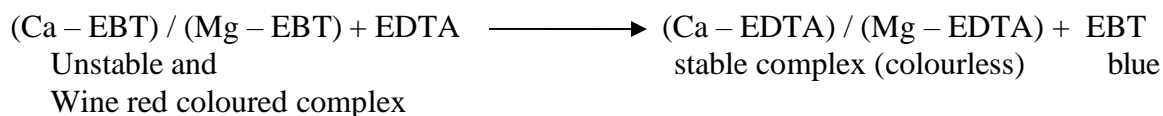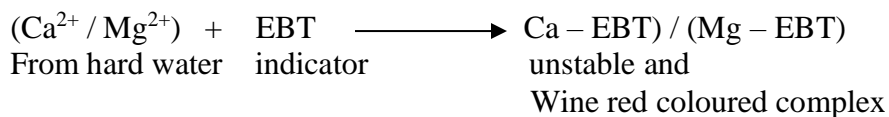- Practically used EDTA is a disodium salt that is fairly soluble in water.

EDTA: Ethylene Diamine Tetra Acetic acid

★Ethylenediamine tetra acetic acid
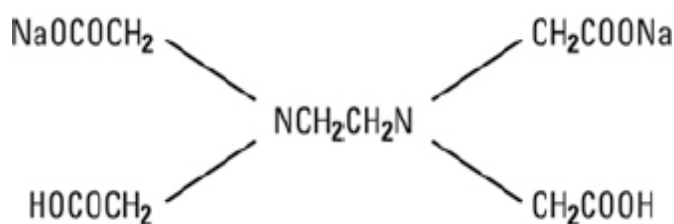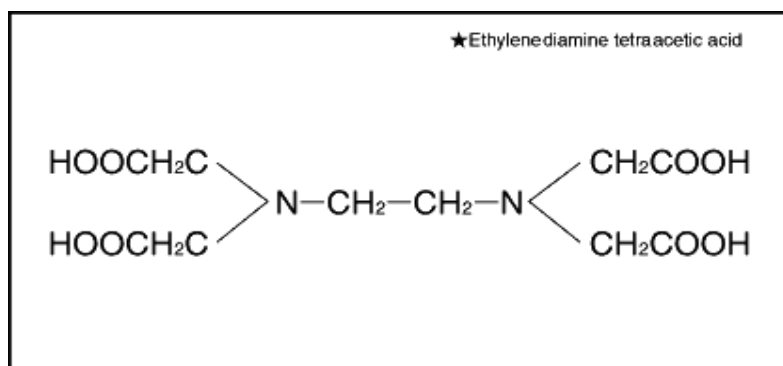
Di sodium salt of EDTA

Basic 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+} / Mg^{2+}) + EBT $\longrightarrow$ Ca – EBT) / (Mg – EBT)
From hard water   indicator   unstable and
                                        Wine red coloured complex

(Ca – EBT) / (Mg – EBT) + EDTA $\longrightarrow$ (Ca – EDTA) / (Mg – EDTA) + EBT
    Unstable and   stable complex (colourless)   blue
    Wine red coloured complex

Experiment:

I. 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.

$$\text{Normality of Standard Hard water} = \frac{\text{Wt.of } CaCO_3}{\text{GEW of } CaCO_3} \times \frac{1000}{(V \text{ in ml})}$$

$$N_1 = 0.01N$$

i. Preparation of EDTA solution: Dissolve 4 g of pure EDTA crystals + 0.1g $MgCl_2$ in 1 Litre of distilled water.

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

iii. 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.

II. Standardization of EDTA solution: Clean 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**.

$$N_1 V_1 = N_2 V_2$$

Where, N_1 = Normality of Standard Hard
water(0.01M), V_1 = Volume of Standard Hard
water (20 ml), N_2 = Normality of EDTA,
V_2 = Volume of EDTA **(Xml)** burette reading

III. Determination of Total Hardness: Clean 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**.

$$N_2 V_2 = N_3 V_3$$

Where, N_2 = Normality of EDTA,
V_2= Volume of EDTA **(Yml)** burette reading
N_3 = Normality of sample water,
V_3 = Volume of Sample water (20 ml).

Total Hardness = $N_3 \times$ GEW of CaCO3 (50) $\times$ One Litre (1000ml)
         = $N_3 \times 10^5$ ppm

IV. 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**.

$$N_2 V_2 = N_4 V_4$$

Where, N_2 = Normality of
EDTA,
V_2= Volume of EDTA (**Z ml**) burette reading
N_4 = Normality of Permanent hard water,
V_4 = Volume of Permanent hard water (20 ml)
Permanent Hardness = $N_4 \times$ GEW of CaCO3 (50) $\times$ One Litre (1000ml)
         = $N_4 \times 10^5$ ppm

V. Determination of Temporary Hardness:

Temporary Hardness = Total Hardness - Permanent Hardness

Problem-1: 50 ml of standard hard water containing 1 gram of pure CaCO3 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:

I. Strength of standard hard watersample (CaCO3 solution) (N_1):

$$N_1 = \frac{\text{Weight of CaCO3} \times 1000}{\text{GEW of CaCO3} \times (\text{V inml})}$$

$$= \frac{1 \text{ gm} \times 1000}{50 \times 1000}$$

$$= 0.02 \text{ N}$$

II. Strength of EDTA solution (N_2):

N_1 = Strength of standard hard water (0.02N), N_2 = Strength of EDTA solution =?
V_1 = Volume of standard hard water (50 ml), V_2 = Volume of EDTA solution (20 ml)

$$N_2 = \frac{N_1 V_1}{V_2} = \frac{50 \times 0.02}{20} = 0.05 \text{ N}$$

III. Calculation of Total hardness (N_3):

N_2 = Strength of EDTA solution= 0.05N, N_3 = Strength of sample hard water =?
V_2 = Volume of EDTA solution (25 ml), V_3 = Volume of sample hard water (50 ml)

$$N_3 = \frac{V_2 N_2}{V_3} = \frac{25 \times 0.05}{50} = 0.025 \text{ N}$$

Total Hardness:

Total Hardness = N_3 x 50 x1000

$$= 0.025 \times 50 \text{ x } 1000 \text{ ppm}$$

$$= 1250 \text{ ppm.}$$

Problem-2: 0.28 grams of CaCO3 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.

Solution:

I. Strength of standard hard water sample (CaCO3 solution) (N_1):

$$= \frac{\text{Weight of CaCO3}}{\text{GEW of CaCO3}} \times \frac{1000}{\text{V in ml}}$$

$$N_1 = \frac{0.28\text{gm}}{50} \times \frac{1000}{1000} = 0.0056 \text{ N}$$

II. Strength of EDTA solution (N_2):

N_1 = Strength of standard hard water (0.0056 N), N_2 = Strength of EDTA solution=?

V_1 = Volume of standard hard water (100 ml), V_2 = Volume of EDTA solution (28 ml)

$$N_2 = \frac{V_1 \, N_1}{V_2} = \frac{100 \times 0.0056}{28} = 0.02 \text{ N}$$

III. Calculation of Total hardness (N_3):

N_2 = Strength of EDTA solution (0.02 N), N_3 = Strength of sample hard water =?
V_2 = Volume of EDTA solution (33 ml), V_3 = Volume of sample hard water (100 ml)

$$N_3 = \frac{V_2 \, N_2}{V3} = \frac{33 \times 0.02}{100} = 0.0066 \text{ N}$$

Total Hardness = $N_3 \times$ 50 (GEW of CaCO$_3$) $\times$ 1000 ppm

$$= 0.0066 \times 50 \text{ x } 1000 \text{ ppm}$$

$$= 330 \text{ ppm}$$

IV. Calculation of Permanent hardness (N_4):

N_2 = Strength of EDTA solution (0.02 N), N_4 = Strength of sample hard water after boiling cooling and filtering =?
V_2 = Volume of EDTA solution (10 ml), V_4 = Volume of sample hard water after boiling cooling and filtering (100 ml)

$$N_4 = \frac{V_2\, N_2}{V_4} = \frac{10 \times 0.02}{100} = 0.002 \text{ N}$$

Permanent Hardness = $N_4 \times 50$ (GEW of $CaCO_3$) $\times$ 1000 ppm

$$= 0.002 \times 50 \times 1000 \text{ ppm}$$

$$= 100 \text{ ppm}$$

Calculation of Temporary hardness:

Temporary hardness = Total hardness - Permanent hardness
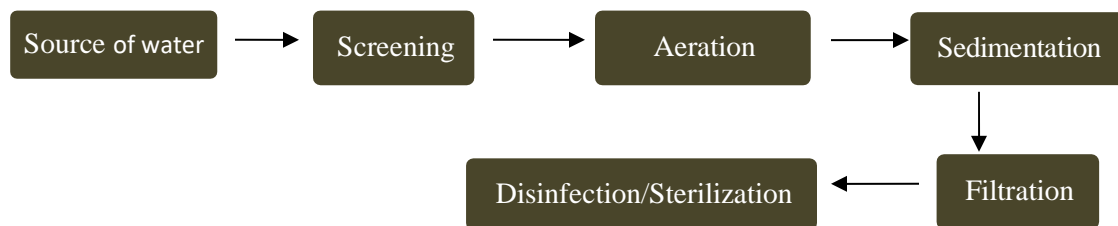
$$= 330 - 100 = 230 \text{ ppm}$$

Potable water:

- Potable water is water which is fit for consumption by humans and animals. It is also called as drinking water.
- Water which is not safe to drink can carry diseases and heavy metals. People who consume this water will become ill.
- Potable water has been filtered, cleaned and treated to meet the standards for drinking water, meaning that it is reasonably clear of contaminates and harmful bacteria. This makes the water safe for drinking and cooking.

Specifications of potable water:

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

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

3. The pH of potable water should be 7.0 to 8.5.

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

500 ppm.

5. The turbidity in drinking water should not exceed 25 ppm.

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

7. The water must be free from pathogenic bacteria

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

Steps involved in the treatment of Potable water (or) Treatment of water for municipal supply (or) Treatment of water for domestic supply:

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.

```
┌─────────────────┐     ┌──────────────┐     ┌──────────────┐     ┌──────────────────┐
│ Source of water │ ──> │  Screening   │ ──> │   Aeration   │ ──> │  Sedimentation   │
└─────────────────┘     └──────────────┘     └──────────────┘     └──────────────────┘
                                                                           │
                                                                           ▼
                        ┌───────────────────────────┐     ┌──────────────┐
                        │ Disinfection/Sterilization │ <── │  Filtration  │
                        └───────────────────────────┘     └──────────────┘
```

Sources of water:
There are two main sources of water – surface water and grand water.
- Surface water is found in lakes, rivers and reservoirs.
- Grand water lies under the surface of the land.

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

Aeration: The water is then subjected to aeration (reacting with air) which helps in
- Exchange of gases between water and air,
- Increases the oxygen content and removes the impurities like iron, manganese and dissolved gases like H_2S, CO_2 and NH_3.

Sedimentation:

Sedimentation is the process of removing suspended impurities by allowing the water to stand undisturbed for 2 to 6 hours in big tanks due to force of gravity most of the suspended impurities settle down at the bottom of the tanks and they are removed.
Sedimentation process removes only 70 to 75% of suspended matter.

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 and sterilization: The process of destroying the harmful bacteria from water is known as sterilization or disinfection.

Disinfection methods:

1) By boiling: By boiling of water for 15 to 20 mints, harmful bacteria are killed. But this process is not possible for the municipal supply of water.

2) By Ozonization: Ozone is a powerful disinfectant and is readily absorbed by water. Ozone is highly unstable and breaks down to give nascent oxygen.
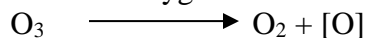
$$O_3 \longrightarrow O_2 + [O]$$
$$\text{Nascent oxygen}$$

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.

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

a. By adding Chlorine: Chlorine gas is a very good disinfectant. The process of applying calculated amount of chlorine to water in order to destroy the pathogenic bacteria is called chlorination. Chlorine is also reacts with water and generates hypochlorous acid, which kills the bacteria.

Chlorine is a powerful disinfectant than chloramine and $CaOCl_2$.

$$Cl_2 + H_2O \longrightarrow HOCl + HCl$$
$$\text{(Hypochlorous acid)}$$
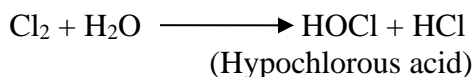
b. By adding Chloramine: When chlorine is mixed with ammonia in the ratio 2:1 a compound chloramine is formed which generates hypochlorous acid with water.

This hypochlorous acid kills the bacteria , chloramine is useful for disinfecting swimming pools.

$$Cl_2 + NH_3 \longrightarrow ClNH_2 + HCl$$
$$\text{Chloramine}$$

$$ClNH_2 + H_2O \longrightarrow NH_3 + HOCl$$
$$\text{(Hypochlorous acid)}$$
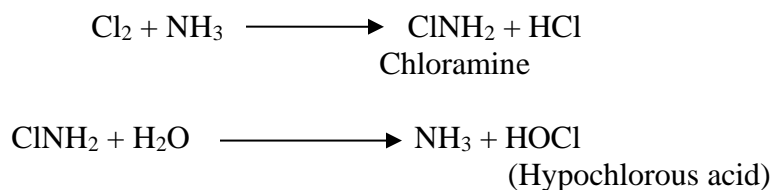
c .By adding bleaching powder : bleaching powder contains 80% chlorine. When it is used as disinfectant, this method is known as hypochlorinationation because the disinfection is due to hypochlorous acid.

$$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$
$$\text{Bleaching}$$
$$\text{Powder}$$

$$Cl_2 + H_2O \longrightarrow HOCl + HCl$$
$$\text{(Hypochlorous acid)}$$
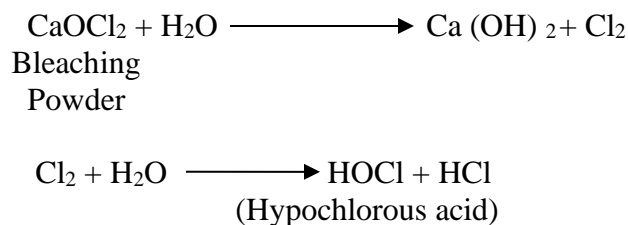
Break-point chlorination:

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

Calculated amount of chlorine must be added to water because chlorine after reacts with bacteria and organic impurities or ammonia, remains in water as residue chlorine which gives bad taste odor and toxic to human beings.

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

From graph it is clear that:
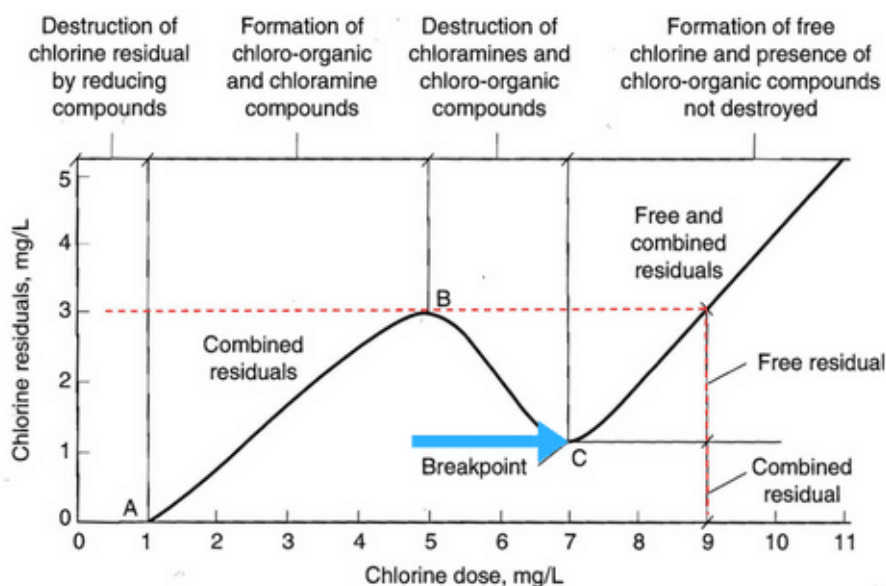
'a' gms of chlorine added oxidizes reducing impurities of water.

'b' gms of chlorine added forms chloramines and other chloro-organic 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 reducing impurities
- It destroys completely (100%) all disease producing bacteria.
- It prevents growth of any weeds in water.

Desalination of water -Reverse Osmosis:

The process of removing common salt (Sodium Chloride) from the water is known as "desalination or demineralization".
The water containing dissolved salts with a salty or brackish taste is called "brackish water". Depending upon the quantity of 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:

When two solutions of unequal concentration are separated by a semi permeable membrane which does not permit the passage of dissolved solute particles. Flow of solvents takes place from dilute solution to concentrated solution. This is called as Osmosis.

If high pressure is applied on the concentrated side of solvent molecules forced to move from higher concentration side to lower concentration side. Thus the solvent flow is reversed, hence this method is called reverse osmosis.

Reverse osmosis cell
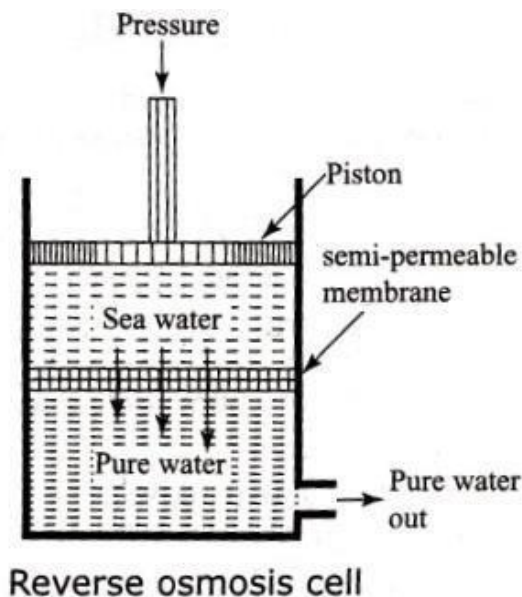
Alkalinity of water and its determination:

Alkalinity is a measure of the water's ability to neutralize acidity. The alkalinity of water is due to the presence of carbonates, bi carbonates and hydroxide ions.

The possible combinations of ions causing alkalinity of water are:

1) Only OH^-

2) Only CO_3^{-2}

3) Only HCO_3^-

4) OH^- and CO_3^{-2} together

5) CO_3^{-2} and HCO_3 together

Alkalinity of water can be classified into two categories based upon the anion present

1. Caustic alkalinity –due to OH^- and CO_3^{-2} ions.

2. Bicarbonate alkalinity (or) temporary alkalinity – due to HCO_3^- ions.

Total alkalinity of water can be determined by titrating water against a standard acid using methyl orange indicator because of it's colour change in the range of 4 – 4.5.

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

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

$$HCO_3^- + H^+ \longrightarrow H_2O + CO_2$$
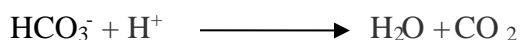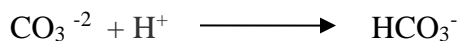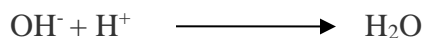
\The titration of water sample against acid using phenolphthalein ($P^H = 8.5$) neutralizes only hydroxide ions and half of the carbonate ions present.

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

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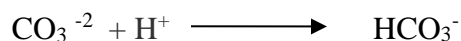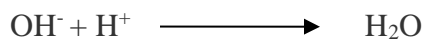
Procedure:

Take 100ml of water sample into a clean conical flask and add 2 or 3 drops of phenolphthalein indicator. The burette is filled with N/50 H_2SO_4. The end point is noted after titrating the acid against the water sample. The end point is the just disappearance of pink colour. Then continue the titration after adding 2 or 3 drops of methyl orange indicator. The end point is the color change from yellow to pink.

Calculations:

Phenolphthalein alkalinity:

| Acid | standard hard water |

$V_{acid} = V_1$ $V_{H2O} = 100ml$

$N_{acid} = N/50$ $N_{H2O} = ?$

$$N_{H2O} = \frac{Nacid \ X \ Vacid}{VH2O}$$

$$= V_1/5000$$

Phenolphthalein alkalinity in terms of $CaCO_3 = N \ X \ 50 \ X \ 1000$

$$= V_1/5000 \ X \ 50 \ X \ 1000$$

$$= 10 \ V_1 ppm$$

Methyl orange alkalinity:

| Acid | standard hard water |

$V_{acid} = V_1 + V_2$ $V_{H2O} = 100ml$

$Nacid = N/50$ $N_{H2O} = ?$

$$N_{H2O} = \frac{Nacid \ X \ Vacid}{VH2O}$$

$$= V_1 + V_2/5000$$

Methyl orange alkalinity in terms of $CaCO_3 = N \ X \ 50 \ X \ 1000$

$$= V_1 + V_2/5000 \ X \ 50 \ X \ 1000$$

$$= (V_1 + V_2)10ppm$$

Boiler feed water: In order to generate steam on a constant basis, boiler should be continuously supplied with water, called as feed water.

Internal treatment of boiler feed water:

The softening of water carried out inside the boiler is called internal treatment of water.

1. Colloidal conditioning:

In low pressure boilers the scale formation can be removed by adding organic substances like kerosene, agar-agar(a gel like substance), they get coated over the scale forming precipitates and can give non-sticky and loose deposits which can be easily removed by blow-down operation.

2. Phosphate conditioning:

In high pressure boilers, scale formation can be avoided by adding sodium phosphate. This can react with hardness producing substances present in the water and forms non-sticky and easily removable soft sludge of calcium and magnesium phosphates. This can be removed by blow-down operation.
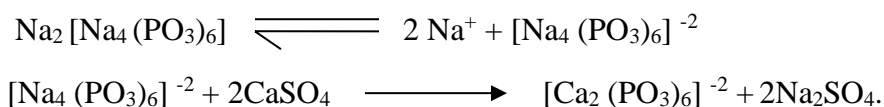
$$3CaCl_2 + 2Na_3PO_4 \longrightarrow Ca_3(PO_4)_2 \downarrow + 6NaCl$$
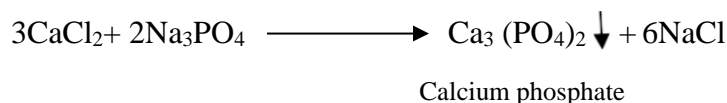
Calcium phosphate

The main phosphates are

i) NaH_2PO_4 (Sodium dihydrogen phosphate)

ii) Na_2HPO_4 (disodium hydrogen phosphate)

iii) Na_3PO_4 (trisodium phosphate)

The choice of salts depends upon the alkalinity of the boiler feed water.
When the boiler water has low alkalinity trisodium phosphate can be used. If boiler water alkalinity is sufficient, then disodium phosphate is used. If the alkalinity of boiler water is too high to reduce this, monosodium phosphate is to be added.

3) Calgon conditioning:

Addition of calgon (sodium hexa meta phosphate) to boiler water is called calgon conditioning. Colgon forms soluble complex compounds with $CaSO_4$.

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

$$[Na_4(PO_3)_6]^{-2} + 2CaSO_4 \longrightarrow [Ca_2(PO_3)_6]^{-2} + 2Na_2SO_4.$$

It prevents the formation of scale and sludge.

External treatment of boiler feed water:

Softening of water by ion-exchange process:-

Ion exchange process includes the exchange of the atoms and ions of the dissolved salts with H^+ and OH^-ions respectively.

Two types of ion exchanges are used

i) Cation exchange resin

ii) Anion exchange resin

i) Cation exchange resin :- (RH)

The cation exchange resins are represented by "RH". These are mainly styrene divinyl benzene, benzene co-polymers containing the functional groups $-COOH, -SO_3H$,

'R' is the general structure of resin and 'H' is the exchangeable with cation.

Cation exchange resins are capable of exchanging there H^+ ions with cations of the dissolved salts.

ii) Anion exchange resin :- (R¹OH)

Anion exchange resins are represented by "R^1OH". These are mainly phenol-formaldehyde or amine formaldehyde co-polymer resins.

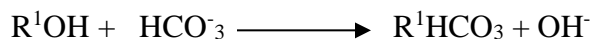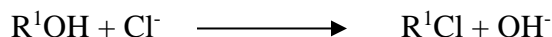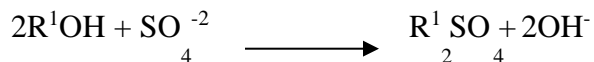'R^1' is the general structure of resin and 'OH' is the exchangeable with anion.

Anion exchange resins are capable of exchanging there OH^- ions with anions of the dissolved salts.
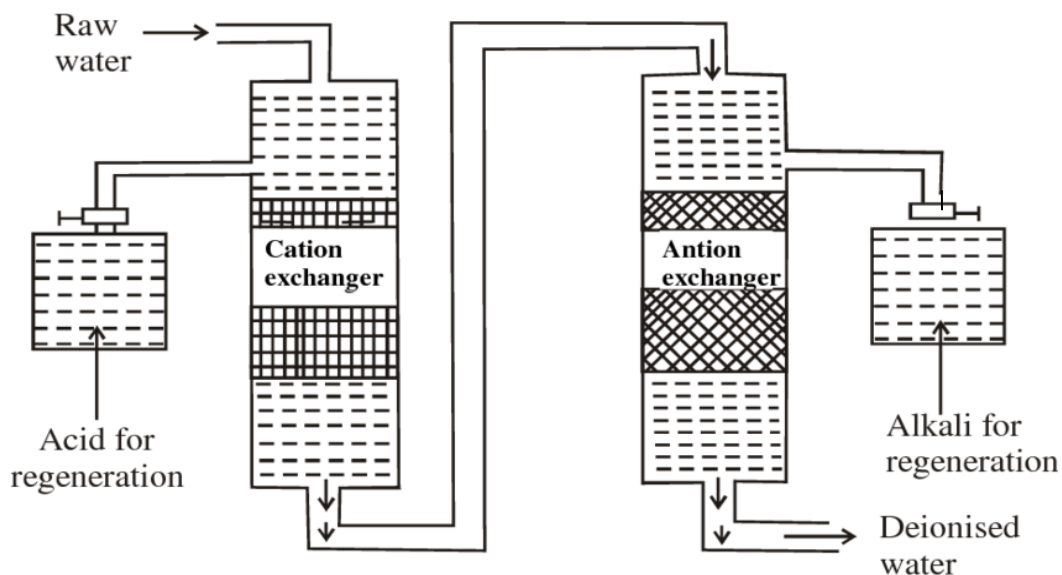
Raw water (or) hard water first passed through a cation exchanges,which removes all the cations like Ca^{+2} and Mg^{+2} from the hard water and equivalent amount of H^+ ions are released into water.

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

$$2RH + Mg^{+2} \longrightarrow R_2Mg + 2H^+$$
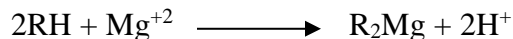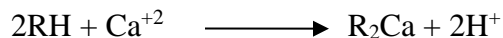
Then the hard water is passed through anion exchanges, which removes all anions like Cl^-, SO_4^{-2}, HCO_3^{-1} from hard water and equivalent amount of OH^- ions are released into water.

$$2R^1OH + SO_4^{-2} \longrightarrow R_2^1SO_4 + 2OH^-$$

$$R^1OH + Cl^- \longrightarrow R^1Cl + OH^-$$

$$R^1OH + HCO_3^- \longrightarrow R^1HCO_3 + OH^-$$

H^+ ions and OH^- ions released from cationic exchanges and anionic exchanges respectively, get combined to form water molecule (H_2O).

$$H^+ + OH^- \longrightarrow H_2O$$
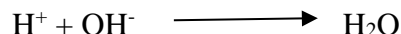
Thus, the water coming out from exchanges is free from all ions known as deionised water.

Regeneration:-

After some time cation and anion exchanges will be exhausted. Hence regeneration of cation exchanges is carried out by passing dilute HCl. Here the H^+ ions of the acid exchanged with the cations (Ca^{+2} and Mg^{+2}) present in cationic exchanges.

$$R_2Ca + 2HCl \longrightarrow 2RH + CaCl_2 \text{ (Washings)}$$

$$R_2Mg + 2HCl \longrightarrow 2RH + MgCl_2 \text{ (Washings)}$$

The washings containing $CaCl_2$ and $MgCl_2$ were passed to sink. Similarly, the anion exchange is treated with dilute NaOH solution. The regeneration can be represented as below.

$$R_2^1SO_4 + 2NaOH \longrightarrow 2R^1OH + Na_2SO_4$$

$$R^1Cl + NaOH \longrightarrow R^1OH + NaCl \qquad \text{(Washings)}$$

$$R^1HCO_3 + NaOH \longrightarrow R^1OH + NaHCO_3$$