

WATER AND ITS TREATMENT

INTRODUCTION:

Water is nature's most wonderful, abundant and useful compound. Water is not only essential for the lives of animals and plants, but also occupies a unique position in industries. It is widely used in drinking, bathing, sanitary, washing, irrigation, fire-fights, air-conditioning and also production of industrial materials. The distribution of water on the Earth's surface is extremely uneven. Only 3% Of freshwater (69% resides in glaciers, 30% underground, and less than 1% is located in lakes, rivers and swamps.) of water on the surface is fresh; the remaining 97% resides in the ocean. Looked at another way, only one percent of the water on the Earth's surface is usable by humans, and 99% of the usable quantity is situated underground.

Types of Impurities present in water:

The natural water is usually contaminated by different types of impurities.

They are mainly three types.

- Physical impurities
- Chemical impurities
- Biological impurities

1. Physical impurities:

- *Colour*: in water is caused by metallic substances like salts.
- *Turbidity*: is due to the colloidal, extremely fine suspensions such as insoluble substances like clay, slit, and micro-organisms.
- *Taste*: presence of dissolved minerals in water produces taste. Bitter taste can be due to the presence of Fe, Al, Mn, Sulphates and lime. Soap taste can be due to the presence of large amount of sodium bicarbonate.
- *Odour*: In water is undesirable for domestic as well as industrial purpose.

2. Chemical impurities:

- *Inorganic chemicals*: Cations(Al^{+3} , Ca^{+2} , Mg^{+2} , Fe^{+2} , Zn^{+2} , Cu^{+2} , Na^+ , K^+), Anions(Cl^- , SO_4^{-2} , NO_3^- , HCO_3^- , F^- , NO_2^-)
- *Organic chemicals*: dyes, paints, petroleum products, pesticides, detergents, drugs textile materials, other organic related materials.

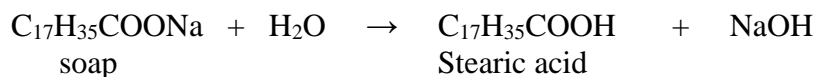
3. Biological Impurities:

- Biological impurities are Algae, pathogenic bacteria, fungi, viruses, pathogens, parasite-worms.

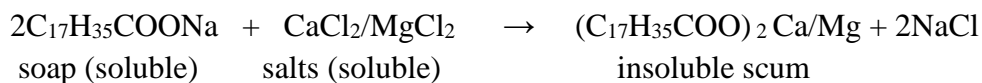
HARDNESS OF WATER

Hardness of water defined as which prevent the lathering of soap. This is due to presence of certain salts like Ca^{+2} , Mg^{+2} and other heavy metals dissolved in water. Soaps (Sodium or Potassium salts of higher fatty acids) like Stearic acids ($\text{C}_{17}\text{H}_{35}\text{COONa}$).

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



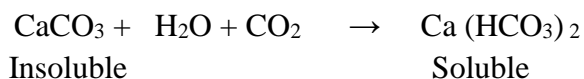
Hard Water: The water which does not give lather with soap is called hard water. This is due to presence of certain salts like Ca^{+2} , Mg^{+2} and other heavy metals dissolved in water



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:

1. When natural water containing CO_2 flows over the rocks of the limestone (CaCO_3) and Dolomite (CaCO_3 & MgCO_3), they get converted into soluble bicarbonates. Thus, water gets hardness.



2. 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

1. 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 quality of 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.

2. 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.

3. Steam generation in Boilers:

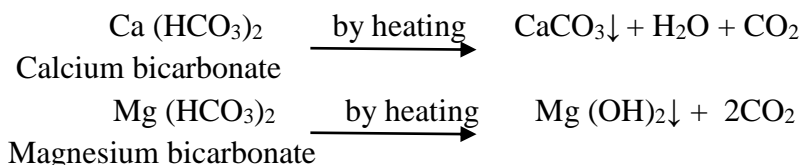
- For steam generation, boilers are almost invariably employed. If the hard water is fed directly to the boilers, there arise many troubles such as: Scales & sludges formation, Corrosion, Priming & Foaming and Caustic embrittlement.

TYPES OF HARDNESS

Hardness of water is mainly two types:

1. Temporary Hardness
2. Permanent Hardness

1. Temporary Hardness: Temporary Hardness mainly caused by the presence of dissolved bicarbonates of Calcium, Magnesium ($\text{Ca}(\text{HCO}_3)_2$, $\text{Mg}(\text{HCO}_3)_2$). Temporary Hardness can be largely removed by boiling of water.



2. 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 , $\text{Al}_2(\text{SO}_4)_3$. 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:

- 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:

$$\text{Degree of Hardness} = \frac{\text{The weight of hardness causing salts}}{\text{Molecular weight of hardness causing salts}} \times 100 \text{ (Molecular weight of } \text{CaCO}_3\text{)}$$

Units of Hardness:

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

$$1\text{ppm} = 1 \text{ part of } \text{CaCO}_3 \text{ eq hardness in } 10^6 \text{ parts of water.}$$

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

$$1 \text{ mg/L} = 1 \text{ mg of CaCO}_3 \text{ eq hardness in 1 litre of water.}$$

But one litre of water weights = 1 kg = 1000g = 1000 x 1000 mg = 10⁶ mg = 1 ppm.

3. Clark's degree (°Cl): The number of parts of calcium carbonate equivalent hardness presents in 70,000 or (7×10⁴) parts of water.

$$1^\circ \text{ Clarke} = 1 \text{ part of CaCO}_3 \text{ eq hardness per 70,000 parts of water.}$$

4. Degree French (°Fr): The number of parts of calcium carbonate equivalent hardness presents in 10⁵ parts of water.

$$1^\circ \text{ Fr} = 1 \text{ part of CaCO}_3 \text{ hardness eq per } 10^5 \text{ parts of water.}$$

Relationship between various units of hardness:

$$\begin{array}{llll} 1 \text{ ppm} & = 1 \text{ mg/L} & = 0.1^\circ \text{ Fr} & = 0.07^\circ \text{ Cl} \\ 1 \text{ mg/L} & = 1 \text{ ppm} & = 0.1^\circ \text{ Fr} & = 0.07^\circ \text{ Cl} \\ 1^\circ \text{ Cl} & = 1.433^\circ \text{ Fr} & = 14.3 \text{ ppm} & = 14.3 \text{ mg/L} \\ 1^\circ \text{ Fr} & = 10 \text{ ppm} & = 10 \text{ mg/L} & = 0.7^\circ \text{ Cl} \end{array}$$

Problem-1: A sample of water is found to contains following dissolving salts in milligrams per litre Mg(HCO₃)₂ = 73, CaCl₂ = 111, Ca(HCO₃)₂ = 81, MgSO₄ = 40 and MgCl₂ = 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

$$\begin{aligned} \text{Temporary hardness} &= \text{Mg(HCO}_3)_2 + \text{Ca(HCO}_3)_2 \\ &= 50 + 50 = 100\text{mgs/Lit.} \end{aligned}$$

$$\begin{aligned} \text{Permanent hardness} &= \text{CaCl}_2 + \text{MgSO}_4 + \text{MgCl}_2 \\ &= 100 + 33.3 + 100 = 233.3\text{mgs/Lit.} \end{aligned}$$

$$\begin{aligned} \text{Total hardness} &= \text{Temporary hardness} + \text{Permanent hardness} \\ &= 100 + 233.3 = 333.3\text{mgs/Lit.} \end{aligned}$$

Problem-2: A sample of water is found to contains following dissolving salts in milligrams per litre Mg(HCO₃)₂ = 16.8, MgCl₂ = 12.0, MgSO₄ = 29.6 and NaCl = 5.0. Calculate temporary and permanent hardness of water.

UNIT-1

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(HCO₃)₂ = 11.50mgs/Lit.

Permanent hardness = MgCl₂ + MgSO₄ = 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(HCO₃)₂ = 14.6, MgCl₂ = 9.5, MgSO₄ = 6.0 and Ca(HCO₃)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 (HCO₃)₂ + Ca (HCO₃)₂] = 10 + 10 = 20mg/Lit
 = 20ppm
 = 20×0.07°Cl = 1.4°Cl
 = 20×0.1°Fr = 2°Fr

Permanent hardness [MgCl₂ + MgSO₄] = 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(HCO₃)₂ = 121.5 ppm, Mg(HCO₃)₂ = 116.8 ppm, MgCl₂ = 79.6 ppm and CaSO₄ = 102 ppm.

Solution:

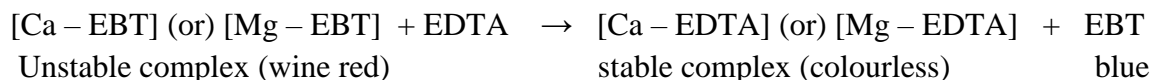
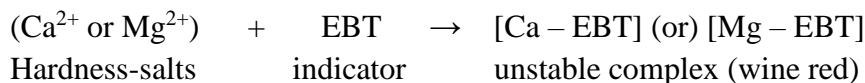
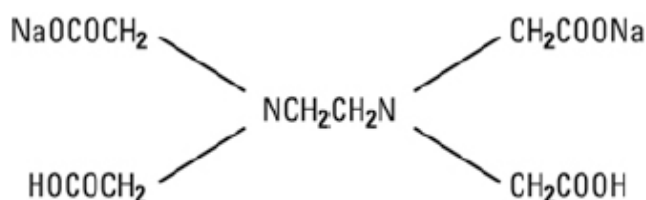
Name of the hardness causing salts	Amount of the hardness causing salts(ppm)	Molecular weight of hardness causing salts	Amounts equivalent to CaCO ₃ (ppm)
Ca(HCO ₃) ₂	121.5	162	121.5×100/162 = 75
Mg(HCO ₃) ₂	116.8	146	116.8×100/146 = 80
MgCl ₂	79.6	95	79.6×100/95 = 3.37
CaSO ₄	102	136	102×100/136 = 75

$$\begin{aligned} \text{Temporary hardness [Mg (HCO}_3)_2 + \text{Ca (HCO}_3)_2] &= 75 + 80 = 155 \text{ ppm} \\ &= 155 \times 0.07^\circ\text{Cl} = 10.85^\circ\text{Cl} \\ &= 155 \times 0.1^\circ\text{Fr} = 15.5^\circ\text{Fr} \\ &= 155 \times 1 \text{mg/Lit} = 155 \text{ mg/Lit} \end{aligned}$$

$$\begin{aligned} \text{Permanent hardness [MgCl}_2 + \text{CaSO}_4] &= 10 + 5 = 15 \text{mg/Lit} \\ &= 15 \text{ppm} \\ &= 15 \times 0.07^\circ\text{Cl} = 1.05^\circ\text{Cl} \\ &= 15 \times 0.1^\circ\text{Fr} = 1.5^\circ\text{Fr} \end{aligned}$$

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.



Chemicals Required:

- i. Preparation of standard hard water (0.01M):** Dissolve 1g of pure, dry CaCO₃ 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 CaCO₃ equivalent hardness.
- ii. Preparation of EDTA solution:** Dissolve 4 g of pure EDTA crystals + 0.1g MgCl₂ in 1 Litre of distilled water.
- iii. Preparation of Indicator (EBT):** Dissolve 0.5 g of Eriochrome Black-T in 100mL alcohol.
- iv. Preparation of Buffer solution:** Add 67.5g of NH₄Cl to 570 ml of Con. Ammonia solution and then dilute with distilled water to 1 Litre.

Various steps involved in this method:

- 1. Standardization of EDTA solution:** Rinse and fill the burette with EDTA solution. Pipette out 20 ml of standard hard water (M₁) 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).

- 2. 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).

$$\begin{aligned} \text{Total Hardness} &= M_3 \times \text{Molecular weight of CaCO}_3 (100) \times \text{One Litre (1000ml)} \\ &= M_3 \times 10^5 \text{ ppm} \end{aligned}$$

- 3. 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)

$$\begin{aligned} \text{Permanent Hardness} &= M_4 \times \text{Molecular weight of CaCO}_3 (100) \times \text{One Litre (1000ml)} \\ &= M_4 \times 10^5 \text{ ppm} \end{aligned}$$

- 4. Determination of Temporary Hardness:**

$$\text{Temporary Hardness} = \text{Total Hardness} - \text{Permanent Hardness}$$

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 (CaCO₃ solution) M₁=

$$\begin{aligned} & \frac{\text{Weight of CaCO}_3 \times 1000}{\text{Mol. wt of CaCO}_3 \quad 1000} \\ & = \frac{1 \text{ gm} \times 1000}{100 \quad 1000} = 0.01 \text{ M} \end{aligned}$$

Strength of EDTA solution M₂ = $\frac{V_1 M_1}{V_2} = \frac{50 \times 0.01}{20} = 0.025 \text{ M}$

V₁ = Volume of standard hard water (50 ml), M₁ = Strength of standard hard water (0.01M)

V₂ = Volume of EDTA solution (20 ml), M₂ = Strength of EDTA solution = ?

Calculation of Total hardness M₃ = $\frac{V_2 M_2}{V_3} = \frac{25 \times 0.025}{50} = 0.0125 \text{ M}$

V₂ = Volume of EDTA solution (25 ml), M₂ = Strength of EDTA solution = 0.025M

V₃ = Volume of sample hard water (50 ml), M₃ = Strength of sample hard water = ?

$$\begin{aligned} \text{Total Hardness} &= 0.0125 \times 10^5 \text{ ppm} \\ &= 0.0125 \times 100 (\text{Mol. Wt of CaCO}_3) \times 1000 (\text{ml})\text{ppm} \\ &= 1250 \text{ ppm.} \end{aligned}$$

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.

$$\begin{aligned} \text{Strength of standard hard water sample (CaCO}_3 \text{ solution) M} &= \frac{\text{Weight of CaCO}_3 \times 1000}{\text{Mol. wt of CaCO}_3 \quad 1000} \\ &= \frac{0.28\text{gm} \times 1000}{100 \quad 1000} = 0.0028 \text{ M} \end{aligned}$$

Strength of EDTA solution M₂ = $\frac{V_1 M_1}{V_2} = \frac{100 \times 0.0028}{28} = 0.01 \text{ M}$

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 = $\frac{V_2 M_2}{V_3} = \frac{33 \times 0.01}{100} = 0.0033 \text{ M}$

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 = ?

$$\begin{aligned} \text{Total Hardness} &= 0.0033 \times 10^5 \text{ ppm} = 0.0033 \times 100 (\text{Mol. Wt of CaCO}_3) \times 1000 (\text{ml})\text{ppm} \\ &= 330 \text{ ppm} \end{aligned}$$

Calculation of Permanent hardness M₄ = $\frac{V_2 M_2}{V_4} = \frac{10 \times 0.01}{100} = 0.001 \text{ M}$

V_2 = Volume of EDTA solution (10 ml), M_2 = Strength of EDTA solution (0.01M)

V_4 = Volume of sample hard water after boiling cooling and filtering (100 ml)

M_4 = Strength of sample hard water after boiling cooling and filtering =?

Permanent Hardness = 0.001×10^5 ppm

= 0.001×100 (Mol. Wt of CaCO_3) $\times 1000$ (ml)ppm

= 100 ppm

Calculation of Temporary hardness = Total hardness - Permanent hardness

= $330 - 100 = 230$ ppm

POTABLE WATER AND ITS SPECIFICATIONS

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

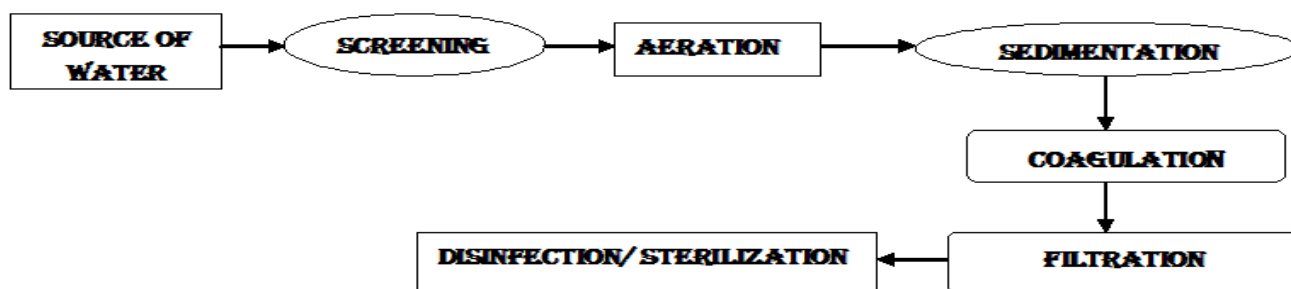
The following are the **specifications of water drinking purpose**.

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

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.

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

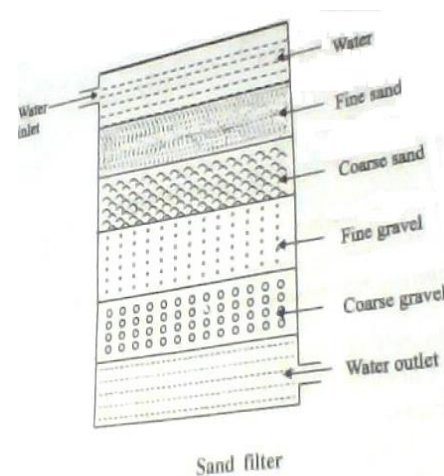


2. Aeration: The water is then subjected to aeration(reacting with air) which helps in exchange of gases between water and air, increases the oxygen content and removes the impurities like iron, manganese and dissolved gases like H_2S , CO_2 and NH_3 .

3. 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.

4. 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.

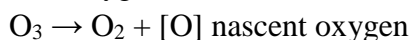
5. The colloidal impurities are retained by the fine sand layer resulting the very slow filtration of water. Periodically the top layers of the fine sand layer is scraped off, washed, dried and introduced into the filter bed for reuse.



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

DISINFECTION OF POTABLE WATER

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

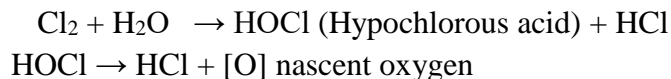


The nascent oxygen is a powerful oxidizing agent and kills the bacteria.

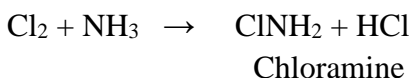
Disadvantages: This process is costly and cannot be used in large scale, due to unstable of ozone cannot be stored for long time.

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

a. 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.



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



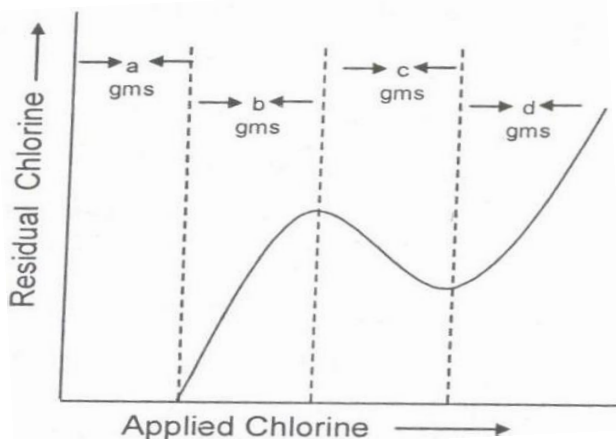


Chloramine compounds decompose slowly to give nascent oxygen which will be act as good disinfectant than the Chlorine. Chloramine gives good taste to the treated water.

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 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 compounds.

‘c’ gms of chlorine added causes destruction 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**.

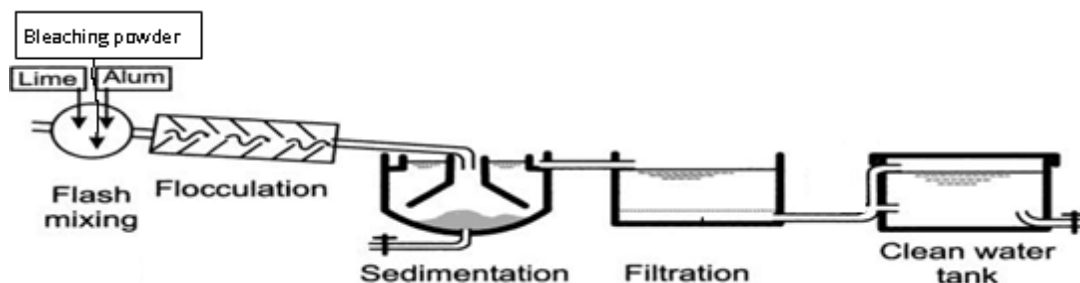
Advantages of break-point chlorination:

- 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.

DEFLUORIDATION - NALGONDA TECHNIQUE

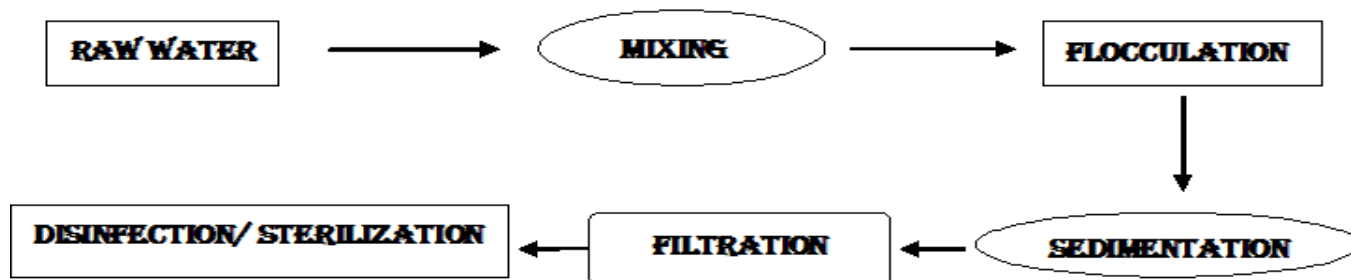
Defluoridation is the removal of excess fluoride from water. Nalgonda technique is simple and economical. Reverse osmosis, activated alumina and distillation methods are used to remove fluorine.

In Nalgonda technique, where fluoride is precipitated using 500 mg/L of alum and 30 mg/L of lime with small amount of bleaching powder (3 mg/L) for disinfection.



Steps involved in Nalgonda technique:

Nalgonda Technique involves rapid mixing (with that chemical interaction is very effective), flocculating, sedimentation, filtration and disinfection. Alum (coagulant) is used to flocculate fluoride ions.



The process is best carried out under alkaline conditions, therefore, lime is added. For disinfecting, bleaching powder is added. After stirring, the chemical elements coagulate into flocks and settle down in the bottom.

- Advantages:**
- i. Nalgonda Technique is adoptable to domestic use because low price.
 - ii. Ease of Handling. Bleaching powder

- Disadvantages:**
- i. It is not suitable if the pH of untreated water is alkaline.
 - ii. It is not suitable when the fluoride concentration is very high.

Sailent features of Nalgonda Technique:

- Nalgonda Technique is adoptable to domestic use.
- Simultaneous removal of colour, odour, turbidity, bacteria and organic contaminants possible.
- Sludge generated is convertible to alum for reuse.
- No handling of caustic acids and alkalis, Local skills/capability readily employable.
- Needs minimum mechanical and electrical equipment and no energy except muscle power for domestic equipment.
- Highly efficient removal of fluoride from 1.5 to 20 mg/L to desirable levels.

DETERMINATION OF F⁻ ION BY ION- SELECTIVE ELECTRODE METHOD.

- An ion-selective electrode (ISE) is defined as an electro analytical sensor with a membrane whose potential indicates the activity of the ion to be determined (fluoride) in a solution.
- Ion-sensitive membrane may be glass, a crystalline inorganic material, or an organic ion exchanger.
- The membrane interacts with the ion of choice, here fluoride, allowing electrical potential of the half cell which is controlled by the fluorine concentration.

- The potential of the ISE is measured against a suitable reference electrode using a pH meter. The electrode potential is related to the logarithm of the concentration of the fluoride ion by the Nernst equation.

$$E = E^0 + \frac{2303 RT}{nF} \log [M]$$

n = ion charge, the equation is valid for very dilute solutions where the ionic strength is constant.

- In this experiment we will use fluoride-sensitive electrode, either a saturated calomel electrode or Ag/AgCl external reference electrode to measure the fluoride ion concentration.
- Fluoride ISEs only respond to free ionized F⁻ in solution and can be used to measure this ion in the presence of other fluorine compounds.

Reagents required:

- NaF(dried at 100°C for 1 hour)
- KCl
- Liquid NaF unknown
- Fluoride ISE and Ag/AgCl reference electrode
- pH meter capable of displaying mV potentials

Procedure:

- Dry the NaF solid for 1 hour at 100°C
- **NaF(10⁻¹ M):** Weigh 0.42 g of NaF, dissolve in deionized water, and dilute to 100 ml in a volumetric flask. This solution is about 10⁻¹ F in NaF.
- Transfer 10 ml of above solution to 100 ml volumetric flask and dilute with deionized water. This solution is about 10⁻² F in NaF.
- **KCl (1 M):** Weigh 7.55 g of KCl on a top loading balance and dissolve in 100 ml deionised water.
- Prepare four 100 ml volumetric standard flasks as follows:

NaF(10 ⁻² M) ml	KCl (1 M) ml	Dilute each flask with deionised water
(a) 1.00	10	
(b) 2.00	10	
(c) 5.00	10	
(d) 10.00	10	

Analysis:

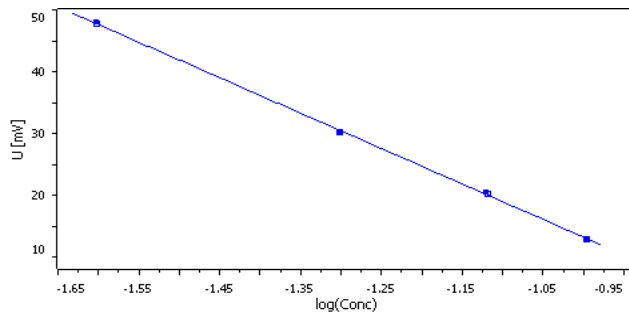
- Take unknown solution into a 100 ml volumetric flask and dilute upto the mark.
- Add 1 ml of prepared unknown solution and add 10 ml of KCl and dilute it to 100 ml with deionised water.
- Measure the potential in MV of the fluoride ISE Vs reference electrode for each of the four standard and for unknown solution.
- Pour about 30 ml of each standard solution (or) unknown into clean 100 ml beaker and immerse the electrode in the solution in the depth of 2 cm and then measure the electrode potential.

- After completion of the experiment rinse the electrodes with deionised water and keep the reference electrode in the appropriate solution.
- The F-ISE should be stored dry and loosely capped.

Calculations:

- Calculate the molarity of NaF accurately.

- Plot a graph of the concentration of NaF Vs potential. Find the best line passing through four standard solution points. Calculate the slope of the calibration curve slope = $dE/d\log[\text{NaF}]$



- By using calibration curve determine the concentration of NaF in your prepared unknown solution. Report this as percent fluoride (% w/v) in the prepared unknown.

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:

1. 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:

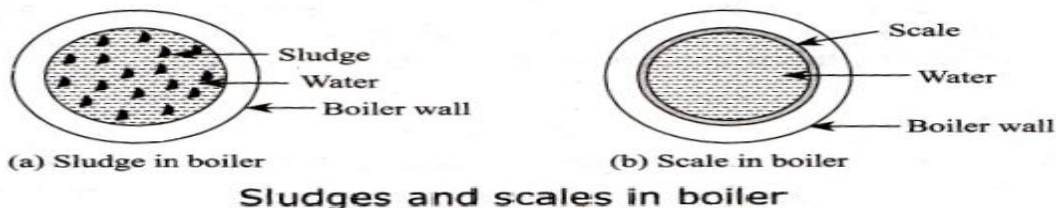
The dissolved salts whose solubility is more in hot water and less in cold water produce sludges.

Disadvantages of sludges:

1. Sludges are bad conductors of heat and results in the wastage of heat and fuel.
2. 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:

- a. 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.
- b. 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:

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



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



- c. **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.

- d. **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:

1. **Wastage of heat and fuels:** Scales poor thermal conductivity so that rate of heat transformation is reduced.
2. **Lowering of boiler safety** is due to overheating of the boiler material becomes softer and weaker, which causes distortion of boiler.

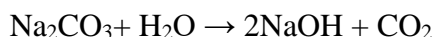
3. **Decrease in efficiency** of the boiler due to scales deposited in the valves and condensers of the boiler cause choking.
4. **Danger of explosion** which happens the formation of the scales, the boiler plate faces higher temperature outside and lesser temperature inside due to uneven expansion. 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:

- a. If the scale formation is soft it can be removed by a scrapper, wire brush.
- b. By giving thermal shocks, by sudden heating and sudden cooling which makes scale brittle and removed by scrubbing with wire brush.
- c. 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”.



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:

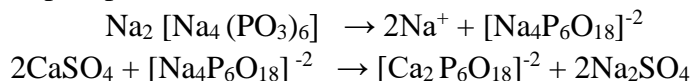
- a. By maintaining the pH value of water and neutralization of alkali.
- b. By using Sodium Phosphate as softening reagents, in the external treatment of boilers.
- c. Caustic embrittlement can also be prevented by adding Tannin or Lignin or Sodium sulphate which prevents the infiltration of caustic-soda solution blocking the hair-cracks.

INTERNAL TREATMENT OF WATER

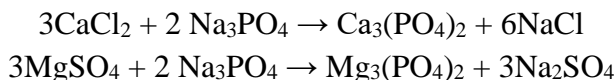
Suitable chemicals are added to the boiler water either to precipitate or to convert the scale into compounds is called **internal treatment** of the boiler feed water. Internal treatment can be done following types.

1. 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 = $\text{Na}_2 [\text{Na}_4 (\text{PO}_3)_6]$



2. 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.



Generally three types of Phosphates are employed.

- i. Tri sodium Phosphate (Na_3PO_4): is too alkaline used for treat to too acidic water.
- ii. Di sodium Phosphate (Na_2HPO_4): is weakly alkaline used for treat to weakly acidic water.
- iii. Sodium dihydrogen Phosphate (NaH_2PO_4): is too acidic used for treat to too alkaline water.

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

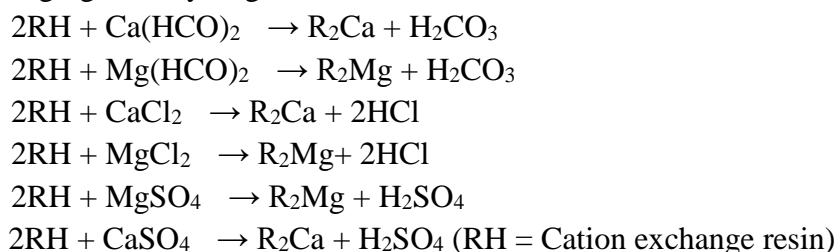
SOFTENING OF WATER BY ION EXCHANGE PROCESS

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.

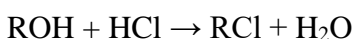
Resins are classified as:

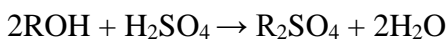
- i. Cation Exchange Resins
- ii. Anion Exchange Resins.

i. Cation Exchange Resins: Cation exchange resins are styrene divinyl benzene co-polymers, which on sulphonation (or) carboxylation, which contains $-\text{COOH}$, $-\text{SO}_3\text{H}$ functional groups which responsible for exchanging their hydrogen ions with cations in water.



ii. 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.





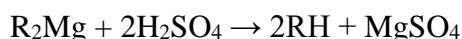
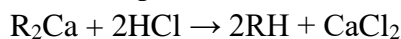
In ion-exchange process, hard water is allowed to pass through cation exchange resins, which remove Ca^{+2} and Mg^{+2} ions and exchange equivalent amount of H^+ ions. Anions exchange resins remove bicarbonates, chlorides and sulphates from water exchange equivalent amount of OH^- ions.

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.

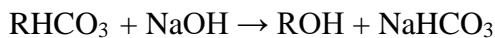
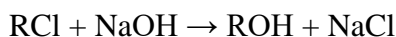
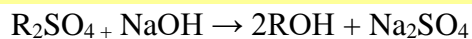
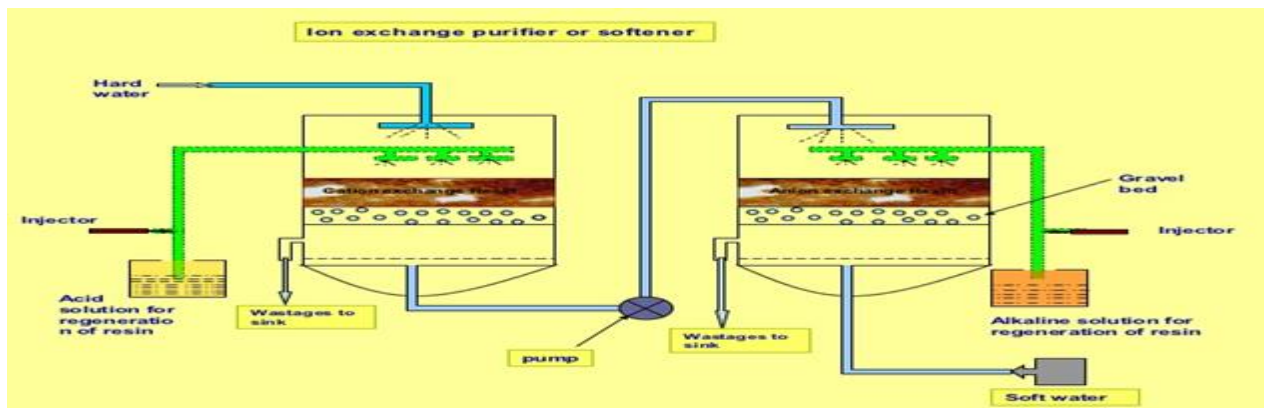


The water coming out from the exchanger is ion free from anions and cations. Thus water of zero hardness is obtained.

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.



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



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 quantity of dissolved solids, water is graded as:

- i. Fresh Water: Contains less than 1000 ppm of dissolved solids.
- ii. Brackish Water: Contains more than 1000 ppm to less than 35000 ppm of dissolved solids.
- iii. Sea Water: Contains more than 35000 ppm of dissolved solids.

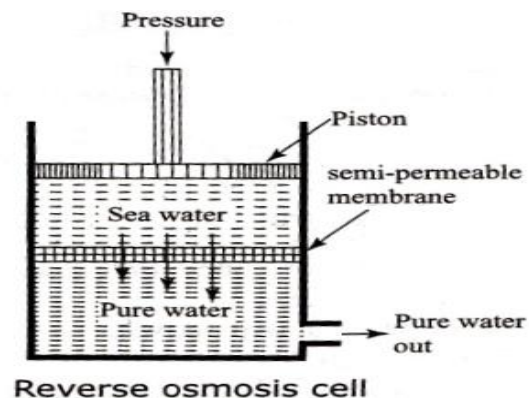
Sea water and brackish water can be made available as drinking water through desalination process. Desalination is carried out either by reverse osmosis or electro dialysis.

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.

In this process pure water is separated from salt water. 15-40 kg/cm² 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.

SEWAGE WATER - STEPS INVOLVED IN THE TREATMENT

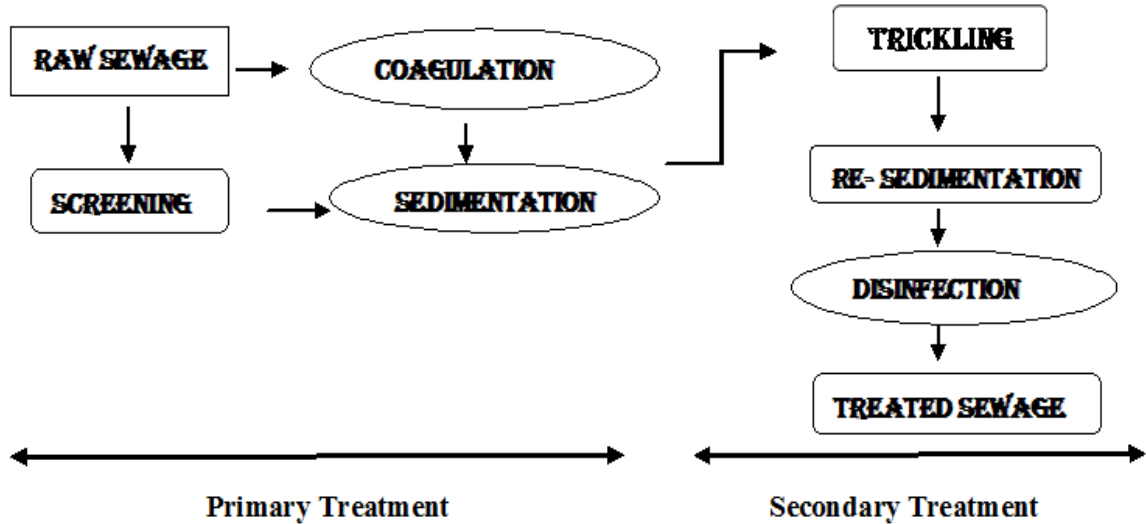
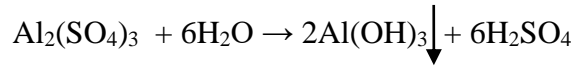
Sewage/Waste water is the water which comes from flushing the toilet, bathing, washing clothes and general cleaning.

Sewage treatment is the process of removing contaminants from waste water. It includes physical, chemical, and biological processes to remove these contaminants and produce environmentally safe treated waste water.

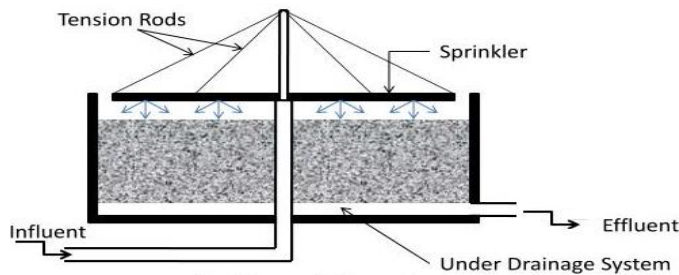
Steps involved in the treatment of sewage water: Waste water goes down the drain and into a pipe, which joins a larger drainage pipe under the road; this water can be send to the treatment center. **Five steps** involved in the treatment of sewage water.

I. Preliminary treatment (Screening): Screening is the first stage of the treatment of the sewage water. Screening removes large objects like, plastics, bottles, sanitary items, papers and damaged equipment.

II. Primary Treatment (or) settling process: This involves the separation of organic solid matter like human waste. This is done by putting the waste water into large settlement tanks for the solids to sink to the bottom of the tank. The settled solids are called sludge, after removing the sludge the rest water is then send to the secondary treatment.



III. Secondary Treatment (or) Biological treatment:



In this stage water is put into larger rectangular tanks, which we called aeration lanes. In this process air is pumped into the water to encourage bacteria to break down biodegradable organic impurities in to the small particles which are separated through scrapping process. This is done by **Trickling filter process**.

IV. Tertiary Treatment: After the secondary treatment the treated water send through settlement tank to separate the remaining sludge. The water at this stage is almost free from harmful substances and chemicals. The water is allowed to flow over a wall where it is filtered through a bed of sand to remove additional particles. The filtered water is then released into the river.

V. Disposal of Sludge: This is the last stage in the sewage treatment. Sludge formed from different steps can be disposed by dumping into low-lying areas, burning of sludge and using it as low grade fertilizers.

Important Questions

1. How temporary hardness differs from permanent hardness?
2. Define hardness and estimate hardness of water by using EDTA solution?
3. Explain Caustic embrittlement, Scale & Sludge.
4. Explain determination of fluoride ions (F^-) by ion selective electrode method.
5. Explain softening of water using Ion exchange process.
6. What is desalination? Explain reverse osmosis process.
7. Explain Steps involved in treatment of sewage water.
8. What is Potable water and what are its specifications.
9. Explain Steps involved in the treatment of potable water.
10. 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.
11. Explain the following?
 - a. Calgon conditioning and Phosphate conditioning of boiler feed water.
 - b. What is defluoridation and explain Nalgonda technique.
12. What is Hardness and calculate 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.

Objective Questions:

1. Hard water may be softened by passing it through: []
(a) Limestone (b) Ion-exchange resins (c) Calgon (d) Rock salt
2. Temporary hardness in water is removed by []
(a) Filtration (b) Sedimentation (c) Boiling (d) coagulation
3. The colour of EBT indicator is []
(a) Wine red (b) Blue (c) Colour less (d) Pink

UNIT-1

4. EDTA method of determining hardness of water can be used to determine: []
(a) All types of hardness (b) Temporary hardness only
(c) Permanent hardness only (d) Alkaline hardness only
5. One part of CaCO_3 equivalent hardness per 10^6 parts of water is also called as []
(a) Degree Clarke (b) Degree french (c) ppm (d) mg/L
6. The hardness of water is 10ppm it can be expressed in degree clark as: []
(a) 0.07°Cl (b) 0.7°Cl (c) 7.0°Cl (d) 0.007°Cl
7. The process of allowing water to stand and undisturbed in big tank for settling of the suspended Particles due to force of gravity []
(a) Coagulation (b) Sedimentation (c) Conditioning (d) Screening
8. The Soft, loose and slimy precipitate formed within the boiler is called []
(a) Scale (b) sludge (c) embrittlement (d) Coagulation
9. The Hard and adherent precipitate formed on the inner walls of the boiler is called []
(a) Scale (b) sludge (c) embrittlement (d) Coagulation
10. Potable water treatment does not involve []
(a) Demineralization (b) sedimentation (c) filtration (d) disinfection
11. Caustic embrittlement is due to the []
(a) NaOH (b) Na_2CO_3 (c) $\text{Mg}(\text{OH})_2$ (d) H_2SO_4
12. Caustic embrittlement can be avoided by using []
(a) Sodium phosphate (b) hydrogen (c) ammonium hydroxide (d) sodium sulphate
13. The exhausted anion exchange resin can be regenerated by the addition of []
(a) dil. HCl (b) dil. NaOH (c) dil. H_2SO_4 (d) dil. $\text{Mg}(\text{OH})_2$
14. Brackish water mostly contains dissolved []
(a) Calcium salts (b) Magnesium salts (c) Turbidity (d) Sodium Chloride
15. The purification of brackish water by reverse osmosis is also ... called []
(a) Super-Filtration (b) Supra-Filtration (c) hypo-Filtration (d) Filtration
16. Which of the following methods separating both ionic and non ionic impurities from water []
(a) electrodialysis (b) Demineralization (c) reverse osmosis (d) ion exchange process

Fill in the blanks:

1. Hardness of water is expressed in terms of _____ equivalents.
2. Temporary hardness of water can be removed by _____.
3. $MgCl_2$ and $MgSO_4$ present in water produces _____ hardness.
4. In the estimation of hardness of water by EDTA method, the wine red colour is due to _____.
5. The process of killing germs in potable water is called _____.
6. _____ is the main advantage of usage of chlorine gas than the Chloramine as a disinfectant.
7. Chlorine, when treated with water produce _____ acid, which act as a powerful germicide.
8. The pH of the potable water should be _____.
9. Sodium aluminate is used as _____ during purification of water.
10. _____, _____ & _____ Chemicals are required in Nalgonda de-fluoridation technique.
11. The chemical name of the calgon is _____.
12. In phosphate conditioning if boiler feed water is too alkaline _____ is used for internal conditioning.
13. Cation and Anion exchange resins are regenerated by using _____ & _____.
14. Best method of removing hardness of water is _____ process.
15. _____ is a measure of oxidizable impurities present in the sewage.

Two Marks and Three Marks Questions

1. Write two balanced equations to describe when hard water is heated.
2. What are the constituents that cause hardness in water? Explain the terms Carbonate hardness and Non-Carbonate hardness.
3. What is the inter relation of units of hardness?

4. Write the principle involved in complexometric method for the determination of hardness of water.

5. What is the need for an alkaline buffer in the determination of hardness of water by EDTA titration?

6. Write the specifications of potable water.

7. Explain disinfection by chlorination.

8. What is Break-point of chlorination?

9. What is meant by defluoridation.

10. How is Nalgonda technique carried out?

11. Write differences between scales and sludges.

12. What is Caustic embrittlement? Explain and also write its prevention.

(or)

Explain the cause of caustic embrittlement in boilers and suggest a remedy.

13. Calgon treatment prevents scale formation in boilers. Give reasons.

14. What is Phosphate conditioning?

15. Write the principle of Ion exchange process of softening water.

16. What are advantages of Ion exchange process?

17. What is ment by Reverse osmosis? How is it applied in the desalination of water?

18. What are advantages of Reverse osmosis?

19. What is sewage water?

Draw the neat diagrams of the following

1. Ion – exchange process:

2. Reverse Osmosis:

Draw the flow charts of the following:

1. Steps involved in the treatment of the “**POTABLE WATER**”:

2. Steps involved in the treatment of the “**Defluoridation – NALGONDA
TECHNIQUE**”:

3. Steps involved in the treatment of the “SEWAGE WATER”: