Introduction:

Like air water is one of the few basic materials which is of prime importance for the preservation of life on this earth. All are aware of the uses of water for drinking, cooking, bathing and farming etc., but few know the importance of water as an engineering material. For the existence of all living beings (humans, animals and plants) water is very crucial. Without water we cannot survive and almost all human activities–domestic, agricultural and industrial demand use of water. Although water is nature's most wonderful and abundant compound but only less than 1% of the world's water resources is available for the ready use. As engineering material water is used for producing steam in boilers to generate hydroelectric power, furnishing steam for engines, for refrigeration and air conditioning, for construction of concrete structures for manufacturing purposes and as a solvent in the chemical process.

SOURCES OF WATER:

The various sources of water are:

1. **Surface water** – It is any source of water body above the ground. It includes rivers, ponds, lakes, reservoirs etc.
2. **Underground water** – Ground water sources are beneath the land surface and include springs and wells.
3. **Rain water** – It is the purest form of water and the main source of water in tropical communities.
4. **Sea water** – Sea water contains number of salts like chlorides, carbonates, bicarbonates, sulfates of sodium, potassium, calcium, magnesium etc. It is neither suitable for drinking nor in industrial applications.

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:

- ❖ They are the suspended solids that are not completely soluble in water and are present as particles. They impart visible turbidity to the water. 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.

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.

4. Colloidal impurities:

- ❖ They are the very finely divided dispersion of particles in water. These particles are so small that these cannot be removed by ordinary filters and are not visible to the naked eye.

Hardness

Hardness of water is defined as the property which prevents the lathering of soap. This is due to presence of certain salts of Ca^{2+}, Mg^{2+} and other heavy metals dissolved in it. Soaps are sodium or potassium salts of higher fatty acids like oleic acid or palmitic acid or stearic acids ($C_{17}H_{35}COONa$). Hard water does not give lather with soap while soft water gives lather readily with soap.
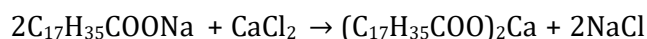
Causes of Hardness: Soap with hard water reactions

When soap comes in contact with soft water lather is produced due to stearic acid.

$$C_{17}H_{35}COONa + H_2O \rightarrow C_{17}H_{35}COOH + NaOH$$
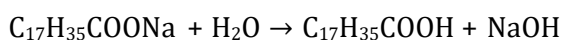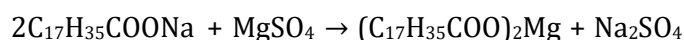
(Sodium stearate)   (Stearic acid)

When soap comes in contact with hard water, sodium stearate will react with dissolved calcium and magnesium salts and produce calcium stearate or magnesium stearate which is white precipitate. This insoluble white precipitate prevents lathering of soap.

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

(Sodium stearate)   (insoluble scum)

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

(Sodium stearate)   (insoluble scum)

Different types of water have different degrees of hardness. The different types of water are commercially classified on the basis of degree of hardness as follows:

Hardness	Name of water
0-70mg/liter	Soft water
70-150mg/liter	Moderate hard water
150-300mg/liter	Hard water
300mg/liter and above	Very hard water

Effects of Hard Water

(a) In domestic uses. For washing and bathing, hard water creates difficulties, since it does not form lather freely with soap. It also creates sticky precipitates that deposit on bath tub, body, clothes etc. until all the Ca/Mg salts get precipitated. Thus a lot of soap gets wasted also.

For cooking hard water creates similar difficulties by producing scum on the bottom of the vessels. Due to the presence of hardness producing salts in hard water, boiling point gets elevated and during cooking a lot of fuel is wasted. Pulses etc. do not cook in hard water. Taste of tea, coffee becomes unpleasant.

Drinking of hard water is also problematic since it affects the digestive system and at the same time the possibility of deposition of calcium oxalate crystals in the urinary tract is alarming.

(b) In industrial uses. For textile industry and dyeing industry, hard water causes the usual problem of deposition of insoluble salts that interfere with the proper dyeing and printing of the fabrics. The stains of iron salts also are undesirable on fabrics. Hard water also hampers the economy by wastage of soap as it does not form good lather.

- For sugar industry, the salts responsible for hardness create difficulties in sugar refining and crystallization of sugar and the sugar becomes deliquescent.
- Calcium and magnesium salts also interfere with the smooth and glossy finish of the papers in the paper industry. Iron salts interfere with the colour of the paper.
- In laundry, hard water causes wastage of costly soap and also interferes with the coloration due to the staining of iron salts.
- The hydration of cement and final hardening of cement are affected by use of hard water in concrete making.
- Hard water is not suitable for preparing drug solutions in pharmaceutical industry.
- For steam generation in boilers, hard water creates many problems like: (i) scale and sludge formation, (ii) corrosion, (iii) priming and foaming and (iv) caustic embrittlement.

Degree of hardness

The total hardness of water is caused by eight different dissolved salts of calcium and magnesium, [$Ca(HCO_3)_2$, $Mg(HCO_3)_2$, $CaCl_2$, $MgCl_2$, $CaSO_4$, $MgSO_4$, $Ca(NO_3)_2$ and $Mg(NO_3)_2$]. Hence the hardness of water is expressed in terms of calcium carbonate equivalents. The weight of different hardness salts causing hardness are converted to weight equivalent to that of calcium carbonate. $CaCO_3$ is selected for expression of hardness because the molecular weight of $CaCO_3$ is 100, which is easy for calculation and it is the most insoluble salt and all the dissolved salts of calcium are precipitated as $CaCO_3$.

Name of the salt	Molecular weight
$Ca(HCO_3)_2$	162
$Mg(HCO_3)_2$	146
$CaCl_2$	111
$MgCl_2$	95
$CaSO_4$	136
$MgSO_4$	120
$CaCO_3$	100

The method for calculating degree of hardness will be clear from the following formula: Hardness of water in terms of calcium carbonate equivalents = (Amount of hardness causing salts/ Molecular weight of hardness causing salts) × 100

Why $CaCO_3$ as reference for Hardness?

(1). $CaCO_3$ is stable, non-hygroscopic and is obtained in pure form. Therefore a standard hard water solution can be prepared by dissolving accurately weighed $CaCO_3$ in dilute HCl and make up to a known volume.

(2). $CaCO_3$ is insoluble in water. Therefore it can be easily precipitated in water treatments.

(3). Molecular weight of $CaCO_3$ is 100, so mathematical calculations are easy.

Expression of hardness – Units

1Parts Per Million: Parts of $CaCO_3$ equivalent hardness per 10^6 parts of water.

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

Milligram per liter: Number of milligrams of calcium carbonate equivalent hardness present in 1 liter of water.

1mg/L = 1 mg of $CaCO_3$ equivalent hardness present in 1 liter of water.

At 4oC, 1 liter of water is equal to 1kg of water.

1L of water weight = 1Kg of water

1Kg = 1000gms

= 1000 x 1000 mg

1L = 10^6 mg

It becomes number of parts of $CaCO_3$ equivalent hardness causing salts in one million parts of water. Therefore 1mg/L is equal to 1ppm.

Degree Clark: (°Cl): It is the number of grains (1/7000 lb) of $CaCO_3$ equivalent hardness per 70,000 parts of water.

1Clark = 1 grain of $CaCO_3$ equivalent hardness per gallon of water.

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

Degree French (°Fr): It is the parts of $CaCO_3$ equivalent hardness per 10^5 parts of water.

1^0French =1 part of $CaCO_3$ per 10^5 parts of hard water

Milliequivalents per litre: No of milliequivalents of hardness present per liter of water.

1m eq./L= 1 m eq. of $CaCO_3$ per / liter of water = 50 mg /L of $CaCO_3$eq. = 50ppm

Relation between various units of hardness:

$$1 \text{ ppm} = 1mg/L = 0.1^0Fr = 0.07\ ^0Cl = 0.02 \text{ m eq./L}$$

Total hardness of the sample water= 121ppm = 121mg/L

121x0.07=8.47^{0}Cl and 121x0.1=12.1^{0}Fr

Permanent hardness= 101mg/l, 101ppm, 7.07^{0}Cl, 10.1^{0}Fr

Temporary hardness=20mg/l, 20ppm, 1.4^{0}Cl and 2^{0}Fr

Types of Hardness

Hardness of water is mainly two types

1. Temporary Hardness

2. Permanent Hardness

1. Temporary Hardness:

It is caused mainly due to the presence of dissolved bicarbonates of calcium, magnesium and other heavy metals. The salts mainly responsible for temporary hardness of water are Calcium bicarbonate $Ca(HCO_3)_2$ and Magnesium bicarbonate $Mg(HCO_3)_2$.

When bicarbonates are decomposed, yielding insoluble carbonates or hydroxides, this gets deposited as a crust at the bottom of vessel. Temporary hardness can be largely removed by mere boiling of water. On boiling bicarbonates converts into corresponding carbonates which are insoluble. They can be removed by filtration.

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

(Calcium bicarbonate)

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

(Magnesium bicarbonate)

2. Permanent Hardness:

It is due to the presence of dissolved chlorides and sulphates of calcium, magnesium, iron and other metals. The salts responsible for permanent hardness 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.

Total hardness of water =Temporary hardness + Permanent hardness

So, How to Remove the Permanent Hardness of Water?

We use certain chemical methods to remove the permanent hardness of water, which are:

1. Treating the Water with Washing Soda

In this method, we add washing soda, i.e., Na_2CO_3 to the hard water. It combines with chloride salts of calcium and magnesium present in the water to form compounds.

2. Calgon's Method

In this method, when Calgon, i.e Sodium Hexametaphosphate ($Na_6P_6O_{18}$) is added to the water, each of its molecules ionizes to give two Na^+ ions and one complex anion. This complex anion further releases Na^+ ions and captures all the Ca^{2+} or Mg^{2+} ions. These ions become a part of the complex anion. In this manner, water is freed from Ca^{2+} or Mg^{2+} ions. Now, it contains only Na+ ions only. Therefore, it no longer remains hard, i.e., becomes soft.

3. Ion-Exchange Method

In this method, we add a Permutit (a complex inorganic salt) called zeolite (Sodium Aluminum Silicate) or ($AlNa_{12}SiO_5$) to the water, which is insoluble in water. On adding this to water, the ion-exchange process starts between it and the Ca^{2+} or Mg^{2+} ions. In this way, water becomes free from Ca^{2+} or Mg^{2+} ions, and no longer remains hard.
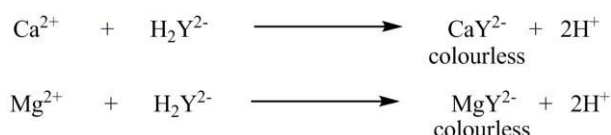
4. Synthetic Resins Method

In this method, we use synthetic ion-exchange resins (RNa^+), which is insoluble in water. When it is added to water, an exchange between RNa^+ and Ca^{2+} or Mg^{2+} ions occurs. This process frees water from Ca^{2+} or Mg^{2+} ions. So, water no longer remains hard, and it becomes soft.

|	Unit No:
Subject: Applied Chemistry	Lecture No:
Faculty: Dr. Monaj Karar	Link to Session
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Topic: WATER and ITS TREATEMENT	Date Conducted:
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Estimation of temporary & permanent hardness of water

Estimation of Hardness of Water by EDTA method (Complexometric titration)

Hardness in water is due to the presence of dissolved salts of calcium and magnesium. It is unfit for drinking, bathing, washing and it also forms scales in boilers. Hence it is necessary to estimate the amount of hardness producing substances present in the water sample.

The estimation of hardness is based on complexometric titration. Hardness of water is determined by titrating with a standard solution of ethylene diamine tetra acetic acid (EDTA) which is a complexing agent. Ethylene Diamine Tetra Acetic acid (EDTA) is a reagent that forms EDTA-metal complexes with many metal ions. In alkaline conditions (pH>9) it forms stable complexes with the

alkaline earth metal ions Ca^{2+} and Mg^{2+}. EDTA can combine with metal ion in 1:1 ratio to form a chelate structure.

$$Ca^{2+} \quad + \quad H_2Y^{2-} \quad \longrightarrow \quad \underset{\text{colourless}}{CaY^{2-}} \quad + \quad 2H^+$$

$$Mg^{2+} \quad + \quad H_2Y^{2-} \quad \longrightarrow \quad \underset{\text{colourless}}{MgY^{2-}} \quad + \quad 2H^+$$

EDTA is Ethylene Diamine Tetra Acetic acid. The structure of EDTA is as shown below. Since, EDTA is insoluble in water; its disodium salt is used as a complexing agent.
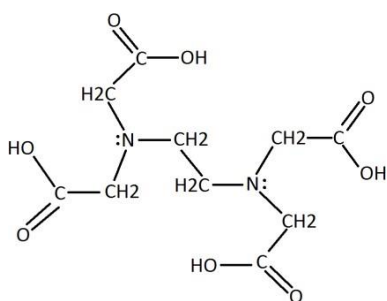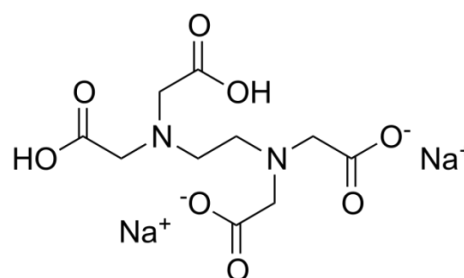

EDTA   **Disodium salt of EDTA**

Basic Principle

Total hardness is due to the presence of bicarbonates, chlorides and sulphates of calcium and magnesium ions. The total hardness of water is estimated by titrating the water sample against

EDTA using Eriochrome Black-T (EBT) indicator. Initially EBT forms a weak EBT- Ca^{2+}/Mg^{2+} wine red coloured complex with Ca^{2+}/Mg^{2+} ions present in the hard water. On addition of EDTA solution, Ca^{2+}/Mg^{2+} ions preferably forms a stable EDTA-Ca^{2+}/Mg^{2+} complex with EDTA leaving the free EBT indicator in solution which is steel blue in color in the presence of ammonia buffer. Thus the end point is the change of color from wine red to blue.
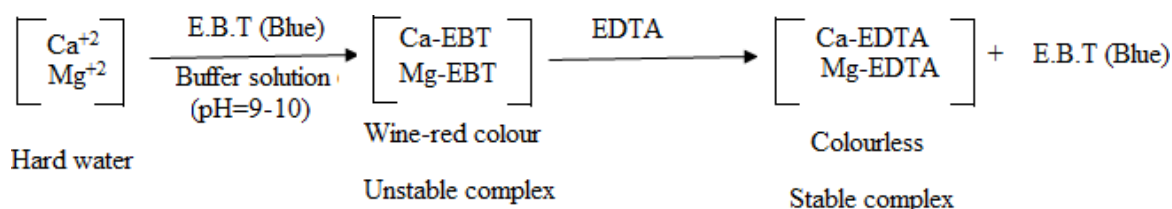
Structure of EBT:
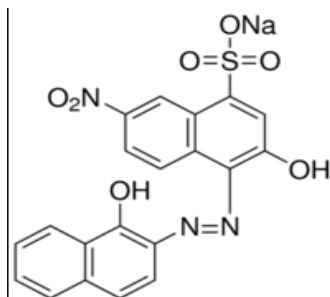
In EDTA methods, the known water sample is titrated against standard EDTA solution using EBT as indicator in the presence of basic buffer solution (NH_4OH-NH_4Cl; pH=10). At the end point the wine red color changes to blue.
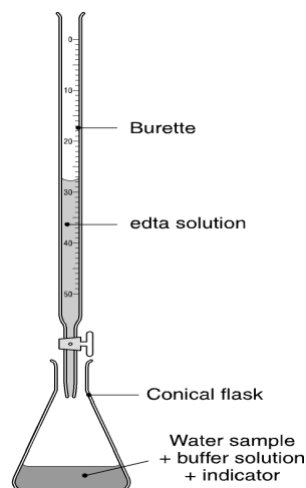
#Role of Buffer NH_4Cl + NH_4OH: To maintain pH10. M-EDTA complex is more stable at pH 10. M-EBT complex formation is more favorable at pH10.

Experimental procedure:

1. Preparation of standard hard water: Dissolve 1.0g of $CaCO_3$ in minimum amount of dil. HCl and make up to 1000ml in a standard flask with distilled water.

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

2. Standardization of EDTA: Add 4g of disodium salt of EDTA to 1L of distilled water. Fill the 50ml burette with the EDTA solution.

Pipette out 20ml of standard hard water into a conical flask. To it add 2ml NH_4Cl-NH_4OH buffer, 4 drops of EBT. Upon adding EBT the water turns into wine red color. The wine red color is due to the formation of the Ca-EBT complex. Upon titration with the EDTA the water color changes from wine red to blue color.

Let the volume of EDTA consumed by standard hard water be 'a' ml. Repeat the titration to get concurrent values.

Molarity of Hard water: $M_1V_1 = M_2V_2$

M_1 = Molarity of Std hard water = 0.01M
V_1 = Volume of Std hard water = 20mL
M_2 = Molarity of EDTA solution =?
V_2 = Volume of EDTA solution - Burette reading = a mL

$$M_2 = \frac{M_1V_1}{V_2} = \frac{0.01M \times 20mL}{a\ mL} = M_2$$

3. <u>Estimation of total hardness of water</u>: Pipette out 20 ml of sample water into a conical flask. To it add 2ml of NH_4Cl-NH_4OH buffer solution and 4 drops of EBT. Titrate with EDTA solution till the wine red color of the solution changes to blue.

Let the volume of EDTA consumed by sample water be 'b' ml. Repeat the titration for concurrent values.

Molarity of Hard water: $M_2V_2 = M_3V_3$

M_2 = Molarity of EDTA solution (from step 2)
V_2 = Volume of EDTA solution - Burette reading = b mL
M_3 = Molarity of Std hard water = ?
V_3 = Volume of Std hard water = 20mL

$$M_3 = \frac{M_2V_2}{V_3} = \frac{M_2 \times b\ mL}{20\ mL} = x\ moles$$

Total hardness of Water = 'x'moles x 10^5 (to convert into ppm)
= 'x'moles x 100 x 1000 = x ppm

4. <u>Estimation of permanent hardness of water:</u> Boil 100 ml of water in a beaker till it reduces to 20 ml. (Boiling remove temporary hardness). Cool & filter into a 100 ml standard flask .Wash the precipitate with distilled water. Pipette out 20 ml of the water sample into a comical flask and add 2ml of buffer solution, 4 drops of EBT. Titrate with EDTA until wine red solution changes to blue color.

Let the volume of EDTA consumed with boiled water be 'c' ml. Repeat the titration for concurrent values.

Permanent Hardness: $M_2V_2=M_4V_4$

M_2 = Molarity of EDTA solution (from step 2)
V_2 = Volume of EDTA solution - Burette reading = c mL
M_4 = Molarity of Std hard water = ?
V_4 = Volume of Std hard water = 20mL

$$M_4 = \frac{M_2V_2}{V_4} = \frac{M_2 \times c\ mL}{20\ mL} = y\ moles$$

Permanent hardness of Water = 'y' moles x 10^5 (to convert into ppm)

= 'y' moles x 100 x 1000 = y ppm

Temporary hardness = Total hardness – Permanent hardness

= (M_3 X 100 X 1000) – (M_4 X 100 X 1000) ppm

Numerical Problems:

Problem-1: *A sample of water is found to contains following dissolving salts in milligrams per liter* $Mg(HCO_3)_2 = 73$, $CaCl_2 = 111$, $Ca(HCO_3)_2 = 81$, $MgSO_4 = 40$ *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 = 100 mgs/Lit.

Permanent hardness = $CaCl_2$ + $MgSO_4$ + $MgCl_2$ = 100 + 33.3 + 100 = 233.3 mgs/Lit.

Total hardness = Temporary hardness + Permanent hardness = 100 + 233.3 = 333.3 mgs/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 CaCO3 (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 = 15 ppm

= 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

Problem-5: *In a hardness estimation by EDTA method 50 ml of a sample water required 30 ml of std EDTA solution. Calculate hardness of sample water? Given that 1ml of EDTA solution is equivalent to 1.8 mg of CaCO$_3$ (Here you are provided with a standardized EDTA).*

Solution: 1 ml of EDTA solution is equivalent to 1.8 mg of CaCO$_3$

Hardness estimation

50 ml sample water consumed 30 ml of EDTA

I.e. 50 ml sample water = 30 x 1.8 mg of CaCO$_3$.

Then, 1 ml of sample water = $\frac{30 \times 1.8}{50}$ mg of CaCO$_3$.

Therefore 1000 ml sample water = $\frac{30 \times 1.8}{50} \times 1000$ mg = 1080 mg of CaCO$_3$

Then hardness = 1080 ppm.

Problem-6: *50 ml of standard hard water containing 1mg of CaCO$_3$/L consumed 20 ml of EDTA. 50 ml of sample water consumed 25 ml of EDTA. Calculate the total hardness. (Here you are provided with standard hard water solution, you have to standardize EDTA then find out the total hardness).*

Solution: Standard Hard water 1mg of CaCO$_3$ per litre

That means 1000 ml Std. Hard water contains 1mg of $CaCO_3$

Then 1 ml Std. Hard water contains 1/1000 mg = 0.001 mg of $CaCO_3$

Standardization of EDTA

20 ml of EDTA for 50 ml standard hard water

I.e. 20 ml of EDTA = 50 ml X 0.001 mg/ml of $CaCO_3$

Then, 1 ml EDTA $= \dfrac{50 \times 0.001}{20} = 0.0025$ mg of $CaCO_3$.

Estimation of total hardness

50 ml sample water consumed 25 ml of EDTA

I.e. 50 ml sample water = 25 x 0.0025 mg of $CaCO_3$.

Then, 1 ml of sample water $= \dfrac{25 \times 0.0025}{50}$ mg of $CaCO_3$.

Therefore 1000 ml sample water $= \dfrac{25 \times 0.0025}{50} \times 1000 = 1.25$ mg of $CaCO_3$

Then hardness = 1.25 ppm.

Problem-7: 50 ml of standard hard water containing 1mg of $CaCO3$/ml consumed 20 ml of EDTA. 50ml of sample water consumed 25 ml of EDTA. Calculate the total hardness. *Here you are provided with standard hard water solution, you have to standardize EDTA then find out the total hardness.*

Solution: Standard Hard water: 1mg of $CaCO_3$ per ml

That means 1ml Std Hard water contains 1mg of CaCO3

Standardization of EDTA

20 ml of EDTA for 50 ml standard hard water

I.e. 20 ml of EDTA = 50 ml X 1 mg/ml of $CaCO_3$

Then, 1 ml EDTA $= \dfrac{50 \times 1}{20} = 2.5$ mg of $CaCO_3$.

Estimation of total hardness

50 ml sample water consumed 25 ml of EDTA

I.e. 50 ml sample water = 25 x 2.5 mg of $CaCO_3$.

Then, 1 ml of sample water $= \dfrac{25 \times 2.5}{50}$ mg of $CaCO_3$.

Therefore 1000 ml sample water $= \dfrac{25 \times 2.5}{50} \times 1000 = 1250$ mg of $CaCO_3$

Then hardness = 1250 ppm.

Problem-8: *Calculate the hardness of 0.01 M $AlCl_3$ solution.*

Solution: Hardness (in ppm) = Molarity x Valency of Hardness causing salt x 50000 ppm

= Normality x 50000 ppm (Al^{3+})

Hardness (in ppm) = 0.01 M x 3 x 50000 = 1500 ppm

Problem-9: *Calculate the hardness of 0.01 N $AlCl_3$ solutions.*

Solution: Hardness (in ppm) = Normality x 50000 ppm (Al^{3+})

Hardness (in ppm) = 0.01 N x 50000 = 500 ppm

Problem-10: Calculate the hardness of 0.01 M $CaCO_3$ solution.

Solution: Hardness (in ppm) = Molarity x Valency of Hardness causing salt x 50000 ppm

Hardness (in ppm) = 0.01 M x 2 x 50000 = 1000 ppm

Problem-11: The hardness of a solution is 1000 ppm. Calculate the molarity solution.

Solution: Hardness (in ppm) = Molarity x Valency of Hardness causing salt x 50000 ppm

= Normality x 50000 ppm (Take standard $Ca^{2+}CO_3^{2-}$ valence)

Molarity = $\dfrac{\text{Hardness in ppm}}{Valancy*50000}$ = $\dfrac{1000}{2*50000}$ = 0.01 M

Problem-12: Calculate the hardness of 0.01 M $Al_2(SO_4)_3$ solution.

Solution: Hardness (in ppm) = Molarity x Valency of Hardness causing salt (Al^{3+}) x 50000 ppm

Hardness (in ppm) = 0.01 M x 3 x 50000 = 1500 ppm

Problem-13: Calculate the temporary and permanent hardness of water sample having the following analysis.

$Mg(HCO_3)_2$	73 mg/L	$CaSO_4$	136 mg/L	$CaCl_2$	111mg/L	SiO_2	10 mg/L
$Ca(HCO_3)_2$	162 mg/L	$MgCl_2$	95 mg/L	NaCl	100 mg/L		

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

Permanent hardness = $CaSO_4$ + $MgCl_2$ +$CaCl_2$

Hardness (in $CaCO_3$ equivalents)

= $\sum$ mass of hardness producing substance × $\dfrac{MW\ of\ CaCO3/valancy}{MW\ of\ Hardness\ producing\ subatance/valancy}$

Total hardness (due to $Mg(HCO_3)_2$ = 73 mg/L, $Ca(HCO_3)_2$ = 162 mg/L, $CaSO_4$ = 136 mg/L, $MgCl_2$ = 95 mg/L, $CaCl_2$ = 111 mg/L)

Total Hardness (in CaCO3 equivalents)

= $73×\dfrac{100/2}{146/2}$ + $162×\dfrac{100/2}{162/2}$ + $136×\dfrac{100/2}{136/2}$ + $95×\dfrac{100/2}{95/2}$ + $111×\dfrac{100/2}{111/2}$

= 50 + 100 + 100 + 100 + 100 = 450 ppm

Temporary hardness (due to $Mg(HCO_3)_2$ = 73 mg/L, $Ca(HCO_3)_2$ = 162 mg/L)

= $73×\dfrac{100/2}{146/2}$ + $162×\dfrac{100/2}{162/2}$ = 50 + 100 = 150 ppm

Permanent hardness = Total – temporary hardness = 450–150 = 300 ppm.

Problem-14: Calculate the hardness of given sample of water, if 50 ml of sample water gives endpoint with 20 ml of EDTA solution. 20 ml of standard hard water of concentration 0.02 M gives end point with 25 ml of EDTA solution.

Molarity of Standard hard water solution M_1 = 0.02 M

Solution:

Standardization (Finding the concentration of EDTA solution using standard hard water)

V_1 = 20 ml V_2 = 25 ml

Standard Hard water (pH 10) Vs EDTA (EBT indicator wine red to blue)

(M_1 = 0.02 M)   (M_2)

$M_1V_1 = M_2V_2$

Then molarity of EDTA: $M_2 = (M_1V_1)/V_2 = (0.02 \times 20)/(25) = 0.016$ M

Estimation of hardness

V3= 50 ml   V4 = 20 ml

Sample water (pH 10) vs EDTA (EBT indicator wine red to blue)

(M_3) $(M_4 = M_2)$

Molarity of sample water M3? Now, $M_3V_3 = M_4V_4$

Then, $M_3 = (M_4V_4)/V_3 = (0.016 \times 20)/(50) = 0.0064$ M

Hardness in ppm is Molarity x 100000 ppm = 0.0064 x 100000 = 640 ppm

Problem-15: 100 ml sample water required 13.5 ml of 0.02 N EDTA solutions for hardness estimation. 100 ml sample water was boiled and removed the precipitate by filtration. This filtrate required 6 ml of EDTA. Calculate temporary hardness

Solution:

Estimation of hardness

V3 = 100 ml; V4 = 13.5 ml

Sample water (pH 10) vs. EDTA (EBT indicator wine red to blue)

(N_3) $(N_4 = 0.02$ N)

Normality of sample water N3? $N_3V_3 = N_4V_4$

Then, $N_3 = (N_4V_4)/V_3 = (0.02 \times 13.5)/(100) = 0.0027$ N

Hardness in ppm = Normality x 50000 ppm = 0.0027 x 50000 = 135 ppm

Estimation of permanent hardness

$V_5 = 100$ ml $V_6 = 13.5$ ml

Sample water (pH 10) vs EDTA (EBT indicator wine red to blue)

(N_5) $(N_6 = 0.02$ N)

Normality of sample water after boiling N5? $N_5V_5 = N_6V_6$

Then, $N_5 = (N_6V_6)/V_5 = (0.02 \times 6)/(100) = 0.0012$ N

Permanent Hardness in ppm is Normality x 50000 ppm = 0.0012 x 50000 = 60 ppm

Temp. Hardness = total – perm = 135-60 = 75 ppm.

Softening of water by Ion exchange resin process or deionization process or demineralization process

- ❖ The process of complete removal of all ions present in water is known as demineralization process
- ❖ The process is done by using ion exchange resin process.
- ❖ These resins are highly insoluble cross linked organic polymers with porous structure.
- ❖ They contain functional groups attached to the polymeric chains are responsible for ion exchange property.
- ❖ The functional groups used are either acidic or basic in nature.
- ❖ Depending on functional groups Ion exchange resins are classified into two types.
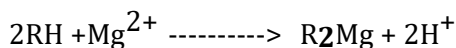
1. Cation Exchange Resins
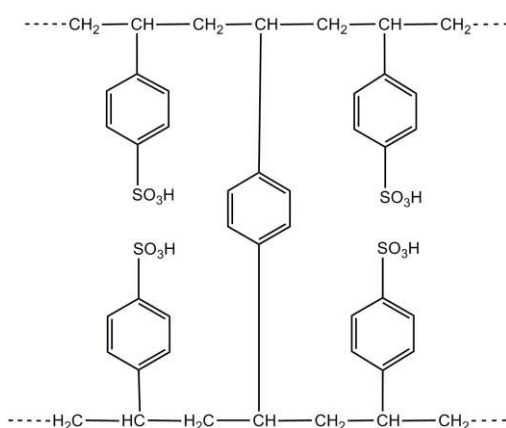
2. Anion Exchange Resins

1. Cation Exchange Resins:

- ➢ These are mainly poly-styrene polymers which contain acidic functional groups (like –COOH or –SO$_3$H).
- ➢ The acidic functional group is capable of exchanging its H$^+$ ions with cations present in water.

$$2RH + Ca^{2+} \text{-----------} > R_2Ca + 2H^+$$
Acidic resin
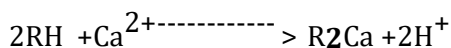
$$2RH + Mg^{2+} \text{----------} > R_2Mg + 2H^+$$
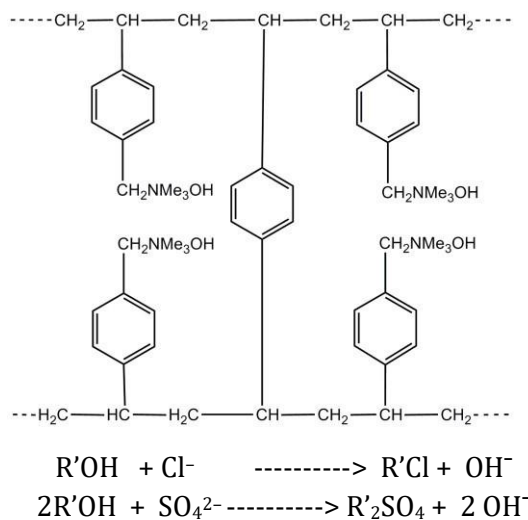Acidic resin

Anion Exchange Resins:

- ➢ These are mainly poly-styrene polymers which contain basic functional groups (like –CH2-NMe$_3$OH).
- ➢ The basic functional group is capable of exchanging its OH$^-$ ions with anions present in water.

$$R'OH + Cl^- \longrightarrow R'Cl + OH^-$$
$$2R'OH + SO_4^{2-} \longrightarrow R'_2SO_4 + 2OH^-$$

Basic resin

Process:

Step1: The hard water is passed through a cylindrical tank packed with cation exchange resin bed. The cation exchange removes cations like Ca^{2+} and Mg^{2+} etc from water and equivalent amount of H^+ ions are released from resin to water.

Step2: The hard water is then passed through another column packed with anion exchange resin. It removes all hardness causing anions like SO_4^{2-}, Cl^- and HCO_3^- from water and equivalent amount of OH^- ions are released from resin to water.

C E R: Cation exchange resin
A E R: Anion exchange resin
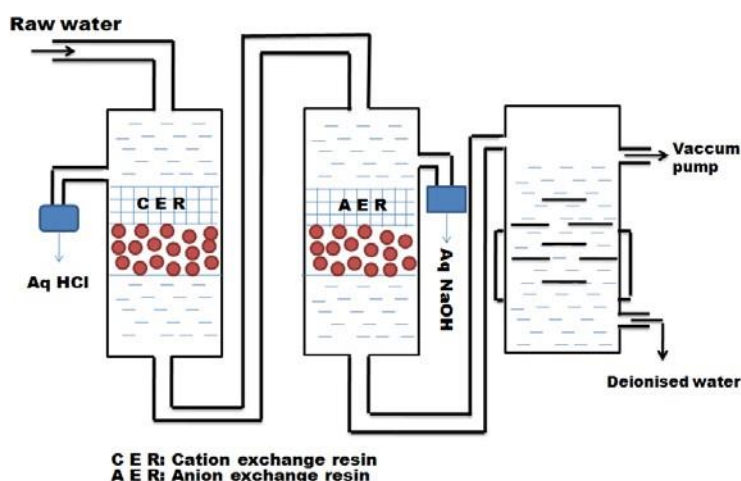
Regeneration

When cation exchanger losses capacity of producing H^+ ions and anion 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.

$$R_2Ca^{+2} + 2H^+ \rightarrow 2RH^+ + Ca^{+2}$$
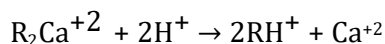
The exhausted anion exchanger is regenerated by passing a dilute solution of NaOH.

$$R_2SO_4^{-2} + 2OH^- \rightarrow 2ROH^- + SO_4^{-2}$$
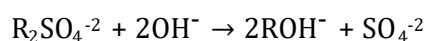
Merits of Ion-exchange process

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

2. It produces water of very low hardness (2ppm). So it is very good for treating water for use in high-pressure boilers.

3. The operational expenses are less because the resins can be regenerated.

Demerits of Ion-exchange process

1. The equipment is costly and more expensive chemicals are needed.

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


POTABLE WATER

The water which is used for drinking is called potable water.

Specification of potable water/drinking water

1. It should be sparkling clear and odorless.

2. It should be pleasant in taste.

3. It should be perfectly cool.

4. Its turbidity should not exceed 10ppm.

5. It should be free from objectionable dissolved gases like hydrogen sulphide.

6. It should be free from minerals such as lead, arsenic, chromium and manganese salts.

7. Its alkalinity should not be high.

8. Its pH should be about 8.0.

9. It should be reasonably soft.

10. Its total dissolved solids should be less than 500 ppm.

11. It should be free from disease-producing micro-organisms.

12. Chloride, fluoride and sulphide contents should be less than 250ppm, 1.5ppm and 250ppm, respectively.

Steps involved in treatment of potable water
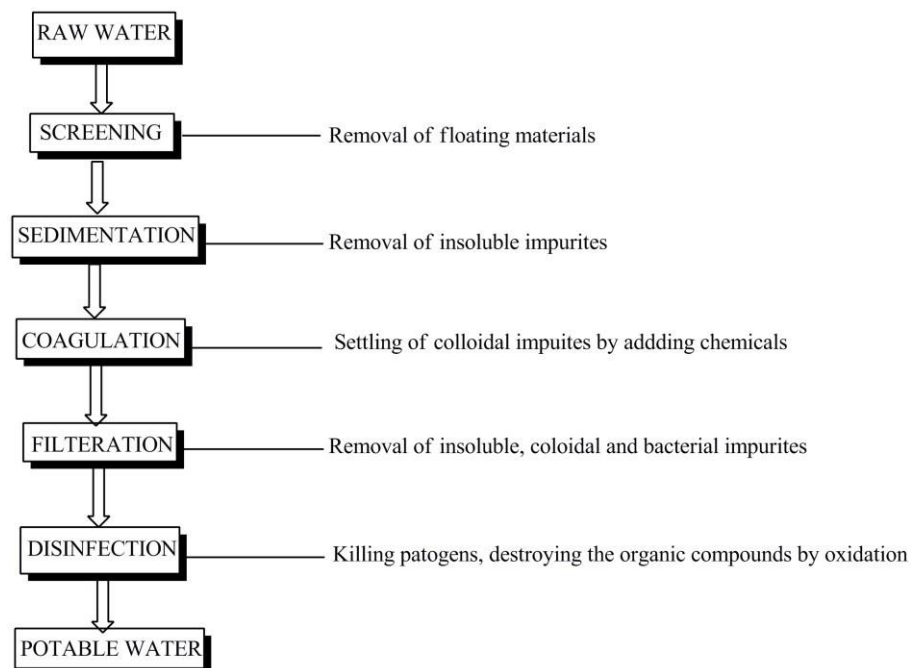
1. Screening

To protect the main units of a treatment plant and to aid in their efficient operation, it is necessary to use screens to remove any large floating and suspended solids that are present in the inflow. These

materials include leaves, twigs, paper, rags and other debris that could obstruct flow through the plant or damage equipment. There are coarse and fine screens.

Coarse screens are steel bars spaced 5–15 cm apart, which are employed to exclude large materials (such as logs and fish) from entering the treatment plant, as these can damage the mechanical equipment. The screens are made of corrosion-resistant bars and positioned at an angle of 60º to facilitate removal of the collected material by mechanical raking.

Fine screens, which come after the coarse screens, keep out material that can block pipework at the plant. They consist of steel bars which are spaced 5–20 mm apart. A variation of the fine screen is the microstrainer which consists of a rotating drum of stainless steel mesh with a very small mesh size (ranging from 15 μm to 64 μm, i.e. 15–64 millionths of a metre). Suspended matter as small as algae and plankton (microscopic organisms that float with the current in water) can be trapped. The trapped solids are dislodged from the fabric by high-pressure water jets using clean water, and carried away for disposal.

2. Aeration

After screening, the water is aerated (supplied with air) by passing it over a series of steps so that it takes in oxygen from the air. This helps expel soluble gases such as carbon dioxide and hydrogen sulphide (both of which are acidic, so this process makes the water less corrosive) and also expels any gaseous organic compounds that might give an undesirable taste to the water. Aeration also removes iron or manganese by oxidation of these substances to their insoluble form. Iron and manganese can cause peculiar tastes and can stain clothing. Once in their insoluble forms, these substances can be removed by filtration.

In certain instances excess algae in the raw water can result in algal growth blocking the sand filter further


down the treatment process. In such situations, chlorination is used in place of, or in addition to, aeration to kill the algae, and this is termed pre-chlorination. This comes before the main stages in the treatment of the water. (There is a chlorination step at the end of the treatment process, which is normal in most water treatment plants). The pre-chlorination also oxidises taste- and odour-causing compounds.

3. Coagulation and flocculation

After aeration, coagulation takes place, to remove the fine particles (less than 1 μm in size) that are suspended in the water. In this process, a chemical called a coagulant (with a positive electrical charge)

is added to the water, and this neutralises the negative electrical charge of the fine particles. The addition of the coagulant takes place in a rapid mix tank where the coagulant is rapidly dispersed by a high-speed impeller.

Since their charges are now neutralised, the fine particles come together, forming soft, fluffy particles called 'flocs'. (Before the coagulation stage, the particles all have a similar electrical charge and repel each other, rather like the north or south poles of two magnets.) Two coagulants commonly used in the treatment of water are aluminium sulphate and ferric chloride.
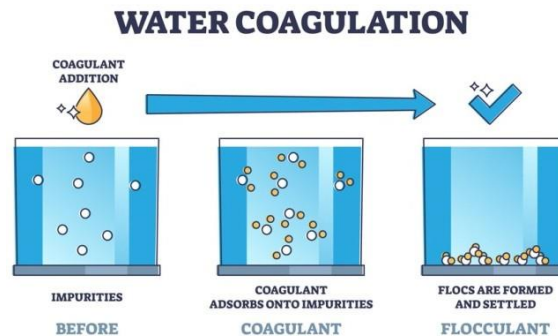
The next step is flocculation. Here the water is gently stirred by paddles in a flocculation basin and the flocs come into contact with each other to form larger flocs. The flocculation basin often has a number of compartments with decreasing mixing speeds as the water advances through the basin. This compartmentalized chamber allows increasingly large flocs to form without being broken apart by the mixing blades. Chemicals called flocculants can be added to enhance the process. Organic polymers called polyelectrolytes can be used as flocculants.

4. <u>Sedimentation</u>

Once large flocs are formed, they need to be settled out, and this takes place in a process called sedimentation (when the particles fall to the floor of a settling tank). The water (after coagulation and flocculation) is kept in the tank for several hours for sedimentation to take place. The material accumulated at the bottom of the tank is called sludge; this is removed for disposal.
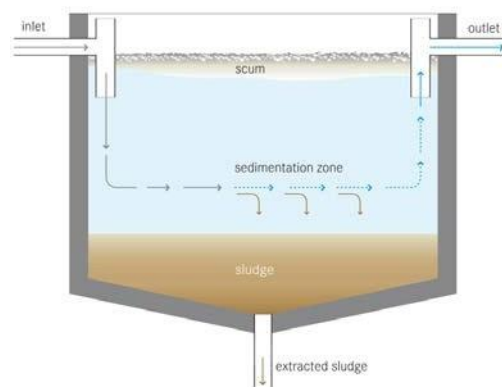
5. <u>Filtration</u>

Filtration is the process where solids are separated from a liquid. In water treatment, the solids that are not separated out in the sedimentation tank are removed by passing the water through beds ofsand and gravel. Rapid gravity filters, with a flow rate of 4–8 cubic metres per square metre of filter surface per hour (this is written as 4–8 $m^{-3} m^{-2} h^{-1}$) are often used.

When the filters are full of trapped solids, they are backwashed. In this process, clean water and air are pumped backwards up the filter to dislodge the trapped impurities, and the water carrying the dirt (referred to as backwash) is pumped into the sewerage system, if there is one. Alternatively, it may be

discharged back into the source river after a settlement stage in a sedimentation tank to remove solids.

6. Sterilization of surface water/Removal of micro-organisms in water (Disinfection):

The process of destroying/killing the disease producing Bacteria, microorganisms, etc. from the water and making it safe for use, is called disinfection.
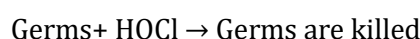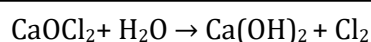
Disinfectants:

The chemicals or substances which are added to water for killing the bacteria are called disinfectants. The chemicals used in this process are called Disinfectants.

It is done by following methods:

1. Boiling: By boiling water for 10-15 minutes, all the disease producing bacteria is killed and the water becomes safe for use.

2. By adding Bleaching powder: 1 kg of bleaching powder is added to 1000 kiloliters of water and left undisturbed for several hours that produces hypochlorous acid (powerful germicide).

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

$$Cl_2 + H_2O \rightarrow HCl + HOCl \text{ (Hypochlorous acid)}$$

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

3. By using Chlorine:

Chlorination is the process of purifying the drinking water by producing a powerful germicide like hypochlorous acid. When this chlorine is mixed with water it produces hypochlorous acid which kills the germs present in water.

$$H_2O + Cl_2 \rightarrow HOCl + HCl$$
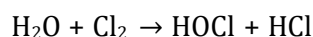
Chlorine is basic (means pH value is more than 7) disinfectant and is much effective over the germs. Hence chlorine is widely used all over the world as a powerful disinfectant. Chlorinator is an apparatus, which is used to purify the water by chlorination process.

Water after Filteration   Chlorine

Baffle Plates

Sterlized Water outlet

Chlorinator Apparatus
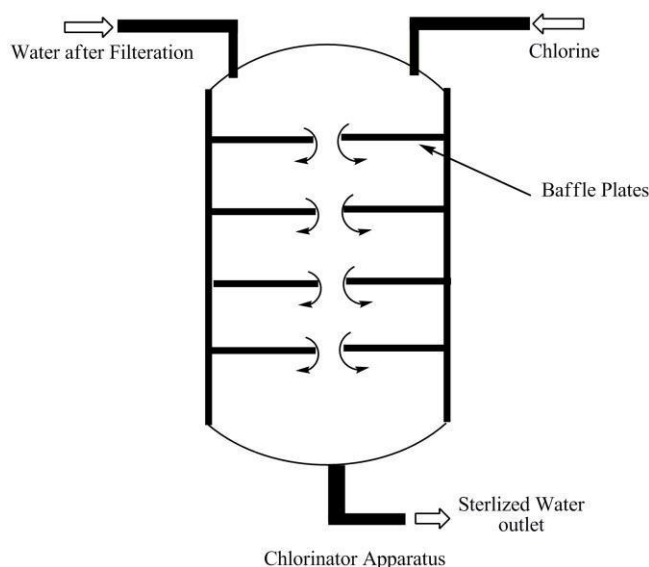
Advantages

(1). Effective and economic

(2). It leaves no salt impurities

(3). Chlorine is available in pure form

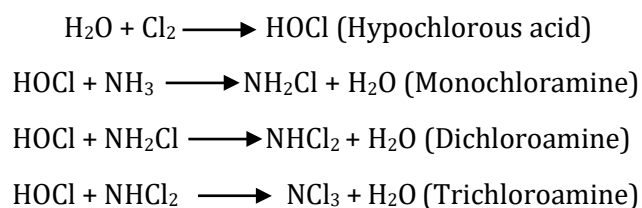(4). It requires little space for storage.

Disadvantages:

(1). Bad taste and unpleasant odour.

(2). Irritation on mucous membrane if used in excess.

(3). Ineffective at high pH value.

Break-Point of Chlorination:

- By chlorination, organic matter and disease producing bacteria are completely eliminated which are responsible for bad taste and bad odour in water.

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

- When certain amount of chlorine is added to the water, it leads to the formation of chloro-organic compounds and chloramines.

- The point at which free residual chlorine begins to appear is known as "Break-Point"

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

- Break point determines whether chlorine is further added or not.
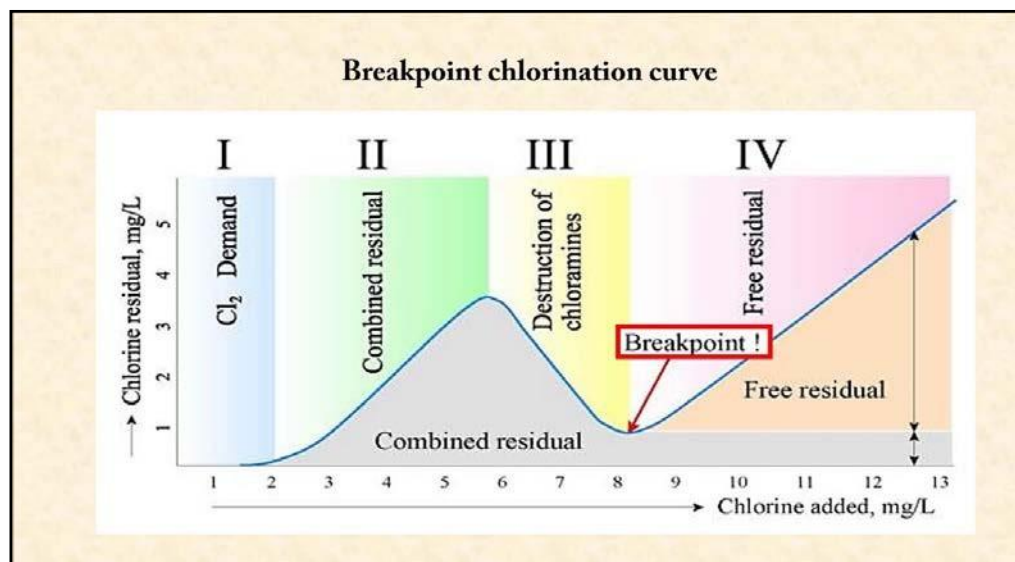
- From the graph, it is clear that :

- In phase I, 'a' gm of chlorine added oxidizes reducing impurities of water.

- In phase II, 'b' gm of chlorine added forms chloramines with nitrogen compounds present in the water.

$$H_2O + Cl_2 \longrightarrow HOCl \text{ (Hypochlorous acid)}$$

$$HOCl + NH_3 \longrightarrow NH_2Cl + H_2O \text{ (Monochloramine)}$$

$$HOCl + NH_2Cl \longrightarrow NHCl_2 + H_2O \text{ (Dichloroamine)}$$

$$HOCl + NHCl_2 \longrightarrow NCl_3 + H_2O \text{ (Trichloroamine)}$$

- The chlorine at this phase is present as the combined chlorine.

- In phase III, 'c' gm of chlorine added causes destruction of chloramines. The trichloroamine on addition of chlorine is eliminated as Nitrogen gas.

- The concentration of the chlorine at this point dips. The addition of chlorine to water at the dip or

break is called break point chlorination.

- The remaining 'd' gm of chlorine added is seen as residual Chlorine. At this point, the chlorine acts as a disinfectant and kills the micro organisms.

Advantages:

- Complete destruction of pathogens.
- Complete oxidation of organic compounds, ammonia and other reducing impurities.
- Prevents weed growth.
- Prevents growth of microbes.

4. By Chloramines: When chlorine and ammonia are mixed in the ratio of 2:1 by volume, chloramine is formed.

$$Cl_2 + NH_3 \rightarrow ClNH_2 + HCl$$

$$ClNH_2 + H_2O \rightarrow HOCl + NH_3$$
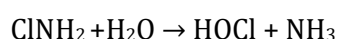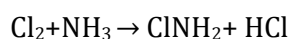
Hypochlorous acid, which is formed by the dissolution of chloramines in water, reacts with micro-organisms and inactivates the enzymes present in it so that the micro-organisms are destroyed.

Dechlorination:

If excess of chlorine is added then it can be dechlorinated by passing it through activated carbon or by adding SO_2 / Na_2SO_3.

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

$$Na_2SO_3 + Cl_2 + H_2O \rightarrow Na_2SO_4 + 2HCl$$
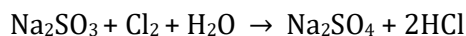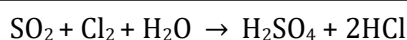
Factors affecting efficiency of chlorine:

- Efficiency increases with rise of temperature.
- Initially, micro-organisms death rate is maximum with time and then keeps on decreasing.
- Kills micro organisms.

UV Light

- 254nm UV light damages the RNA & DNA in bacteria.
- Also destroys chemical contaminants present in water.
- The water should be free from turbidity if you choose UV light

|	Unit No:
Subject: Applied Chemistry	Lecture No:
Faculty: Dr. Monaj Karar	Link to Session
	Planner (SP):S.No. .....of SP
Topic: WATER and ITS TREATEMENT	Date Conducted:
	Page No:

Desalination of Brackish water

The process of removing common salt from the water, is known as desalination. Water containing high concentration of dissolved solids with peculiar salty or brackish taste is called brackish water. Sea water is an example for brackish water as it contains about 3.5% of dissolved salts.

Depending upon the quantity of dissolved salt, water is graded as:

1. Fresh water: less than 1000 ppm of dissolved solids.

2. Brackish water: more than 1000 ppm and less than 3500 ppm of dissolved solids.

3. Sea water: more than 3500 ppm of dissolved solids.

Commonly used methods for the desalination of brackish water is:

1. Reverse Osmosis (Pressure) 2. Electrodialysis (Electrical) 3. Thermal Distillation (Thermal)
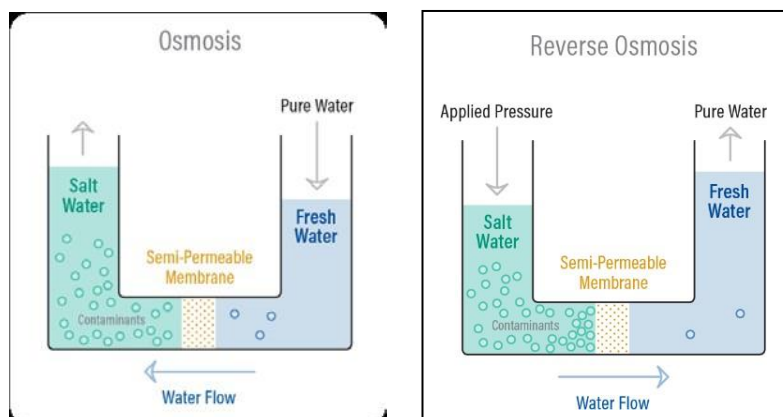
Osmosis:

When two solutions of different concentrations are separated by a semi-permeable membrane, which does not permit the flow of dissolved salts, then the solvent flows from lower concentration to higher concentration.

Reverse Osmosis

When two solutions of unequal concentrations are separated by a semi permeable membrane, flow of solvent takes place from dilute to concentrated sides, due to osmosis. If, however, a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated side, the solvent flow is reversed, i.e. solvent is forced to move from concentrated side to dilute side across the membrane. This is the principle of reverse osmosis. This membrane filtration is also called 'super-filtration' or 'hyper–filtration. The membrane consists of very thin films of cellulose acetate, affixed to either side of a perforated tube. However, more recently superior membranes made of polymethacrylate and polyamide polymers have come into use.

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

Advantages:

1. Reverse osmosis possesses a distinct advantage of removing ionic as well as non-ionic, colloidal and high molecular weight organic matter.

2. It removes colloidal silica, which is not removed by demineralization.

3. The maintenance cost is almost entirely on the replacement of the semi permeable membrane.

4. The life time of membrane is quite high, about 2 years.

5. The membrane can be replaced within a few minutes, thereby providing nearly uninterrupted water supply.

6. Due to low capital cost, simplicity, low operating cost and high reliability, the reverse osmosis is gaining ground at present for converting sea water into drinking water and for obtaining water for very high pressure boilers.