

# **UNIT-I**

## **WATER CHEMISTRY**

# CHARACTERSTICS OF WATER

## Introduction

- ✚ Water is one of the few basic materials which are of prime importance for the preservation of life on earth.
- ✚ Water is not only essential for the lives of animals and plants but also occupies a unique position in industries.
- ✚ It's most important use as an engineering material.
- ✚ 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 chemical processes.

## Sources of water

**Rain water:** It is the most important sources of water and the purest form of natural water. It is naturally distilled water.

**River water:** Water in the form of rivers comes from rain water which is not absorbed into the soil and melting of snow on the mountains.

**Spring and well water:** About one third of rain water falls on the surface of earth seeps inside the soil and goes down through it till it is prevented by impervious rock etc. After some time it then moves up and appears in the form of deep well water or spring water.

**Sea water:** Sea is the largest source of water. The river water which carries many dissolved and suspended impurities finally collects in to sea. The percentage of impurities in sea water is around 3.6 in which about 2.7% is the common salt.

## Impurities of water

Chemically pure water is composed of two parts of hydrogen and one part of oxygen by volume and dissolves many substances. So natural water is not pure. It dissolves various impurities.

**1. Suspended impurities:** It is of two types:

- ✚ Inorganic suspended impurities, like clay and sand.
- ✚ Organic suspended impurities like animal and vegetable impurities. River water mainly contains suspended impurities, which is responsible for turbidity of water.

**2. Dissolved impurities:** The dissolved impurities are classified as:

- ✚ Inorganic salts like bicarbonates, chlorides, sulphates of calcium and magnesium in the dissolved form causes hardness to water.
- ✚ The dissolved impurities like salts of sodium, potassium causes alkalinity to water.
- ✚ The other dissolved salts include iron, silica and alumina.
- ✚ Dissolved gases like CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>S are responsible for the odour and acidity in water. The presence of O<sub>2</sub> causes corrosion in boilers.

**3. Colloidal impurities:** The impurities which exists in very finely divided state such that their small quantities are not visible to naked eye is called colloidal impurities, which comprise of very finely divided silica, clay, aluminum hydroxide and micro-organisms.

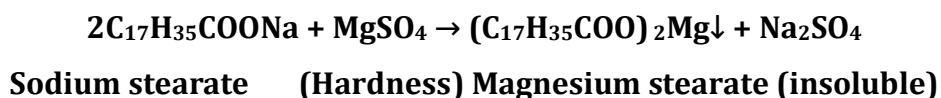
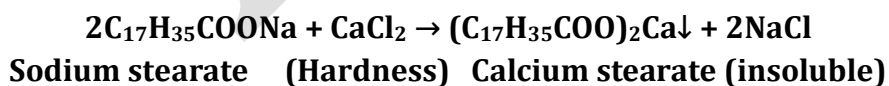
**4. Organic impurities:** The organic impurities include algae, fungi and plant matter etc., which are vegetative by origin and microorganisms, bacteria and animal by their origin.

### Sources of impurities

- ✚ When rain water floods to near stream it carries floating impurities along with it.
- ✚ Gases like CO<sub>2</sub>, O<sub>2</sub> etc. are picked up from atmosphere.
- ✚ When water percolates through the layers of soil it dissolves the salts of calcium, magnesium, potassium, sodium etc. which remain as dissolved salts in the composition of water.
- ✚ The organic impurities are introduced into water due to the decomposition of plant and animal remains in water.

### Hardness

Soap consuming character of water is known as hardness of water. It is the main characteristics of water which prevents the lathering of soap due to the presence of certain salt of Ca and Mg.



Water can be divided into two types based on soap reaction.

**1. Soft water:** water which gives lather easily with soap is known as soft water. Soft water is free from all the minerals.

**2. Hard water:** Water which does not produce lather with soap solution readily is called hard water. Hard water contains high concentration of minerals. It contains bicarbonates, chlorides and sulphates of calcium and magnesium. Hence it does not produce lather with soap solution. Soap is sodium (Na) or potassium (K) salts of fatty acids. Example stearates, palmates and oleic acids etc. which gives cleaning action with soaps.

### Types of hardness:

**Temporary hardness:** It is caused by the presence of dissolved bicarbonates of Ca and Mg. It can be easily removed by simple boiling of water, when bicarbonates are decomposed, yielding insoluble carbonates or hydroxides, which are deposited as a crust at the bottom of vessels.



**Permanent hardness:** It is present due to the presence of chlorides and sulphates of Ca and Mg. Unlike temporary hardness, permanent hardness is not destroyed on boiling.



But it can be removed by

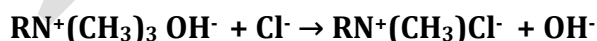
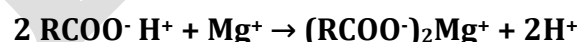
i) Lime-soda process



ii) Zeolite process:



iii) Ion exchange process:



### Units of Hardness:

**Parts per million:** ppm is the parts of calcium carbonate equivalent hardness per  $10^6$  parts of water.

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

**Mg/L:** Milligram per liter is the number of milligrams of  $\text{CaCO}_3$  equivalent hardness present per liter of water.

$$1 \text{ mg/L} = 1 \text{ mg of CaCO}_3 \text{ equivalent hardness of 1 L of water}$$

**Clark's degree ( $^\circ\text{Cl}$ ):** It is the parts of  $\text{CaCO}_3$  equivalent hardness per 70000 parts of water.

$$1^\circ\text{Cl} = 1\text{part of CaCO}_3 \text{ equivalent hardness per 70000 parts of water}$$

**Degree French (°Fr):** It is the parts of CaCO<sub>3</sub> equivalent hardness per 10<sup>5</sup> parts of water.

1°Fr = 1 part of CaCO<sub>3</sub> hardness equivalent per 10<sup>5</sup> parts of water

### Relationship between various units of hardness

	ppm	mg/L	°Fr	°Cl
ppm	1	1	0.1	0.07
mg/L	1	1	0.1	0.07
°Fr	10	10	1	0.7
°Cl	1/0.07	1/0.07	1/0.7	1

### Degree of hardness (Equivalents of Calcium Carbonate):

The concentrations of hardness as well as non-hardness constituting ions are usually expressed in terms of equivalent amount of CaCO<sub>3</sub>, since this mode permit the multiplication and division of concentration, when required. The choice of CaCO<sub>3</sub> in particular is due to its molecular weight is 100 (equivalent weight is 50) and moreover, it is the most insoluble salt that can be precipitated in water treatment.

Name of the H.C.S	Molecular weight	Multiplication factor in CaCO <sub>3</sub> equivalents
Ca(HCO <sub>3</sub> ) <sub>2</sub>	162	100/162
Mg(HCO <sub>3</sub> ) <sub>2</sub>	146	100/146
CaCl <sub>2</sub>	111	100/111
MgCl <sub>2</sub>	95	100/95
CaSO <sub>4</sub>	136	100/136
MgSO <sub>4</sub>	120	100/120
Ca(NO <sub>3</sub> ) <sub>2</sub>	164	100/164
Mg(NO <sub>3</sub> ) <sub>2</sub>	148	100/148

The method of calculating degree of hardness will be clear from the following formula.

Hardness of the H.C.S (hardness causing salt) in terms of CaCO<sub>3</sub>

$$= \frac{\text{amount of the hardness causing salt} \times 100}{\text{molecular weight of the hardness causing salt}}$$

## Industrial water characteristics


S.No.	Purpose	Characteristics of Water	Remarks
1	Boiler Feed water	Very soft, It contains small amount of nitrate and organic matter.	Hard water form scale on boiler walls, which reduce the working of the boiler. Hard water may cause priming and foaming.
2	Pharmaceutical industries	Very pure, free from any diseases causing bacteria, confirming to the standards of potable water.	Salts present in hard water may react with the chemicals to form unsuitable products.
3	Sugar Industries	Free from sulphates, carbonates and nitrates. Free from micro-organisms.	In the process of these anions the crystallization becomes difficult and sugar obtained is deliquescent. The micro-organisms may decompose the sugar partly.
4	Textiles	Free from hardness causing substances and Fe, Mn salts	Hard water precipitates basic dyes and decreases the solubility of acidic dyes. These salts produce insoluble precipitates which stain the cloth and cause uneven dyeing
5	Paper mills	Free from hardness and alkalinity, $\text{SiO}_2$ , lime and magnesia.	Hardness producing ions may react with the chemicals used for paper. $\text{SiO}_2$ may produce cracks in paper.

### Softening of water:

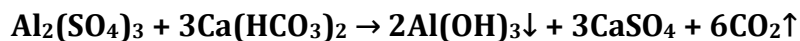
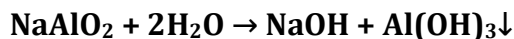
**External treatment methods:** It involves the removal of hardness causing salts from the water before feeding it into the boiler. The following are external treatment methods.

1. Lime -soda process
2. Zeolite or Permutit process
3. Ion- exchange process or Deionization

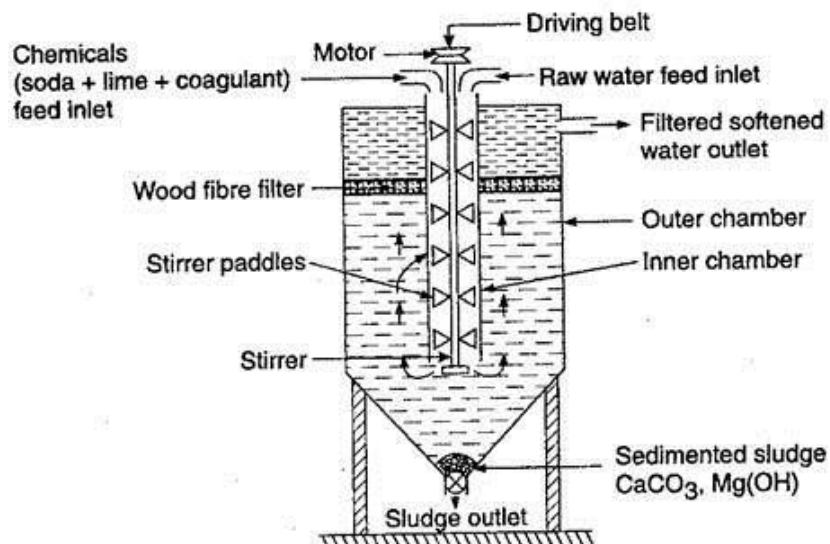
**1. Lime-soda process:** In this process the soluble calcium and magnesium salts in water are chemically converted into insoluble compounds, by adding calculated amounts of lime  $[\text{Ca}(\text{OH})_2]$  and soda  $[\text{Na}_2\text{CO}_3]$ . Calcium carbonate and magnesium hydroxide so precipitates are filtered off. Lime -soda process is of two types.

 **Cold lime-soda process:** In this method calculated quantity of lime and soda are mixed with water at room temperature. The precipitates formed are finely divided, so they do

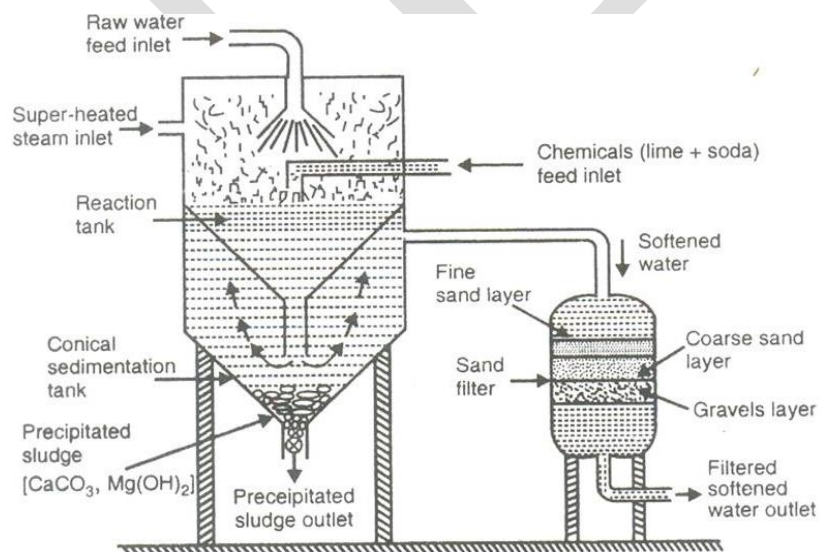
not settle down easily. The coagulant is added which hydrolyze and form precipitate of aluminum hydroxide.



**Coagulant      Hardness**



#### Hot lime-soda process:



Essential parts of plant

- (i) Reaction tank
- (ii) Conical sedimentation vessel
- (iii) Sand filter

- This process involves in treating water with softening chemicals at 80-150°C.
- Reaction proceeds faster.
- Softening capacity is increased.
- Precipitate and sludge settle down rapidly hence no coagulants are needed.
- Dissolved gases are also removed.
- Viscosity of softened water is lower so filtration of water becomes easier.

☉ **Advantages:**

- Very economical
- Lesser amount of coagulants are need
- Minerals in water are reduced
- Pathogenic bacteria is considerably reduced (due to alkaline water)

☉ **Disadvantages :**

- Careful operation and skilled supervision is required
- Disposal of sludge poses problem
- This process removes hardness only up to 15 ppm, which is not good for high pressure boilers.

## 2. Zeolite or Permutit process

The term zeolite stands for boiling stones (zeo-boiling, olite-stone). Zeolites are porous, when water passes through zeolite it gives the appearance as boiling. The chemical formula of zeolite is hydrated sodium aluminium silicate, represented as  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{XSiO}_2 \cdot \text{YH}_2\text{O}$  where  $\text{X} = 2-10$  and  $\text{Y} = 2-6$ . The sodium ions which are loosely held in  $\text{Na}_2\text{Ze}$  are replaced by  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions present in water.

**Types:**

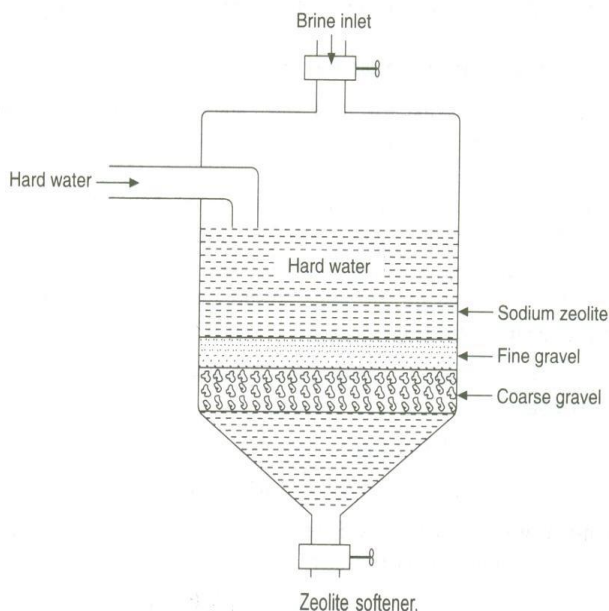
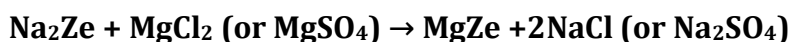
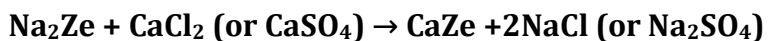
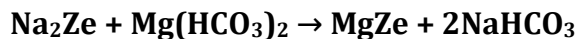
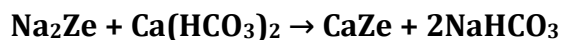
- **Natural zeolites:** Non-porous,  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
- **Synthetic zeolites:** Porous and possess gel structure. They are prepared by heating together china clay, feldspar and soda ash. Synthetic zeolites possess higher exchange capacity per unit weight than natural zeolite.

**Process:**

When hard water is passed through a bed of zeolite placed in a closed cylinder, the hardness causing ions like  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions are taken up by zeolite. Sodium salts are released during the reaction as byproduct. For softening of water by zeolite process, hard



water is percolated at a specified rate through a bed of zeolite, kept in a cylinder. The hardness causing ions like  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are retained by the zeolite as  $\text{CaZe}$  and  $\text{MgZe}$ . While the outgoing water contains sodium salts.



**Regeneration:** After some time the zeolite is completely converted into calcium and magnesium zeolite and it stop to softening water. Zeolite is reclaimed by treating the bed with 10%  $\text{NaCl}$ .



#### Advantages of Zeolite process:

- ✚ It reduces hardness up to 10 ppm.
- ✚ The equipment is quite compact.
- ✚ It requires less time for softening.
- ✚ It requires less skill for maintenance and operation.

#### Disadvantages of zeolite process:

- ✚ Highly turbid water cannot be treated by this method.
- ✚ This process removes only the cations ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ).

### 3. Ion-exchange or de-ionization process:

In this process almost all the ions both anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ) and cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) present in hard water are removed. This process is also called “deionization process”. In the deionization process, the ions present in water are removed by ion exchangers. 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. They are of two types.

(i) Cation exchangers. (ii) Anion exchangers.

**i) Cation exchangers:** Materials capable of exchanging cations are called cation exchangers. Cation exchanger resins containing acidic groups ( $-\text{COOH}$ ,  $-\text{SO}_3\text{H}$ ) are capable of exchanging their  $\text{H}^+$  ions with other cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) of hard water. Cation exchange resin is represented as  $\text{RH}_2$  (or)  $\text{RH}$ .

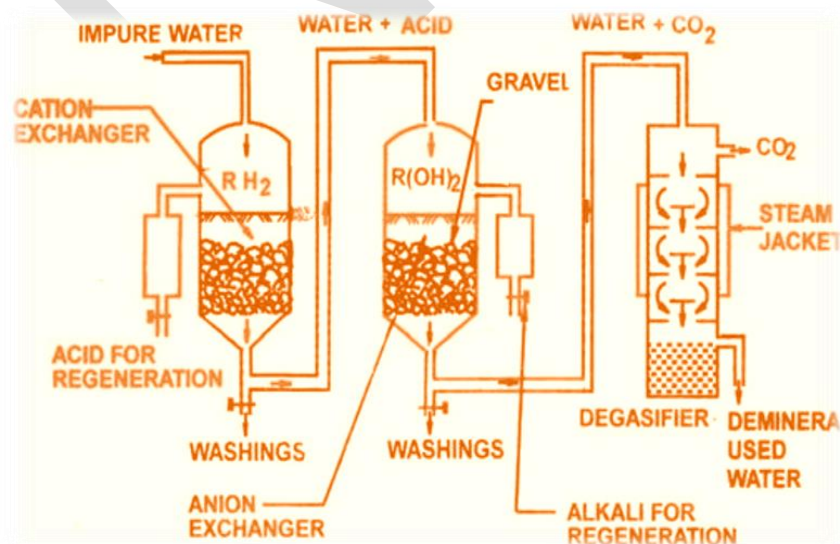
**Eg:** Styrene divinyl benzene.

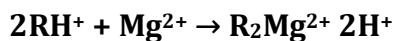
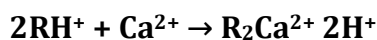
**ii) Anion exchangers:** Materials capable of exchanging anions are called anion exchangers. Anion exchanger resins containing basic groups ( $-\text{NH}_2$ ,  $-\text{OH}$ ) are capable of exchanging their  $\text{OH}^-$  ions with the other anions of hard water. Anion exchange resin is represented as  $\text{R}'(\text{OH})_2$  (or)  $\text{R}'\text{OH}$ .

**Eg:** Phenol-formaldehyde resin.

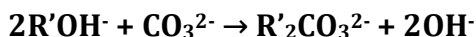
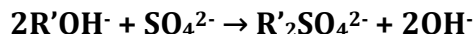
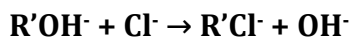
#### Process:

The hard water is passed first through cation exchange column, which remove cations.





After cation exchange column, the hard water is passed through anion exchange column.



$\text{H}^+$  and  $\text{OH}^-$  ions get combined to produce water molecules.

**Regeneration:** When capacity of cation and anion resin to exchange ions are lost then they are said to be exhausted. The regenerated ion exchange resins are then used again.



#### Advantages:

- The process can be used for highly acidic or alkaline waters.
- It produces water of very low hardness (2ppm).
- It is very good for treating water for used in high pressure boilers.

#### Disadvantages:

- The equipment is costly and more expensive chemicals are needed.
- If water contains turbidity, then the output of process is reduced. The turbidity must be below 10 ppm.

#### Desalination of brackish water:

**Brackish water:** The water containing high concentrations of dissolved salts with a salty or brackish taste is called brackish water, which contains about 3.5% of dissolved salts. This water cannot be used for domestic and industrial applications unless the dissolved salts are removed by desalination.

**Desalination:** The process of removal of dissolved salts like NaCl from saline water is known as desalination of water.

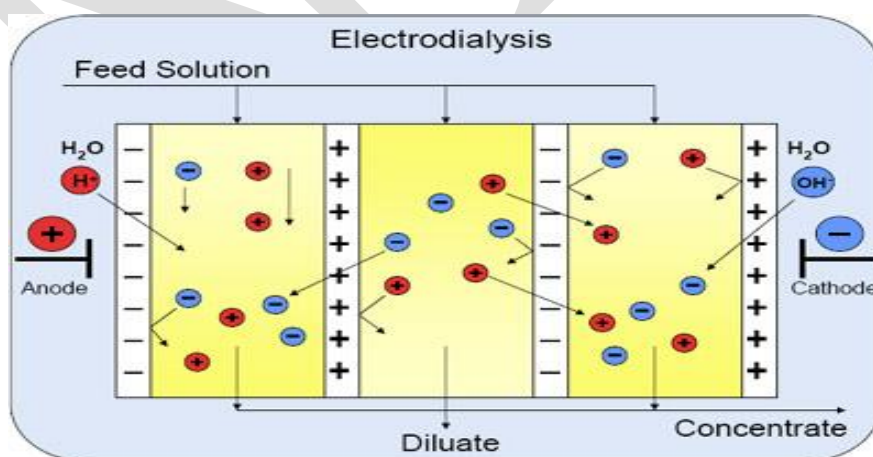
The methods used for desalination of brackish water are:

1. Electrodialysis
2. Reverse osmosis

## 1. Electrodialysis

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

- ✚ The unit consists of a chamber with two electrodes.
- ✚ The chamber is divided into three compartments with the help of thin, rigid, ion-selective membranes which are permeable to either cation or anion.
- ✚ The anode is placed near anion selective membrane while the cathode is placed near cation selective membrane.
- ✚ The *anion selective membrane* is containing positively charged functional groups such as  $R_4N^+$  and is *permeable to anions only*.
- ✚ The *cation selective membrane* consists of negatively charged functional groups such as  $RSO_3^-$  and is *permeable to cations only*.
- ✚ Under the influence of applied e.m.f. across the electrodes the cations move towards cathode through the membrane and the anions move towards anode through the membrane.
- ✚ The net result is depletion of ions in the central compartment while it increases in the cathodic and anodic compartments.
- ✚ Desalinated water is periodically drawn from the central compartment while concentrated brackish water is replaced with fresh sample.



### Advantages of electro dialysis:

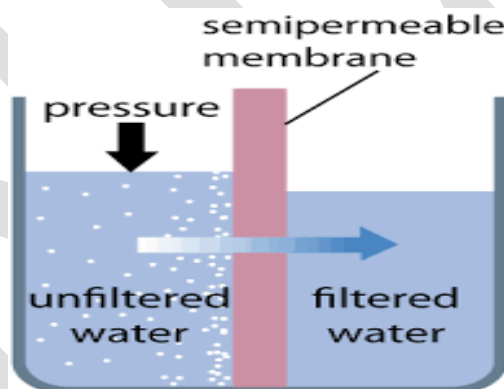
- The unit is compact.
- The process is economical as far as capital cost and operational expenses are concerned.

## 2. Reverse osmosis

- ✚ When two solutions of *unequal concentration* are separated by a *semipermeable membrane* which does not permit the passage of dissolved solute particles, (i.e. molecules and ions) flow of solvent takes place from the dilute solution to concentrated solution is called Osmosis.
- ✚ If a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated side of the solvent, the solvent flow is reversed hence this method is called reverse osmosis. Thus in reverse osmosis pure water is separated from the contaminated water. This membrane filtration is also called “super filtration” or “hyper filtration”.

### Method of purification:

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



### Advantages:

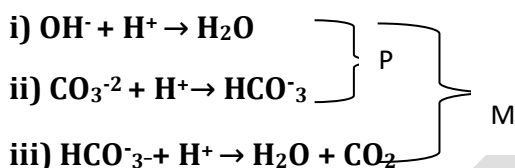
- Ionic and non-ionic, colloidal and high molecule weight organic matter is removed from the water sample.
- Cost of purification of water is less and maintenance cost is less. This water can be used for high pressure boilers.

## **WATER ANALYSIS TECHNIQUES**

### **Determination of alkalinity of water**

Alkalinity of water, which is a measure of the ability of water to neutralize the acids, is due to presence of bicarbonates, carbonates & hydroxides of Ca & Mg. Determination of alkalinity due to different ions is based on the titration of the water sample against a standard acid making selective use of indicators. The indicators used are phenolphthalein & methyl orange.

The reaction taking place is as follows:



#### **Procedure:**

1. Take 50ml of water sample in a 250ml conical flask. Add 2-3 drops of phenolphthalein indicator.
2. The colour of the solution will become pink. Now titrate this solution against 0.1 N HCl taken in a burette till colour of the solution disappears.
3. It shows all the carbonates have been converted in to bio-carbonates. Note the titrate value of the phenolphthalein and point [P].
4. Add 2-3 drops of Methyl orange indicator to the same solution and continue the titration until the sharp colour changes from yellow to rose red takes place.
5. Note the total titre value from the beginning of the experiment as methyl orange end point [M].

$$\text{Phenolphthalein alkalinity [P]} = \frac{E \times N \times V \times 1000}{\text{volume of water sample}} \text{ ppm}$$

$$\text{Methyl orange alkalinity [M]} = \frac{E \times N \times V \times 1000}{\text{volume of water sample}} \text{ ppm}$$

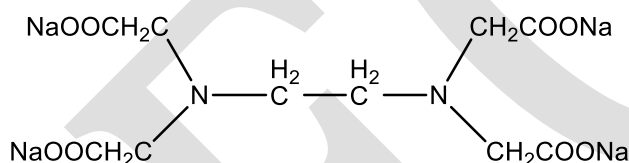
Case	OH-	CO <sub>3</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	Case
<b>P=0</b>	NIL	NIL	M	<b>P=0</b>
<b>P=M</b>	P or M	NIL	NIL	<b>P=M</b>
<b>P=½ M</b>	NIL	2P	NIL	<b>P=½ M</b>
<b>P&gt;½ M</b>	(2P-M)	2(M-P)	NIL	<b>P&gt;½ M</b>

## Estimation of hardness by EDTA Method

Water hardness is generally caused by the presence of  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  ions present in water. An excellent way to determine water hardness is to perform a complexometric titration using standard solution of EDTA (ethylene diamine tetra acetic acid) a weak acid forms a soluble complex with  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$ . Hence the amount of EDTA consumed in the reaction gives the amount of calcium and magnesium salts present in the hard water.

### Ethylene diamine tetra acetic acid (EDTA)

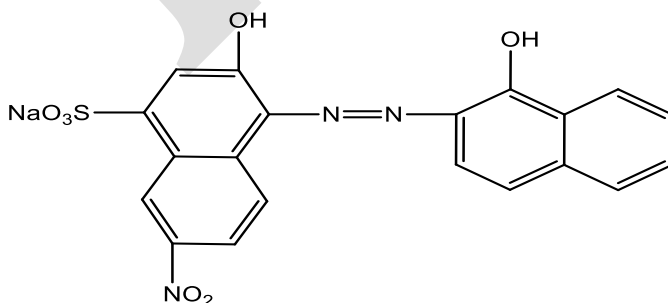
For simplicity it is represented by symbol  $\text{H}_4\text{Y}$ . Because of its limited solubility, it is not used directly. It is usually used as its disodium salt dihydrates  $\text{Na}_2\text{H}_2\text{Y} \cdot 2\text{H}_2\text{O}$ , because it can be obtained in high state of purity and is primary standard. The solution of EDTA is very valuable titrant because the reagent combines with metal ion in 1:1 ratio.



Structure of  $\text{Na}_2\text{EDTA}$

### Eriochrome Black T (EBT) is used as indicator

It is a typical metal ion indicator chemically it is sodium 1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulphonate. The indicator Eriochrome Black T (a dye stuff) is effective between the pH (8-11). It is therefore, essential while performing the titration of hard water with EDTA solution, the pH of the solution must be made ( $\text{pH} = 10$ ) by adding a suitable buffer solution.



sodium 1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulphonate

**Buffer solution:** The optimum pH for the experiment is 10 and is adjusted by  $\text{NH}_4\text{OH}$  and  $\text{NH}_4\text{Cl}$  buffer solution (Alkaline buffer).

Take 17.5 gms of  $\text{NH}_4\text{Cl}$  and add 14.2 ml. conc.  $\text{NH}_3$  solution to it. Dilute the solution to 250 ml with distilled water.

**Necessary Requirement:**

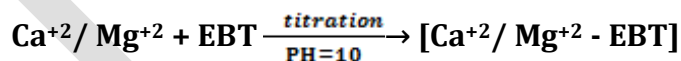
Glasswares, Burette, Pipette, Conical flask, EDTA solution, Standard water sample, Buffer solution, Eriochrome Black-T, Unknown water sample.

**Procedure:**

1. Wash the burette with water, rinse it with given EDTA solution and then fill with EDTA solution.
2. Wash the pipette with water, pipette out 20 ml of water sample & transfer it in the conical flask.
3. Add 5ml of buffer solution and 2 drops of Eriochrome Black-T indicator.
4. Titrate the solution with EDTA solution from the burette until the colour changes from wine red to clear sky blue at the end point.
5. Repeat the same procedure till we get the concordant reading.

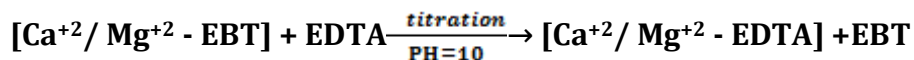
**Metal- indicator unstable complex (wine red color)**

When a small amount of the indicator is added to a hard water sample, whose pH has been controlled by the addition of the buffer solution. The indicator reacts with  $\text{Ca}^{+2}$  /  $\text{Mg}^{+2}$  ions produce wine red colour. As EDTA is added, combines free  $\text{Ca}^{+2}$  /  $\text{Mg}^{+2}$  ions to give very stable, colourless and water soluble Metal-EDTA complex.



**Metal- EDTA stable complex**

After all the free metal ions are consumed the next drop of EDTA solution displaces the indicator EBT from M-EBT Complex.



Thus, at the equivalence point, there is change in color from wine red to blue. Completion of the above reaction makes the end point of the titration.

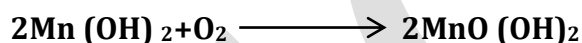
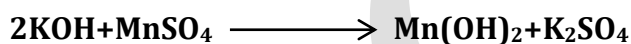


## Dissolved oxygen (DO)

The amount of oxygen present in water is called dissolved oxygen. It is expressed in ppm or mg/lit. DO is needed for living organisms to maintain biological process. Determination of DO is important for boiler feed water

### Theory:

It is usually determined by "Winkler's method". The method is based on the fact that in presence of  $\text{MnSO}_4$  (act as  $\text{O}_2$  carrier to bring about the reaction between  $\text{KI}$  &  $\text{O}_2$ ) dissolved oxygen, oxidises  $\text{KI}$  to Iodine. And the liberated iodine is titrated against standard hypo solution using starch as indicator.



(Sodium tetrathionate)



(Blue colour)

### Procedure:

1. Take 300ml of water in a BOD bottle. Now add 2ml of alkaline iodide-azide reagent and 2 ml of  $\text{MnSO}_4$  solution.
2. Stopper the bottle and shake it well. Keep the bottle in dark for 5 min and add conc.  $\text{H}_2\text{SO}_4$  till the brown precipitates are dissolved.
3. Take 100 ml of the above solution in a conical flask. Titrate against N/100 hypo till the color changes to light Yellow.
4. Add 3-4 drops of starch in to it and the color changes to blue. The blue color solution is titrated against hypo solution till blue color disappeared. This is end point of the titration. The titer value V is noted.

**Calculation of DO:** The DO content of the water sample can be calculated as follows..

$$\text{DO} = V \times N \times \frac{1}{200} \times 8 \times 1000 \frac{\text{mg}}{\text{lit}} \text{ or ppm}$$

Where V is titer value, N is Normality of Hypo solution

## Biological Oxygen Demand (BOD)

BOD is defined as the quantity of dissolved oxygen required by aerobic bacteria for the oxidation of organic matter under aerobic conditions. BOD is considering as the major characteristic used in stream pollution control. It gives valuable information regarding the self-purification capacity of the streams and serves as guide line for the regulatory authorities to check the quality of the effluents discharged in to water bodies. The demand for O<sub>2</sub> is proportional to the amount of organic waste to degrade aerobically. When the BOD is high DO become low. Hence greater the BOD, grater is the pollutants.

S.No	Source of Effluent	BOD(PPM)
1	Domestic sewage	320
2	Cow shed sewage	3010
3	Paper mill	8190
4	Tannery effluent	12360

### Procedure:

1. The BOD test essentially consists of measurement of DO content of water sample, before and after incubation at 20°C for 5 days.
2. Take the diluted sample in two stoppered bottles. The DO content of one of the bottles is determined. The bottle is incubated at 20°C for 5 days.
3. Then it's DO content is determined. The depletion in DO caused is used as measure of BOD.

### Calculation of BOD:

$$\text{BOD (mg/lit)} = \frac{(DO_0 - DO_5 - B) \times 100}{\% \text{ of the sample used}}$$

Where

DO<sub>0</sub>= initial DO content in mg/lit

DO<sub>5</sub>= DO content after incubation at 20°C for 5 days in mg/lit

B= dilution factor

## Chemical Oxygen Demand (COD)

COD is defined as the amount of oxygen consumed under specified conditions in the oxidation of organic and oxidisable inorganic matter, corrected for the influence of chlorides.

The COD is a measure of the O<sub>2</sub> equivalent to the portion of organic matter present in the waste water sample that is susceptible to oxidation by K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. This is an important and quickly measurable parameter for streams, sewage and industrial waste samples to determine their pollution strength.

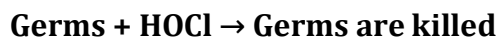
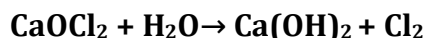
The principle involved in the determination of COD is that when a waste water sample is refluxed with a known excess of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in a 50% of H<sub>2</sub>SO<sub>4</sub> in presence of AgSO<sub>4</sub>(as catalyst) and HgSO<sub>4</sub> to eliminate interference due to chloride, the organic matter, present in the sample is oxidized to CO<sub>2</sub>, H<sub>2</sub>O and NH<sub>3</sub>. The excess dichromate remaining unreacted in the solution is titrated against a solution of Mohr's salt. The COD of waste water sample is calculated as follows.

$$\text{COD} = \frac{(V_1 - V_2) \times N \times 8}{x} \times 1000 \text{ mg/lit}$$

Where V<sub>1</sub> & V<sub>2</sub> are the volumes of Mohr's salt of the normality N, rundown in the blank and test experiments respectively, and x is the volume of sample taken for the test. Since in the COD test, both biologically oxidisable and the biologically inert matter are oxidized, the COD value for a sample is always higher than the BOD value.

### Free chlorine:

Chlorine is widely used for disinfection of potable water to remove bacteria, fungus and other pathogenic micro-organisms. The sterilising action of chlorine is due to its reaction with water, producing hypo chlorous acid and nascent oxygen both of which have powerful germicidal properties.

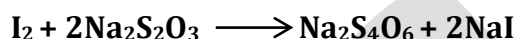
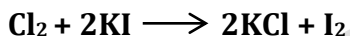


However, excess of free chlorine in drinking water is undesirable not only because of unpleasant taste but also because it is injurious to human metabolism. Hence, free

chlorine present in municipal water is generally estimated prior to the domestic supply for adjusting the chlorine dose rate.

### Procedure:

When the water sample containing free chlorine is treated with KI, free chlorine oxidises KI and liberates  $I_2$  in equivalent amount. The liberated  $I_2$  is titrated against Hypo solution using starch indicator. At the end point blue colour disappeared.



(Hypo)                      (Sodium tetrathionate)

The free chlorine present in the water sample can be calculated as follows..

$$\text{Free chlorine} = \frac{V_1 \times N_1}{V_2} \times 35.5 \times 1000 \text{ ppm}$$

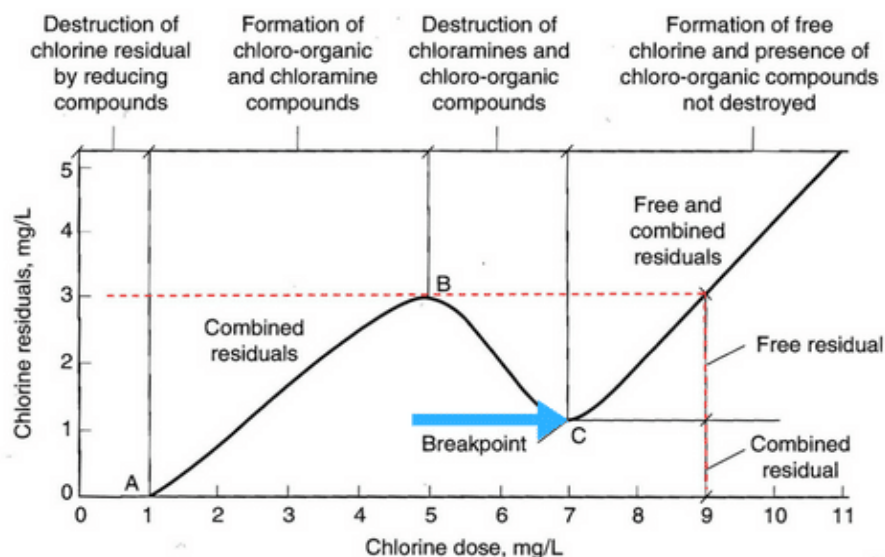
Where  $V_1$  = Volume of standard hypo solution rundown at the end point

$N_1$  = Normality of hypo solution (N/20) and

$V_2$  = Volume of water sample used for the test (100 ml)

### Breakpoint of chlorination (Free residual chlorination):

- ✚ It involves the addition of sufficient amount of chlorine to Oxidize: a) organic matter
- b) reducing substances c) free ammonia in raw water leaving behind mainly free chlorine, which possesses disinfecting action against disease-producing (pathogenic) bacteria.



- ✚ The addition of chlorine at the break is called “break-point”. This indicates the point at which free residual chlorine begins to appear. All tastes, odours (chlorines and others) disappear at break-point, resulting in appearance of water free from bad tastes and odours.

**Advantages of break-point chlorination:**

- 1) It oxidizes completely organic compounds, ammonia and other reducing compounds.
- 2) It removes colour in water, due to presence of organic matters.
- 3) It destroys completely (100%) all the disease-producing bacteria.
- 4) It removes both odour and taste from the water.
- 5) It prevents the growth of any weeds in water.

**UNIT-1**  
**WATER CHEMISTRY**  
**IMPORTANT QUESTIONS**

1. How do you estimate the hardness of water by EDTA method?
2. Describe the zeolite (Permutit) process used for softening of water.
3. With neat diagram explain the Ion-exchange (de ionization) process for the purification of water. Discuss the merits and demerits of the process.
4. Explain the different methods used for the desalination of brackish water.
5. Describe the Lime-Soda (Cold & hot) process used for softening of water.
6. Give an account of industrial water characteristics. Explain break point chlorination.
7. Write a brief note on determination of free chlorine present in water.
8. How would you estimate the amount of dissolved oxygen present in water?
9. Explain the determination BOD & COD and its significance.
10. How do you estimate the alkalinity of water?