WATER TREATMENT

Introduction:

Water is the most wonderful and precious gift from nature to all the living beings on the earth. It is an essential element for the existence of human beings, animals and plants. Water rated to be of the greatest importance. It is the most abundant and useful compound on the earth. It covers nearly 72% of the earth’s surface. Water gets evaporated continuously from ocean, rivers and lakes which goes into the atmosphere as clouds and comes down to the earth surface in the form of rain.

Water distributed throughout the world as follows: 97 % locked in the oceans, 2.1 % is present in the form of Ice, 0.6 % of water abundant in the form of fresh water in lakes, rivers and underground, and remaining 0.1 % in the form of well water and salty water.

- Water is the most widely used chemical compound in earth
- Its one of the most essential requirements in life (Air, Food and Water)
- It is not only essential for human beings, but also for animals and plants
- Human body containing about 65% by weight of water in the form of blood and other fluids
- The average intake of water per day to a human body is nearly 2.5 to 3 litres.

Water is most needful element for many domestic usages such as “Drinking, cooking, washing and agriculture and Industrial processes and productions and power generators.

Health and wealth of the nation depends the resources and abundant of quality of water.

Sources of Water: The sources of water classified as follows

Surface water Underground water

Rain water, River water, Lake water, Seawater Springwater Well water

- Rainwater: Purest form of water contains many dissolved gases and suspended solid particles.
- River water: Contains dissolved minerals of soil such as chlorides, sulphates, bicarbonates of sodium, calcium, Magnesium, Iron etc. It is also containing the organic matters, small particles of soil and Sand suspension.

- Lake water: It contains less dissolved minerals but high quality of organic matters.
- Seawater: It is the most impure form of natural water. It contains dissolved salts such as NaCl, sulphates of sodium, bicarbonates of potassium, Magnesium &Calcium,
- Underground water: clear in appearance but contains many dissolved salts and organic matter.

Impurities in water

The water found in nature is never pure which contains large number of impurities in varying amount. These impurities mainly depend up on its source and are classified into four different types.

- Dissolved gases: Presence of NH_3 CO_2, SO_2,(NO)all of which derived from Atmosphere in water impart foul smell. Presence of nitrogen oxides and CO2 lead boiler corrosion.
- Dissolved solids these includes salts like bicarbonates, chlorides and sulphates of Ca, Mg, &Na in addition to that small amount of nitrates, nitrites, silicates, ammonia and ferrous salt etc.
- Suspended impurities: Suspended impurities are the dispersed solids which can be removed by filtration. These are the insoluble matters in suspension which import turbidity, colour and odour to water.

  Suspended impurities are two types,
  a) Inorganic Impurities: Clay, silica, sand, MnO_2 and Fe_2O_3 etc.
  b) Organic Impurities: Wood, leaves, twigs, animals, dead waste, bacteria and algae and protozoa etc.
- Dissolved Salts: Bicarbonates, carbonates, chlorides, nitrates sulphates of sodium, calcium and potassium etc. (These salts presence in water causes "**Hardness**").
  - Colloidal impurities: Impurities in finely divided and suspended state organic wastes likes emulsified oil, dyes, proteins, amino acids clay, $Fe(OH)_2$ (It causes the turbidity).

Hardness of Water:

Hardness in water is that characteristics, which "prevents the lathering of soap" this is due to presence of certain salts of calcium, magnesium and other heavy metals dissolved in water. Hard water does not give lather easily with soap but produces a white scum or precipitate with soap.

This because of the fatty acid of the soap in presence of calcium and magnesium ions in hard water, quickly replaces the sodium ions forming calcium and magnesium salts of fatty acid. Neither calcium nor magnesium are strongly attracted to water and so they precipice out as soap scum.

$$\underset{\text{Sodium stearate (Sodium soap)}}{2C_{17}H_{35}COONa} + \underset{\text{Hardness}}{CaCl_2} \longrightarrow \underset{\text{Calcium stearate (insoluble)}}{(C_{17}H_{35}COO)_2Ca} \downarrow + 2NaCl$$

$$2C_{17}H_{35}COONa + MgSO_4 \longrightarrow \underset{\text{Magnesium stearate (insoluble)}}{(C_{17}H_{35}COO)_2Mg} \downarrow + Na_2SO_4$$

Hence it required large quantity of soap to produce later

Type of Hardness

Hardness classified into two types (1) Temporary Hardness (2) Permanent Hardness

S. No	Temporary Hardness (Carbonate Hardness)	Permanent Hardness (Non-Carbonate Hardness)
1	Caused by dissolved bicarbonates of calcium and magnesium	Caused by dissolved salts of Calcium &Magnesium, other than bicarbonates.like Chlorides, sulphates, nitrates etc.
2	This hardness is removed by boiling, when bicarbonates are convered in to insoluble carbonates $Ca(HCO_3) \longrightarrow CaCO_3 + H_2O \downarrow + CO_2 \uparrow$	Unlike temporary hardness, permanents hardness cannot remove by boiling. Removal of permanent hardness requires various chemical treatments.

- ***The amount of temporary and permanent hardness of water is referred to as the total hardness of water.***

Units of Hardness:

It is expressed in the term of equivalent of calcium carbonate (*One mole of any hardness causing salt of Calcium and Magnesium is equivalent of one mole of $CaCO_3$*)

(1) Parts per million (**ppm**): It is the number of parts of equivalents of $CaCO_3$ hardness causing salt present in one million parts (***10^6 parts***) of water.

(2). Milligram per litre(**mg/L**): It is the number of milligrams of equivalent of $CaCO_3$ per litre of hard water. E.g.: 1mg/Litre means 1 mg of equivalent$CaCO_3$ present in one litre of hardwater.

(3) Degree Clarke (**°*Cl***): It is the number of gains of (1/7000 *l* b) of $CaCO_3$ equivalents of hardness per gallon (10 ***l b***) of water. (Or) It is parts of $CaCO_3$ equivalent hardness causing salt in 70,000 parts of water.

(4) Degree French (**° Fr**): It is a French unit. The number of parts of $CaCO_3$ equivalent hardness causing substance in 10^5 parts of water.

(5) Milliequivalent per litre (**meq/L**) : Is the number if milli equivalent of hardness present per litre.

$$1 \text{ meq/L} = 1 \text{ meq of } CaCO_3 \text{ per litre of Water}$$

$$= 10^{-3} \times 50 \text{ g of } CaCO_3 \ \mathbf{eq/L}$$

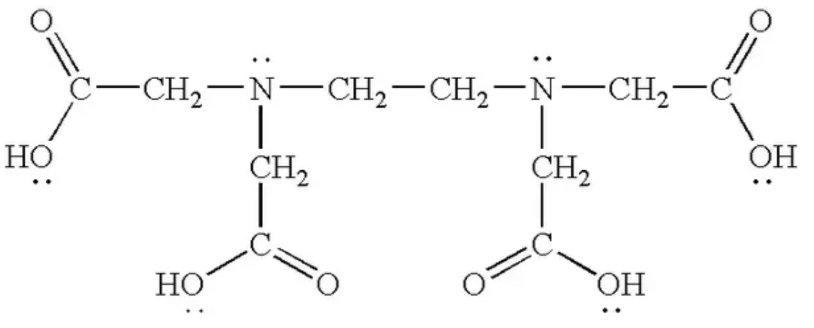
$$= 50 \text{ mg of } CaCO_3 \text{ eq per litre}$$

$$= 50 \text{ mg/L of } CaCO_3 \text{ eq} = \underline{\mathbf{50\ ppm.}}$$

Inter conversion: - 1ppm =1mg/L = 0.07 ° Cl = 0.10 Fr = 0.02 meq/L

Determination of total hardness of water in given water sample by EDTA method

This is a complexometric titration method. Ethylene diamine tetra acetic acid (EDTA),

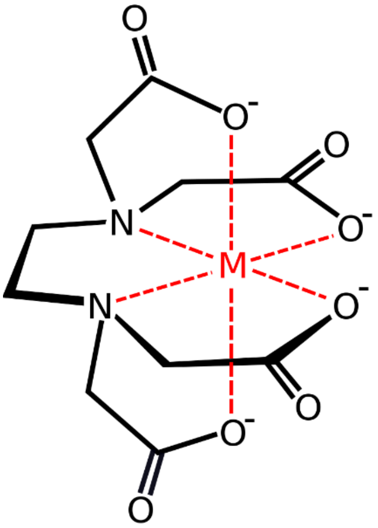


ethylenediaminetetraacetic acid (EDTA)

In the form of its sodium salts yields the anion:

$$[_2(^-OOC.CH_2)\text{-}N\text{-}CH_2\text{-}CH_2\text{-}N\text{-}(CH_2\text{-}COO^-)_2]$$

The above EDTA anion forms complex ions with Ca^{2+} and Mg^{2+}



[Where M = Ca or Mg. It may be pointed the EDTA is employed as its disodium salt.]

(Molecular weight = 372.24, Eq. weight = 186.14)

To determine hardness of given water, hard water is buffered to a **pH** value of 10, for that reason using NH_4OH-NH_4Cl buffer and few drops of Erichrome black -T indicator (EBT) are added. EBT forms a weak unstable wine-red complex with metal ions.

M^{2+} + EBT $\longrightarrow$ (M-EBT) complex

(Blue) ***(Unstable complex) Wine red colour***

Where M = Ca and Mg ions.

During titration of water sample against EDTA, EDTA combines with free Calcium and Magnesium ions to give very stable metal Metal -EDTA complex which is colourless.

(M-EBT) complex + EDTA $\longrightarrow$ (M-EDTA)complex + EBT

Wine red colour *Stable complex* *(Blue colour)*

Thus, at equivalent point, there is a change in colour from wine red (due to M-EBT complex) to blue complex (Due to free EBT).

Various steps involved in this titration method, Refer to Lab manual for detail procedure.

Disadvantages of Hard water

Domestic Usages

- ***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. Hard water reacts with soap it produces sticky precipitates of calcium & Magnesium soaps. These are insoluble formations.

- ***Bathing***: Hard water does not produce 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.

Industrial usages

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

- *Sugar Industry*: Water containing sulphates, nitrates, alkali carbonates etc. if used in sugar refining, causes difficulties in the crystallization of sugar. Moreover, the sugar so produced may be de-liquescent.

- *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.

- *Concrete making*: Water containing chlorides and sulphates, if used for concrete making, affects the hydration of cement and the final strength of the hardened concrete.

- *Laundry*: Hard water, if used in laundry, causes much of the soap used in washing to go as waste iron salts may even causes coloration of the cloths.

Scale and Sludge formation in Boilers

In boilers, water evaporates continuously, and the concentration of the dissolved salts increases progressively. When their concentrations reach saturation point, they are thrown out of water in the form of precipitates on the inner walls of the boiler. The precipitation takes place in the form of loose and slimy, it is called **sludge**.

If the precipitate matter forms a hard and adhering/ coating on the walls of the boiler, it called **scale.**

Boiler feed water:

Water is mainly used in boilers for the generation of steam for industries and power house. Boiler feed water should correspond with the following composition.

1) Its hardness should be below 0.2ppm

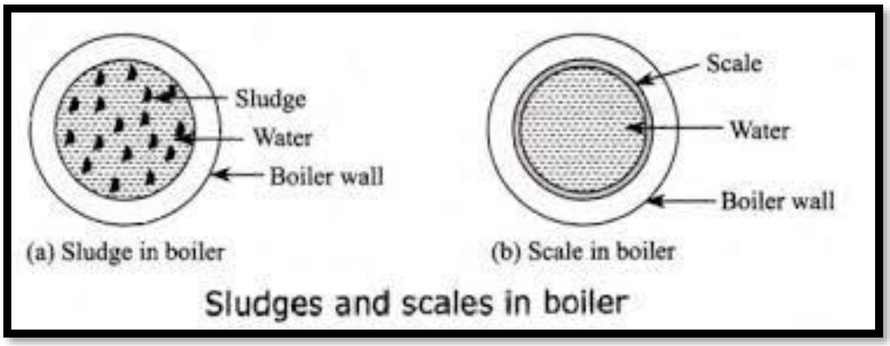
2) Its caustic alkalinity (due to – OH) should lie in between 0.15 and 0.45 ppm

3) Its soda alkanity (due to Na_2CO_3) should be 0.456 to 1ppm. If excess of impurities present they lead to the formation of scales, sludges, foaming, Corrosion and caustic embattlement.

Sludge formation in boilers: The resultant precipitate is called as scale. If it is in the form of thick adherent deposit. The precipitate is known as sludge and it is in the form of loose precipitate. Sludges are formed by substances which have greater solubility in hot water than in cold water. Ex: $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$ etc.

They are collected at place, Where the flow rate is slow, they can be easily removed with a wire brush.

Disadvantages of Sludge: Sludge has greater solubility in hot water than in cold water. They are poor conductors of heat and they tend to waste a portion of heat generated and hence decreases the efficiency of boiler. Excessive sludge formation disturbs the working of the boiler. it settles in the region of poor water circulation such as pipe connection plug opening etc.



Sludges and scales in boiler

Causes of scale formation in boilers If the precipitate is hard and strongly adhering on the inner walls of the boilers is known as scale.

Which is difficult remove even with the help of hammer. Scaler are formed due to

- Decomposition of Calcium bicarbonate.

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

$CaCO_3$ is soft and it is the main cause of scale formation in low pressure boilers. In high pressure boilers $CaCO_3$ is soluble due to formation of $Ca(OH)_2$.

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

- In high pressure boilers, $CaSO_4$, $CaSiO_3$ and $MgSiO_3$ are sparingly soluble in cold water. They are nearly insoluble in high temperature.
- Hydrolysis of magnesium salts.

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

Presence of Silica: If small quantity of Silica is present it will deposit as calcium silicate or $MgSiO_3$.

Disadvantages of Scale formation:

1) It is due to wastage of fuel.

2) It is due to lowering of boiler safety.

3) Due to Decrease in efficiency.

4) Due to danger of explosion.

Prevention of Boilers

The scale formations is mainly due to the presence of salts of Calcium and magnesium ions. Therefore, the scale formation in boilers can be prevented if these metal ions are eliminated from the boiler feed water.

The scale forming impurities can be eliminated by subjecting the boiler feed water to suitable treatments.

a) Using software for boiler operations
b) Removing concentrated salty water from time to time so that deposition of sludge is prevented.

Calgon Conditioning:

It involves adding sodium hexametaphosphate (also called Calgon) to boiler water to prevent Scale and Sludge formation. Calgon converts the scale forming impurities into highly soluble complexes.

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

$$\mathbf{2CaSO_4 + [Na_4(PO_3)_6]^{2-} \longrightarrow \underset{\text{Soluble complex ion}}{[Ca_4(PO_3)_6]^{2-}} + 2Na_2SO_4}$$

$$\mathbf{2Na^+ + [Ca_2(PO_3)_6]^{2-} \longrightarrow \underset{\text{Soluble complex}}{Na_2[Ca_2(PO_3)_6]}}$$

Softening of water by ion exchange process:

It is the process of removing all the dissolved metal ions and their counter anions from water, thereby reducing the hardness. An ion exchange resin is a cross linked Organic Polymer network with some ionisable group. Two types of ion exchange resins

- Cation exchanger: Resins which have $-SO_3H$, -COOH, phenolic group as the ionisable group. Since these resins exchange the Cationic portion of minerals by their $\mathbf{H^+}$.
- Anion exchanger: Resins which have $-NH_2$, $-NHCH_3$, $N(CH_3)_2OH$ as the ionisable group. Since these resins exchange the Anionic portion of minerals by $\mathbf{OH^-}$ ion.

Ion exchange Softening Process:

- In ion exchange process the impure water is pass through cation exchange resin and anion exchange resin. Cation exchange resin is capable of exchanging cations present in water for $\mathbf{H^+}$ ions, i.e., when the water passes through the cation exchanger, the cations present in the water as impurities are retained by the resin and $\mathbf{H^+}$ ions are released into water.

- Anion exchange resin is capable of exchanging anions present in water for **OH^-** ions. i.e., when water passes through anion exchanger, the anions present in the water are retained by the resin and **OH^-** ions are released in to water.

Function of Cation exchanger: Water is passed through a tank having cation exchanger which absorbs all the cations present in water and leaves behind the hydrogen. [Cation exchange resin is expressed in **RH**]

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

$$2RH + Mg^{2+} \longrightarrow R_2Mg + 2H^+$$

The water coming out of the cation exchange resin is acidic as H^+ ions introduced into water in place of metal ions.

Function of anion exchanger: The anion resins are copolymers styrene and divinyl benzene containing active quaternary amino groups these resins are represented as ROH and they exchange anions present in water for **OH^-** ions.

$$ROH + Cl^- \longrightarrow RCl + OH^-$$

$$2ROH + SO_4^{\ 2-} \longrightarrow R_2SO_4^{\ 2-} + 2OH^-$$

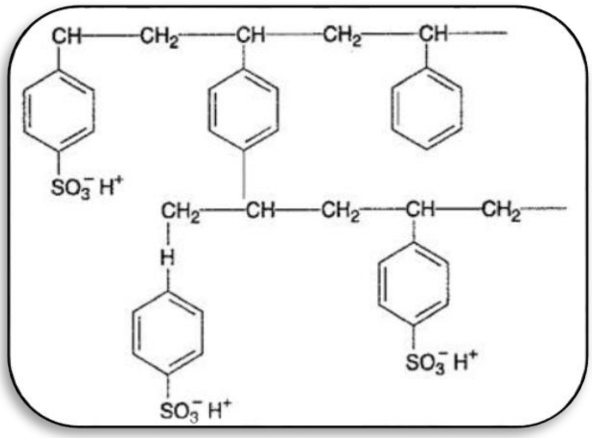
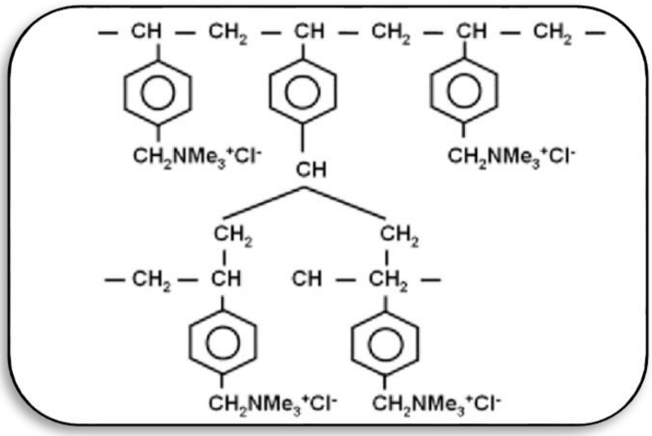


Fig: Cation exchange resin

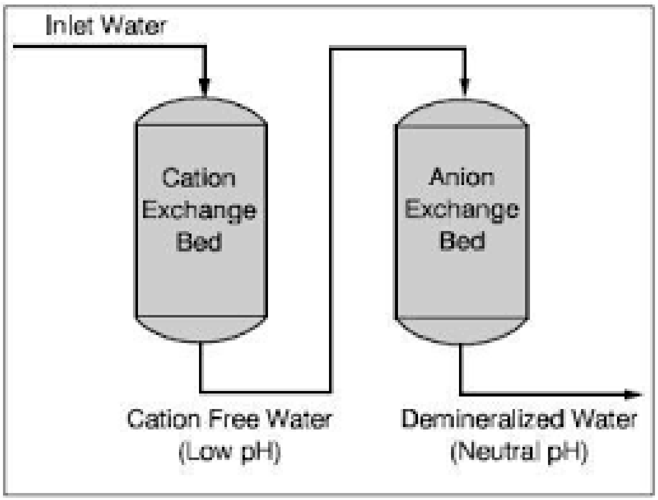


Anion Exchange resin

As cations are replaced by H+ ions and anions by OH-, the net effect is introduction of water in place of metal salts presents in water.

$$\mathbf{H^+ + OH^- \longrightarrow H_2O}$$

The arrangement for demineralization of water shown the below figure.



Regeneration

When the resins get exhausted, they can be regenerated by passing HCl and NaOH solution through cation and anion exchanger resins respectively.

Ion exchange Process: The raw water is first passed through the column containing cation exchanger resin, in which the cations present in water are retained and $\mathbf{H^+}$ ions are released into water. The water coming out of the cation exchanger is acidic. The effluent from the cation exchanger column is then passed through the anion exchange column. The column retains the anion present in water releasees $\mathbf{OH^-}$ ions.

➢ *Advantages:*

- The apparatus once gets installed, is easy to operate and control
- Acidic and alkaline water can be softened
- Residual hardness is very low and thus water is suitable for high pressure boiler

♣ Disadvantages:

- Equipment and process is costly
- Turbid water needs to be filtered first before softening.

Desalination of water:

It is the process of removal if dissolved salts present in water. The process of partial or complete removal of NaCl salt from highly saline water such as sea water is known as desalination. Desalination can be carried out by different techniques which are

- **Electro dialysis**
- **Reverse osmosis**

Reverse Osmosis (RO)

If pure water and salt water are separated by a semipermeable membrane, the water molecules flow from pure water (diluted solution) to salt water (concentrated solution). This process of movement of solvent (Water) molecules from a diluted solution in to concentrated solution through a semi permeable membrane is called osmosis. Pressure exerted due to osmosis is called as osmotic pressure. Water can be made to flow in reverse direction (From salt water to pure water) by applying pressure on salt water which is greater than the osmotic pressure. This process is called as reverse osmosis. Through this, sea water can be converted into potable water.

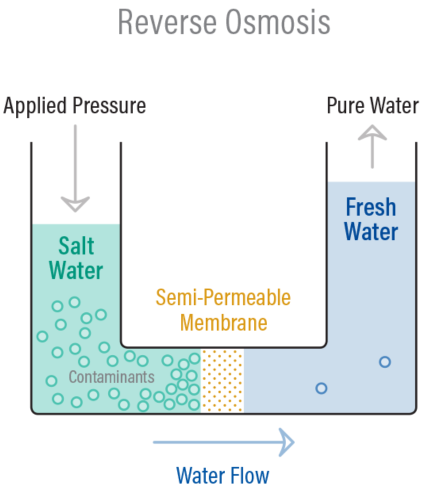


Fig: Reverse Osmosis Process.

Reverse Osmosis unit consists of a vessel, a membrane and a high-pressure pump. The membrane is generally made of cellulose acetate or Nylon. Pressure in the range of 410-540 psi is usually applied to bring about reverse osmosis.

Electrodialysis:

In this method, salts present in water are removed using ion selective membranes by applying direct current. An electro dialysis unit consists of several compartments partitioned by alternating cation and anion selective membranes. These membranes specifically allow the passage of either cations or anions. These membranes are selective as they are made up of materials containing fixed functional groups. Two electrodes, a cathode and an anode are placed at two extreme ends. Salt water is taken in the compartments and direct current is applied under the influence of electric current anions move towards anode through anion selective membrane and are passed on to next compartment. However, these anions cannot pass through next immediate membrane which is permeable to only cations.

Similarly, cations move towards cathode through cation selective membrane and are passed on to next compartment. These cations cannot pass through next membrane which is permeable to only anions. Thus, each alternate compartment gets concentrated with anions and cations. Meanwhile, other adjacent alternate compartments get filled with desalination water. Finally, concentrated water and desalinated water are removed separately as shown in the diagram.

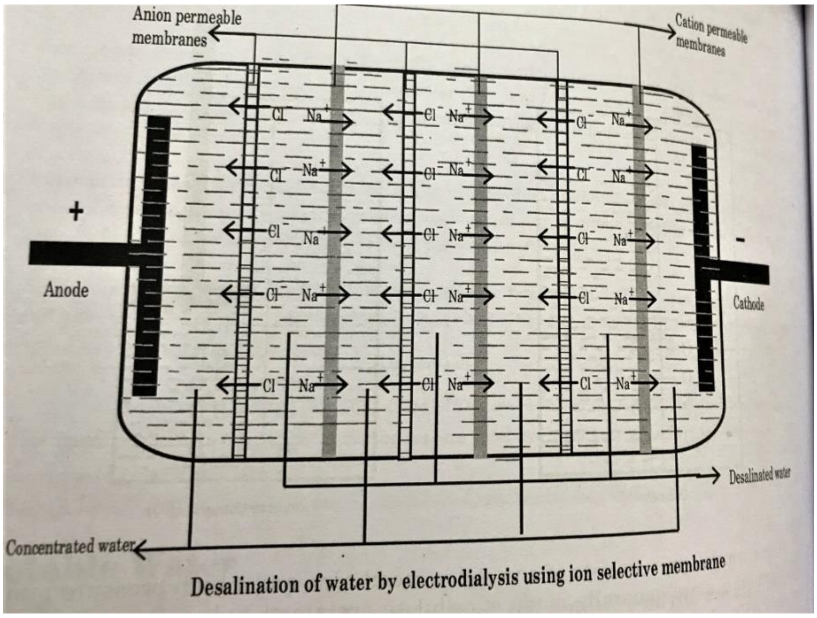


Fig: Desalination of Water by Electrodialysis

Forward osmosis

Forward osmosis (FO) is an osmotic process that, like reverse osmosis (RO), uses a semi-permeable membrane to effect separation of water from dissolved solutes. The driving force for this separation is an osmotic pressure gradient, such that a "draw" solution of high concentration (relative to that of the feed solution), is used to induce a net flow of water through the membrane into the draw solution, thus effectively separating the feed water from its solutes. In contrast, the reverse osmosis process uses hydraulic pressure as the driving force for separation, which serves to counteract the osmotic pressure gradient that would otherwise favour water flux from the permeate to the feed. Hence significantly more energy is required for reverse osmosis compared to forward osmosis. (FO) processes

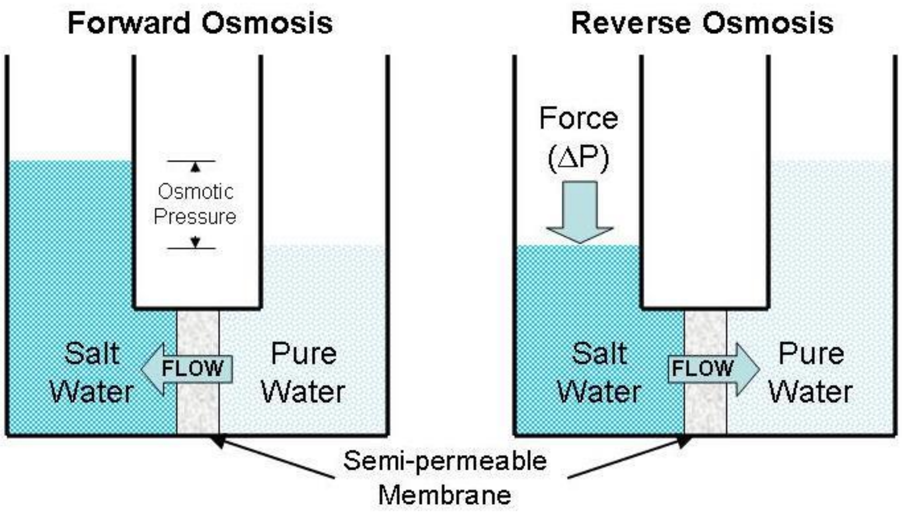


Figure 1: Water flows for FO and RO

In Forward osmosis processes solute diffusion in both directions depending on the composition of the draw solution and the feed water. This does two things; the draw solution solutes may diffuse to the feed solution and the feed solution solutes may diffuse to the draw solution. Clearly these phenomena have consequences in terms of the selection of the draw solution for any Forward osmosis process.

An additional distinction between the Reverse osmosis (RO) and Forward osmosis (FO) processes is that the permeate water resulting from a RO process is in most cases fresh water ready for use. In this process, this is not the case. The membrane separation of the FO process in effect results in a "trade" between the solutes of the feed solution and the draw solution. Depending on the concentration of solutes in the feed (which dictates the necessary concentration of solutes in the draw) and the intended use of the product of the FO process, this step may be all that is required.

Dissolved oxygen:

Pure water contains about 8-9 ppm of molecular oxygen dissolved in it which is called as dissolved oxygen (DO). It is very much essential for the survival of aquatic life. If any oxidizable organic impurities is released to water as a pollutant, then this impurity will be oxidized by DO. Hence, oxidizable impurities are mainly responsible for decreasing level of DO in water. Dissolved oxygen level of water can be determined by Winkler’s method.

The amount of oxidizable impurities present in polluted water is measured in two ways:

- Biological Oxygen Demand (BOD)
- Chemical Oxygen Demand (COD)

Biological Oxygen Demand (BOD)

It is a measure of dissolved oxygen required to oxidize biologically oxidizable impurities present in water. These are the impurities which are oxidized by the microorganisms present in polluted water by utilizing dissolved oxygen present in water.

"BOD **is defined as "the amount of dissolved oxygen consumed by the microorganisms to oxidize the biologically oxidizable impurities present in 1 litre of water over the period of 5 days at 20°C"**

BOD is determined by measuring DO of water in the beginning [DO1] and after the period of 5 days [DO2]. The amount of DO consumed for oxidations over the period of five days is BOD water.

$$\boxed{\mathbf{BOD= [DO_1\text{-}DO_2]mg\ of\ O_2/dm^3}}$$

Chemical Oxygen Demand (COD)

COD is defined as **"the amount of oxygen required to oxidize all oxidizable impurities present in 1 litre o waste water using a strong oxidizing agent such as acidified $K_2Cr_2O_7$"**

Potassium dichromate is a strong oxidizing agent under acidic conditions. Acidity is usually achieved by the addition of sulfuric acid. The reaction of potassium dichromate with organic compounds is given by

$$\boxed{3[CH_2O] + 16H^+ + 2\ K_2Cr_2O_7^{2-} \xrightarrow{Ag_2SO_4\ or\ HgSO_4} 4Cr^{3+} + 3CO_2 + 11H_2O}$$

Ag_2SO_4 is used as catalyst for the oxidation of straight chain aliphatic compounds. However, Ag^{2+} ions become ineffective in the presence of chloride ions (present in waste water) due their precipitation as silver halide (ex: AgCl, AgBr). This difficulty is overcome by treating the waste water with mercuric sulphate. Mercuric sulphate binds the halide ions and makes them unavailable.

Determination of COD of a Waste Water Sample:

A known volume of the waste water sample is refluxed with $K_2Cr_2O_7$ solution in sulphuric acid medium. $K_2Cr_2O_7$ oxidizes oxidizable impurities. The amount of unreacted $K_2Cr_2O_7$ is determined by titration with standard solution of ferrous ammonium sulphate. The amount of $K_2Cr_2O_7$ consumed corresponds to the COD of the waste water sample. To find out this, a blank titration without waste water sample is carried out.

Procedure:

Back Titration: Pipette out 25 cm3 of the waste water sample and 25 cm^3 of $K_2Cr_2O_7$into a 250 cm^3 conical flask. Add one test tube full of 1:1 sulphuric acid (containing Silver sulphate and Mercuric sulphate). Reflux the mixture for half an hour and cool. Add 2 -3 drops of ferroin indicator and titrate against the standard ferrous ammonium sulphate solution until the colour changes from bluish green to reddish brown.

Let the normality of the FAS solution be 'z' N

Let the volume of FAS solution consumed in titration be 'y' cm^3.

Blank Titration: Pipette out 25 cm^3 of $K_2Cr_2O_7$ solution. Add one test tube full of 1:1 H_2SO_4 followed by 2-3 drops of ferroin indicator and titrate against the standard FAS solution till the colour of solution turns bluish green to reddish brown.

Let the volume of FAS solution consumed in titration be x cm^3.

Calculation:

1 cm^3 of 1N FAS solution = 1 milli equivalent of oxygen = 8 mg of oxygen

(x-y) cm3 of z N FAS solution = 8 × (x-y) × z mg of Oxygen

i.e., 25 cm3 of waste water sample = 8 × (x-y) × z mg of Oxygen

1000 cm3 of the waste water sample = $\frac{8 \times (x-y) \times z \times 1000}{25}$ mg of Oxygen

COD of waste water sample = $\frac{8 \times (x-y) \times z \times 1000}{25}$ mg of O_2/dm^3

Comparison between BOD and COD

- *BOD is a slower process. It takes more than five days for estimation of BOD value of water sample. Where as COD value can be estimated in about 3 hours.*
- ***Any water sample COD value is always greater than its BOD values. Because BOD is the measure of only biologically oxidizable impurities present in water whereas COD is the measure of all oxidizable impurities***
- *Bothe BOD and COD are expressed in mg of O_2/dm^3 of waste water.*

Aerobic and Anaerobic oxidation

Larger number of bacteria's present in sewage, are of two types, depending upon the way they satisfy their oxygen demands.

a) ***Aerobic bacteria's***: *Which live on free oxygen or on oxygen dissolved in water.*
b) ***Anaerobic Bacteria's***: *Which live and develop in the absence of free oxygen. They extract oxygen from oxygen containing radicals of organic compounds and minerals such as nitrates, nitrites, and sulphates.*

Aerobic Oxidation: In the presence of oxygen, organic compounds are oxidized by aerobic bacteria's and the oxidation products are nitrites, nitrates, sulfates, phosphates, etc., which do not produce any offensive smell. This kind of oxidation is known as aerobic oxidation.

Anaerobic Oxidation: When the oxygen content is below a certain value, the sewage is said to be stale and the organic compounds are decomposed by anaerobic bacteria's, producing methane, Hydrogen sulphide, phosphine, etc., which give offensive odour. This type of oxidation is called anaerobic oxidation.

When the anaerobic decomposition is continuing the sewage is known as septic sewage.

WATER POLLUTION

Discharge of certain substance into water that affects the physical, biological and chemical properties of water which in turn decreases the utility of water is known as water pollution. The matter which is responsible for these unhealthy changes in water is known as water pollutants. E.g. Pd, Hg, CN, As, Cu, acids alkalis pesticides, insecticides, fungicides, animal matter, human excreta, radioactive wastes etc. *The contaminated in water is called sewage water or effluent.*

Depends on the sources of water Pollutant, sewage water is classified into two type

1. Domestic Sewage 2. Industrial sewage

Domestic sewage:

It is waste discharge away from residence, Institutes, Hospitals etc. These include certain organic wastes, pathogenic bacteria, plant materials Pesticides, detergents and other materials. Domestic sewage causes water borne diseases like dysentery, cholera typhoid, and hookworm infection.

Industrial sewage:

The water released by industries contains Pd, Hg, CN, As, Cu, acids, alkalis, pesticides, detergents, insecticides, fungicides, soap, phenol etc. The industrial sewage also causes several environmental problems. The sewage can be render harmless by suitable treatments.

Sewage treatment

Removal of harmful contamination from waste water completely or partially is known as water treatment or sewage treatment. The treatment of sewage water is carried out by three different stages. 1.***Primary treatment 2. Secondary treatment 3. Tertiary treatment***

Primary treatment: Primary treatment involves following processes

- *Screening*
- *Slit and grit removal*
- *Oil and Gas removal*
- *Sedimentation*

a) ***Screening***: It is physical process which removes large suspended or floating matter in the sewage. This is accomplished by using mesh screens which retain the floating and suspended particles when sewage water is passed through it.

b) ***Slit and grit removal:*** Sand, broken glass, etc, are removed by passing sewage through grit chambers, in which the velocity if flow of sewage is reduced. Being heavier, silt and grit particles settle down at the bottom.

c) ***Removal of oil:*** Oil, grease, etc, , are removed in in skimming tanks. They are converted into a soapy mixture by blowing compressed air through sewage water in skimming tanks and lifted to the surface in the form of a foam. The floating substance is skimmed off.

d) ***Sedimentation process:*** It removes finer suspended impurities. This is brought about by plain sedimentation in a continuous flow type sedimentation tank with coagulation. *The coagulants used are alum, ferrous sulfate.* Etc. which help in the easy settlement of the finely suspended particles.

Secondary treatment

Secondary treatment is *expressed as biological treatment it involves following process*

- *Trickling filter method*
- *Activated sludge process*

This process involves an aerobic biochemical oxidation. The sewage water, after sedimentation, is subjected to aerobic oxidation, during which the organic matter is converted into CO_2, the nitrogen into ammonia, and finally into nitrites and nitrates. Bases present in the sewage water form salts like ammonium nitrite, ammonium nitrate, calcium nitrate, etc.

The biological treatment is generally accomplished by either ***Trickling filter method and Activated sludge process.***

Trickling filter method:

Tricking filter consists of a rectangular or circular vessel, with a filter bed made up of broken rock, broken bricks or large anthracite coal. Sewage is sprayed over this bed by means of a rotating distributor. As the sewage trickles or percolates downwards through the filter bed, micro-organisms grow on the surface of aggregates, using organic materials of the sewage as food. Aerobic conditions are maintained, and the purified sewage is removed from the bottom. The process removes 90% of biologically oxidizable impurities.

The treated water effluent from industrial wastewater trickling filters is typically processed in a clarifier to remove the sludge that sloughs off the microbial slime layer attached to the trickling filter media as for other trickling filter applications. Some of the latest trickle filter technology involves aerated biofilters of plastic media in vessels using blowers to inject air at the bottom of the vessels, with either downflow or up flow of the wastewater.

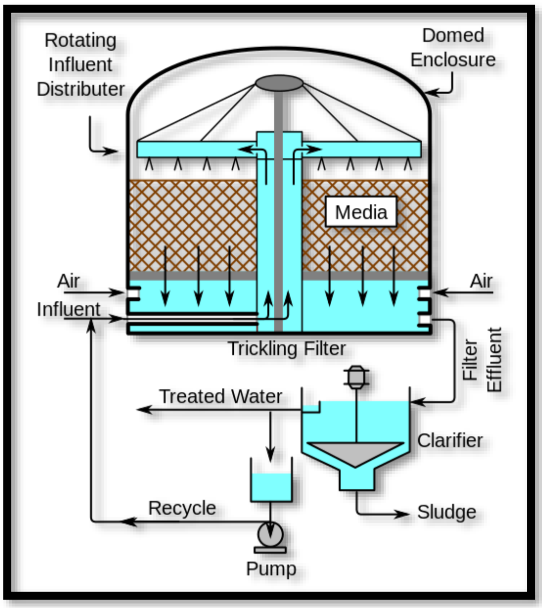


***Fig.Trickling filter Process*.**

***Activated sludge method*:**

The waste water after primary treatment is allowed to flow into a large tank where biological treatment is carried out. Here the water is sprayed with activated sludge, the microorganism present in sludge form a thin layer on water and break down all organic impurities into simpler compounds. The air is passed from the centre of tank vigorously in order bring effective aerobic oxidation. The residual water is chlorinated to kill bacteria and then treated with potash alum to settle the impurities. The water is then filter and discharge into drainage.

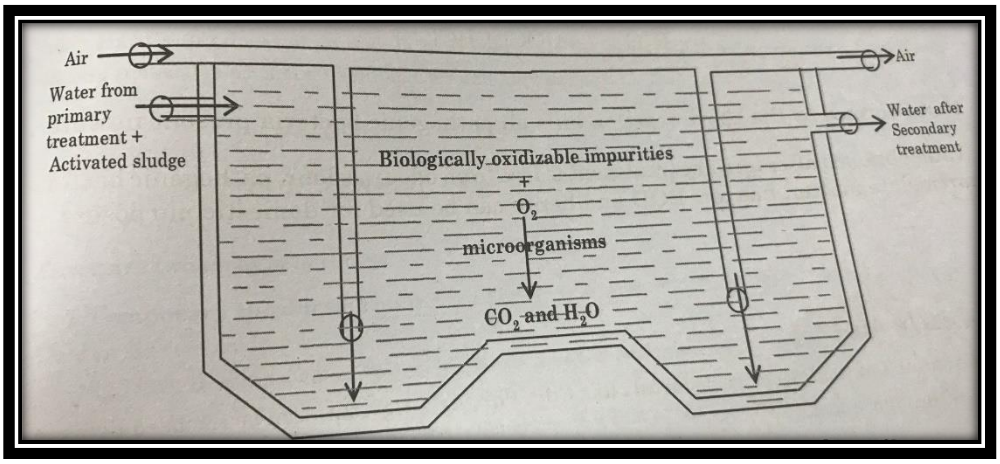


Fig: *Activated sludge process for Sewage treatment.*

Tertiary Treatment:

In this stage, chemical impurities, bacteria, remaining suspended matter and dissolved gases are removed from waste water. Treatment in this stage depends on the type of impurity present in water. Tertiary treatment generally involves the following process

I. ***Removal of Phosphates***: Treating waste water with lime at pH above at 11, phosphate is removed as a precipitate of calcium phosphate.

$$Ca(OH)_2 + PO_4^{3-} \longrightarrow Ca_3(PO_4)_2$$

II. ***Sedimentation with Coagulation***: The fine suspended particles are removed by sedimentation in the presence of coagulating agents like Aluminium sulphate, Ferrous sulphate, etc. These compounds produce gelatinous precipitate of their metal hydroxides. This gelatinous precipitate adsorbs fine suspended particles on its surface and settle at the bottom of the tank.

$$FeSO_4 + 2H_2O \longrightarrow Fe(OH)_2 + H_2SO_4$$

III. ***Filtration***: The last traces of suspended matter is removed by filtering the water through sand filter beds or carbon filter.

Disinfection

It is the process of removing pathogenic bacteria, viruses and protozoa from water. Number of methods are utilized; few examples is given below.

- **Boiling**: It is the simplest method to disinfect water. But it is useful only for small quantities of water. For proper disinfection, water should be boiled vigorously for 20-25 minutes.

IV. ***Disinfection***: Finally, water is chlorinated to kill the pathogenic bacteria

$$Cl_2 + H2O \longrightarrow HOCl + HCl$$

HOCl formed the above reaction kills all pathogenic bacteria present in water.

Water obtained after tertiary treatment is free from odour, colour, pathogenic bacteria, particulate matter, and has low BOD and hence can be used for domestic purposes.

- **By adding Chloramine ($ClNH_2$):** Chloramine is formed by reacting chlorine and ammonia in the ration of 2:1

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

  It is more lasting than chlorine alone, hence it is a better disinfectant.

  $$ClNH_2 + H2O \longrightarrow HOCl + NH_3$$

Advantages: Excess of chloramine does not produce irritating odour

It imparts good taste to treated water

Application of Nanotechnology in Water treatment:

Nanotechnology can be defined as the manipulation of atoms or molecules at nanoscale level (5-100nm) to produce system or devices at superior properties. The materials having at least one dimension in the nanoscale are called nanomaterials. When bulk materials are reduced to nanoscale size the properties exhibit a tremendous efficiency. For example, insoluble substance become soluble (gold), opaque material express transparency (copper), stable materials become combustible (Aluminium). Gold is chemically inert in bulk, but gold nanoparticles act as a good catalyst.

Properties of Nanoparticles:

- The nanoparticle surface to volume ratio is very high. Its increases the chemical reactivity and strength, electrical and chemical properties of the materials at nanoscale level. Zinc oxide nanoparticles shows very superior UV blocking properties compare to the bulk zinc oxide materials. This is one of the major reasons to use for the preparation of sunscreen lotions.
- Nanoparticles always containing unexpected optical properties as they are small enough to confine their electrons and produce quantum effects. Example for this reaction " gold nanoparticles appear deep red to black in solution.

- ***Silver nanoparticles [Ag-N]:***

Very recently Indian Institute of Technology Madras (IIT M) devised a cost effective and highly efficient method to produced a clean drinking water which is affordable nearly 10 -12 rupees per month for a family of five. [The report published in May 7th of national academy of sciences].

- ***Silver nanoparticles coated on a composite do not required electricity or hydrostatic press to form potable water.***
- ***It can operate at ambient temperature with in the range of 5 – 32°C.***
- ***It uses sustained release of silver nanoparticles (nearly 50 ppb) to kill microorganisms.***
- ***The amount of silver ions released is well below the maximum permissible limit of 100 ppb.***
- ***Silver ions are known for the ability to destroy the integrity of cell membrane and damage DNA.***

Even there are report in the literature revealed that silver nanoparticles laced with the filter paper to clean dirty water. This provides simple and inexpensive filtering system that could provide water for millions of people who have short supply of clean water, especially following natural disaster and other emergencies. People without a reliable resource of potable water could use filter paper, which is impregnated with small particles of silver to kill disease causing bacteria as they pass through it.

- ***Nano titanium dioxide [NTO]:***

Titanium oxide is a very good photocatalytic material, due to the excellent photocatalytic activity Nano level titanium dioxide particles used in water treatment.

Nanocrystalline titanium dioxide is a well-known advanced oxidation process for environmental remediation, with insitu generation upon irradiation with light. NTO can mineralize a wide range of organic compounds into harmless end products such as CO_2, H_2O and inorganic ions.

Solved numerical of Hardness

1. A sample of water on analysis was found to contain $(CaHCO_3)_2$ = 4 mg/L, Mg $(HCO_3)_2$ = 6 mg/L, $CaSO_4$ = 8 mg/L, $MgSO_4$ = 10 mg/L. ***Calculate the temporary and permanent and total hardness of water in ppm, °Fr and °Cl***. [Mol.wt of $Ca(HCO_3)_2$ = 162, $Mg(HCO_3)_2$ =146, $CaSO_4$ = 136, $MgSO_4$ = 120]

Solution: Conversion into $CaCO_3$ equivalent.

S.No	Constituent	Amount	Equivalent of $CaCO_3$
1	**$(CaHCO_3)_2$**	**4 mg/L**	**4×100/162 = 2.469 mg/L**
2	**Mg $(HCO_3)_2$**	**6 mg/L**	**6 ×100/146 = 4.10 mg/L**
3	**$CaSO_4$**	**8 mg/L**	**8 × 100/136 = 5.88 mg/L**
4	**$MgSO_4$**	**10 mg/L**	**10 × 100/120 = 8.34 mg/L**

Temporary hardness is due to Ca $(HCO_3)_2$ and $Mg(CHO_3)_2$.

Hence, temporary hardness = 2.46 + 4.10 = 6.57 mg/L or **6.57 ppm.**

Since **1 mg/L = 1 ppm = 0.07 °Cl = 0.1 °Fr.**

= 6.57 × 0.1 °Fr = 0.657 °Fr

= 6.57 × 0.07 °Cl = 0.4605 °Cl

Permanent Hardness is due to salts of $CaSO_4$ and $MgSO_4$,

Hence = 5.88 + 8.34 = 14.21 mg/L or **14.21 ppm**

= 14.21 × 0.1 = **1.421°Fr.**

= 14.21 × 0.07 oCl = **0.995 °Cl.**

Total hardness = Temporary hardness + Permanent hardness

= 6.579 + 14.215 = **20.794 mg/L**

Total hardness expressed in ppm = **20.794 ppm**

Total hardness expressed in °Fr = 20.79 × 0.1 = **2.79 °Fr**.

Total hardness expressed in °Cl = 20.79 × 0.07 = **1.455 °Cl**

2. A sample of water on analysis was found to contain $(CaHCO_3)_2$ = 162mg/L, Mg $(HCO_3)_2$ = 7.3 mg/L, $CaSO_4$ = 136 mg/L, $MgCl_2$= 95 mg/L. ***Calculate the temporary and permanent and total hardness of water in ppm.***

Solution: Conversion into $CaCO_3$ equivalent.

S.No	***Constituent***	***Amount***	***Equivalent of $CaCO_3$***
1	***$(CaHCO_3)_2$***	***4 mg/L***	***162×100/162 = 100 mg/L***
2	***$Mg(HCO_3)_2$***	***6 mg/L***	***73 ×100/146 = 50 mg/L***
3	***$CaSO_4$***	***8 mg/L***	***136 × 100/136 = 100 mg/L***
4	***$MgSO_4$***	***10 mg/L***	***95 × 100/95 = 100 mg/L***

Temporary hardness is due to Ca $(HCO_3)_2$ and Mg $(CHO_3)_2$.
Hence, temporary hardness = (100 + 50) = 150 mg/L or **150 ppm.**

Permanent Hardness is due to salts of $CaSO_4$ and $MgCl_2$

Hence = (100+100) = 200 mg/L or **200 ppm**

Total hardness = Temporary hardness + Permanent hardness
= (150+200 mg/L) = **350 mg/L**

Total hardness expressed in ppm = 350 ppm

EDTA Problems:

1] 25 mL of a sample water consumed 12.5 mL of 0.02 M EDTA before boiling.

7.5 mL of the same EDTA after boiling. Calculate total hardness, Permanent hardness and temporary hardness of the waste water sample.

Solution:

Before boiling: $M_{H2O:}$ 12.5 × 0.02 / 25 = 0.01

Hence, CaCO3 equivalent of hardness = 0.01 ×100 ×1000 = **1000 ppm**

Total Hardness = 1000 ppm

After Boiling, M_{H2O} = 7.5 × 0.02 / 25 = 0.006

Hence, CaCO3 equivalent of hardness = 0.006×100 ×1000 = **600**

Permanent Hardness = 600

Temporary Hardness = (Total hardness – Permanent hardness)

Temporary Hardness = (1000-600) = 400 ppm

2] 50 mL of a sample water consumed 15 mL of 0.01 M EDTA before boiling.

5 mL of the same EDTA after boiling. Calculate total hardness, Permanent hardness and temporary hardness of the waste water sample.

Solution:

Before boiling: $M_{H2O:}$ 15 × 0.01 / 50 = 0.003

Hence, CaCO3 equivalent of hardness = 0.003 ×100 ×1000 = **300 ppm**

Total Hardness = 300 ppm

After Boiling, M_{H2O} = 5 × 0.01 / 50 = 0.001

Hence, CaCO3 equivalent of hardness = 0.001×100 ×1000 = **100**

Permanent Hardness = 100

Temporary Hardness = (Total hardness – Permanent hardness)

Temporary Hardness = (300-100) = 200 ppm

3] 25 cm^3 of hardwater sample required 15.5 cm^3 of 0.02M EDTA solution for titrating using EBT as indicator. Under the similar condition another 25 cm3 of same sample water after boiling and cooling required 8.3 cm3 of EDTA solution. Calculate Temporary, permanent and total hardness of the water sample

Solution:

Total Hardness:

Before boiling: $M_{H2O:}$ 15.5 × 0.02 / 25 = 0.0124

Hence, CaCO3 equivalent of hardness = 0.0124 ×100 ×1000 = **1240 ppm**

Total Hardness = 1240 ppm

Permanent Hardness:

After Boiling, M_{H2O} = 8.3 × 0.02 / 25 = 0.00664

Hence, CaCO3 equivalent of hardness = 0.00664 ×100 ×1000 = **664**

Permanent Hardness = 664

Temporary Hardness = (Total hardness – Permanent hardness)

Temporary Hardness = (1240-664) = 576 ppm

4]0.5 g of $CaCO_3$ was dissolved in HCl and the solution made up to 500 mL with distilled water. 50 mL of the solution required 48 mL of EDTA for titration. 50 mL of hardwater sample required 15 mL of EDTA and after boiling and filtering required 10 mL of EDTA solution. Calculate hardness.

Solution:500 m L of SHW = 0.5 mg or 500 mg $CaCO_3$ eq [SHW = Standard Hard water]

If 1 mL SHW = 1 mg $CaCO_3$

Now 48 mL of EDTA solution = 50 mL SHW = 100 mg $CaCO_3$

So 1 mL of EDTA solution = 50/48 mg $CaCO_3$

Calculation of total hardness of water:

50 mL hard water = 15 mL EDTA = 15 × (50/48) mg $CaCO_3$ eq

= 15.6 mg $CaCO_3$ eq

If 1000 mL hardwater = 15.6×1000 / 50 = 312.5 mg /L CaCO3 eq.

Hence: total hardness = 312.5 mg/L

Total Hardness in ppm = **312.5 ppm**

Calculation of noncarbonate hardness:

50 mL boiled hard water = 10 mL EDTA solution

= 10× (50/48) mg $CaCO_3$ eq.

= 10.417 mg $CaCO_3$ eq.

: 1000 mL boiled hard water = 10.417×1000 / 50 mg $CaCO_3$ eq

= 208.3 mg $CaCO_3$ eq or 208.3 mg/L = 208.3 ppm

Hence, Carbonate hardness = (312.5-208.3) = **104 ppm.**

Ans: 104 ppm

COD Numerical Problems:

1. 30 cm^3 of Industrial effluent consumes 8 cm^3 of 0.05 N $K_2Cr_2O_7$ solution. Calculate COD of the effluent.

   Solution: Vol. of effluent = 30 cm^3

   Vol.of 0.05 N $K_2Cr_2O_7$ consumed = 8 cm^3

   COD =?

   $N_1V_1 = N_2V_2$ **[$V_1 = 30\ cm^3$, $V_2 = 8$, $N_2 = 0.05$]**

   N1 = 0.05 × 8 / 30

   COD = Normality of waste water × Equ.wt of Oxygen × 1000

   $$COD = \frac{0.05\times8}{30} \times 8 \times 1000 = 106.5\ mg/L$$

Ans: COD of the effluent = **106.5 mg/L**

2. 25 cm^3 of waste water sample mixed with 25 cm^3 of potassium dichromate solution. Acidified and refluxed. 30 cm^3 of FAS solution was required by unreacted acidified $K_2Cr_2O_7$ solution. Blank titration was performed to estimate the amount of $K_2Cr_2O_7$ at beginning. 20 Cm^3 of acidified potassium dichromate requires 10.8 cm^3 of the same 0.2 N FAS solution. Calculate COD.

Solution:

Volume of waste water: 25 cm^3

Volume of FAS used for Blank titration V1= 10.8 cm^3

Volume of FAS used for sample titration V2 = 30 cm^3

The volume of FAS equivalent to $K_2Cr_2O_7$ used for oxidation of impurities = V1-V2

= 10.8-30 = 19.2 cm^3

Normality of FAS = 0.2 N

Calculation of COD:

N1V1 = N2V2

N1 = Normality of O2 in waste water; V1 = Volume of Waste water

N2 = Normality of FAS; V2 = Volume of FAS used

$N1 \times 25 = 0.2 \times 19.2$

So

$N1 = 0.2 \times 19.2 / 25$

= 0.1536

$$COD = \frac{0.2 \times 19.2 \times 8 \times 1000}{25} = 1288 \text{ mg/L}$$

COD = 1288 mg/L