WATER TECHNOLOGY

Introduction:

- Water is the most basic and fundamental component of life.
- It is the most wonderful substance gifted by nature to all the living beings on the earth.
- 72% of the earth"s surface is covered by water. It is distributed as follows:

Oceans - 97.23% Ice - 2.14% Fresh Water - 0.01% Other - 0.01%

- Among the three essentials of life i.e., air, water and food, water occupies the second position.
- Health and wealth of a nation largely depends on the availability and utilization of quality of water.

Sources of water:

- Surface water which involves rain water, river water, lake water and sea water.
- Ground water which involves springs and well.

Impurities in water:

The water found in nature is never pure and it is associated with impurities in varying amounts. The major impurities found in water are of the following types.

- a) Dissolved gases: The water contains mainly CO₂ and oxygen as dissolved gases.
- b) Dissolved salts: The water contains dissolved salts of Ca, Mg, Na.
- c) Suspended impurities: They are the dispersion of solid particles which can be removed by filtration or setting. There are two types i) Organic impurities which includes wood, leaf ii) Inorganic impurities which includes clay, silica.
- d) Microscopic matter: They are pathogenic bacteria and microorganisms present in water. They are the main causes for the water borne diseases.

By the action of soap with water, water can be classified into two types: a) Soft water b) Hard water The Water which gives leather very easily and readily by the action of soap is called soft water. The Water which doesn't produce leather very easily and readily by the action of soap is called hard water. This is because hard water usually contains dissolved salts of Ca and Mg. These Ca and Mg ions react with soap to form white scum or precipitate.

$$2C_{17}H_{35}COONa + Ca^{2+}$$
 \longrightarrow $(C_{17}H_{35}COO)_2 Ca + 2Na^+$
 $2C_{17}H_{35}COONa + Mg^{2+}$ \longrightarrow $(C_{17}H_{35}COO)_2 Mg + 2Na^+$

The salts which are responsible for hardness of water are: $MgCl_2$, $CaCl_2$, $MgSO_4$, $CaSO_4$, $Mg(HCO_3)_2$, $Ca(HCO_3)_2$, $Mg(NO_3)_2$ $Ca(NO_3)_2$.

Depending upon the kind of negative ion present along with Ca and Mg ions, hard water can be classified into two types. i) Temporary hard water ii) Permanent Hard water

The water which contains dissolved salts of $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$ is called temporary hardness of water, which can be softened by boiling.

The water which contains dissolved salts of $MgCl_2$, $CaCl_2$, $MgSO_4$, $CaSO_4$, $Mg(NO_3)_2$, $Ca(NO_3)_2$. i.e., other than bicarbonates are called permanent hard water. It cannot be softened by boiling.

"Total hardness of water is the sum of Temporary harness of water and Permanent hardness of water."

Boiler feed water:

Boilers are operated under different pressures, the major troubles caused by the use of unsuitable water are.

1. Scale and sludge formation 2. Boiler Corrosion

1. Scale and sludge formation:

Salts formed in the boilers due to evaporation can be removed in the form of precipitation. If the precipitated matter is soft, loose and slimy, it is called **sludge**. If the precipitated matter is hard and adherent on the inner walls of the boiler, it is called **scale**.

Sludge can easily be scrapped off with a wire brush. Sludges are formed by substances which have grater solubility in hot water than in cold water. Example, MgCO₃, MgCl₂, CaCl₂, MgSO₄ etc.

Disadvantages of sludge formation:

- i) Sludge"s are poor conductor of heat, so they tend to waste a portion of heat generated.
- ii) If sludges are formed along with scales, then sludge gets entrapped in the scales and both get deposited as scales.
- iii) Excessive sludge formation settles in the regions of poor water circulation such as pipe connection, plug opening etc., thereby causing choking of the pipes.

Disadvantages of scale formation:

- i) **Wastage of fuel:** Scales acts as insulator and hence reduced rate of heat transfer and evaporative capacity of the boiler. Thus scale formation will result in wastage of the fuel and reduction in boiler efficiency. The wastage of fuel depends upon the thickness and the nature of scale.
- ii) **Lowering of boiler safety:** Overheating is done in order to maintain a constant supply of steam, makes the boiler material softer and weaker and this causes distortion of boiler tube and makes the boiler unsafe to bear the pressure of steam. Rapid reaction between water and iron occurs at high temperature, causing additional thinning of the tube wall.
- $3 \text{ Fe} + 4 \text{ H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4(s) + 4 \text{ H}_2(g)$
- iii) **Decrease in efficiency:** Excessive scaling may cause clogging of tubes. Considerable quantities of sludges may also be entrapped in the scale which may reduce the water circulation and impair the efficiency of the boiler.
- iv) **Danger of explosion:** When thick scales crack, due to uneven expansion, the water suddenly in contact with over-heated iron plates, resulting in the formation of a large amount of steam. So suddenly high pressure is developed, which may cause even explosion of the boiler.

2. Boiler Corrosion:

Boiler corrosion is destruction / deterioration of boiler tubes, plates, pipelines by chemical or electrochemical attack by its environment.

Reason for boiler corrosion:

i) **Dissolved oxygen:** Dissolved oxygen in water in presence of high temperature, attacks boiler material.

$$2 \text{ Fe} + 2 \text{ H}_2\text{O} + \text{O}_2 \rightarrow 2 \text{ Fe (OH)}2 \downarrow$$

2 Fe (OH)₂
$$\downarrow$$
 + O₂ \rightarrow 2 [Fe₂O₃. 2 H₂O] \downarrow

Rust

ii) **Dissolved CO₂:** $H_2O + CO_2 \rightarrow H_2CO_3$ which has slow corrosive effects on the boiler material. CO_2 is also released inside the boiler of water contains bicarbonates

$$Mg (HCO_3)_2 \rightarrow MgCO_3 + H_2O + CO_2$$

H₂CO₃ is responsible for pitting corrosion.

iii) Acids from dissolved salts: water containing dissolved magnesium salts liberate acids on hydrolysis.

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

The liberated acid reacts with boiler producing HCl again and again.

$$Fe + 2 HCl \rightarrow FeCl_2 + H_2$$

 $FeCl2 + 2 H_2O \rightarrow Fe(OH)_2 \downarrow + HCl$, Presence of even a small amount of $MgCl_2$ will cause corrosion of iron to a large extent.

Determination of Dissolved Oxygen:

Dissolved oxygen content in water is determined by Winklers method.

Principle:

In this method, the given water sample is treated with $MnSO_4$ and Alk. KI solution. In alkaline condition, the dissolved oxygen in water sample oxidizes Mn^{2+} salts into brown precipitate of hydrated manganese dioxide (Mn^{4+}).

$$MnSO_4 + 2KOH \rightarrow Mn(OH)_2 + K_2SO_4$$

 $Mn(OH)_2 + O_2 \rightarrow MnO.(OH)_2 \text{ or } MnO_2.H_2O$

On acidification hydrated manganese dioxide (Mn⁴⁺) oxidize iodide to iodine and the liberated iodine is then titrated with Std. Sodium thiosulfate solution using starch as indicator.

$$MnO_2.H_2O + 4H_2SO_4 \rightarrow MnSO_4 + 3H_2O + [O]$$

 $KI + H_2SO_4 + [O] \rightarrow I_2 + K_2SO_4 + H_2O$
 $I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$

Procedure:

Add 2ml of MnSO4 and 3 ml of alk.KI solution to the bottle containing 250 ml of water sample. The bottle is stoppered and shaken well for 10-15 min and allow to stand for 2 min for the precipitation to settle down and then add 1 ml of con. H_2SO_4 . Then the solution is stoppered and shaken well. Then, 100 ml of the solution pipetted into conical flask and titrated with Std. $Na_2S_2O_3$ solution using starch as indicator till the discharges of violet colour. Note down the titre value.

Dissolved oxygen (mg/dm³) =
$$\frac{(V \times N)_{Na, \S_{3}O} \times 8 \times 1000}{V_{\varsigma}}$$

Determination of Chemical oxygen demand (COD):

BOD values accounts only for biologically oxidisable impurities but doesnt account for biologically non-oxidisable impurities. Therefore COD is introduces to measure the total oxidisable impurities present in sewage.

"It is defined as the amount of oxygen used for the oxidation of total organic load in the water sample with a strong chemical oxidant like $K_2Cr_2O_7$ in acid medium. It is expressed in terms of mg dm⁻³ or ppm.

Characteristics of COD parameters:

- It is a satisfactory and quantitative method for measuring total organic load.
- Results are reliable compared to BOD
- Rapidly measurable parameter

Determination of COD:

Principle:

A suitable waste water or aliquot of the sample is refluxed with a known excess of K₂Cr₂O₇ solution in H₂SO₄ medium and in the presence of Ag₂SO₄ and HgSO₄. K₂Cr₂O₇ oxidizes all oxidisable impurities; Ag₂SO₄ catalyses. HgSO₄ avoids the interference of Cl⁻ ions by forming solution complex with them.

The amount of unconsumed $K_2Cr_2O_7$ is determined by titration with Std. FAS solution. The amount of $K_2Cr_2O_7$ solution consumed corresponds to the COD of the sewage sample.

Procedure:

25 ml of waste water sample is pipette out into a round bottomed flask. Add 10 ml of K₂Cr₂O₇ along with 1 test tube of dil. H₂SO₄ and 1g of HgSO₄ and 1g of Ag₂SO₄ to the same flask.

The flask is fitted with a reflux water condenser and the mixture is refluxed for 2 hrs. The contents are cooled and transferred to a conical flask. Add drops of Ferroin indicator.

The solution mixture is titrated against Std. FAS taken in burette till the colour changes from blue green to reddish brown.

Blank titration (A):

Same volume of K₂Cr₂O₇ is taken out, mixed with H₂SO₄, Ferroin and titrated against same Std.FAS to set blank titre

$$COD = \frac{(A - B) \times N \times 8000}{V_S} \text{ mg/L}$$

Sewage treatment:

Sewage contains liquid waste from industry, baths and kitchens etc. It also contains both organic and inorganic impurities. So, sewage treatment is involved in order to remove organic impurities, suspended and floating materials etc., the function of sewage treatment is to Kill pathogens and to eliminate harmful chemicals.

Sewage treatment carried out in 3 stages:

- Primary treatment
- Secondary treatment
- Tertiary treatment

Primary treatment:

It is used to remove suspended and floating solids from waste water by physical and chemical methods. It involves following steps:

- a) Screening: In this step, bar screens and mesh screens are used to remove floating and suspended particles by passing sewage water through it.
- b) Slit and grit removal: By this step, sand, powdered glass etc., are removed by slowly passing sewage through grit chambers.
- c) Removal of oil grease: They are converted into soapy mixture (foam) by blowing air through sewage water in a large tank. The floating substance is skimmed off.

d) Sedimentation process: This process removes finer suspended particles by adding coagulants like alum into the sewage water. Coagulants help in easy settlements of the finely suspended particles.

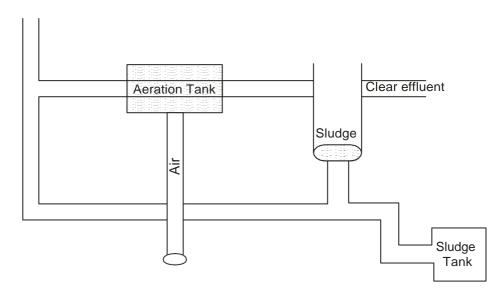
Secondary treatment (Biological treatment):

In this treatment, after the sedimentation of sewage water is subjected to aerobic oxidation. During which organic substances are converted into CO₂, nitrogen into Ammonia.

Secondary treatment is generally described by "Activated Sludge method".

Wash sewage water after sedimentation is mixed with required quantity of activated sludge (containing microorganisms and aerobic bacteria) in a aeration tank as shown in Fig. The mixture is aerated by blowing air through it for several hours. Due to the aerobic condition, the organic matter in the sewage is fully oxidized.

The purified water + sludge sent to the tank where it settles down. A part of the sludge is used for purification of fresh batch of sewage, while the rest is pumped to sludge disposal tank. Purified water is pumped out and collected separately.



Tertiary treatment:

The aim of tertiary treatment is further purification of waste water as well as recycling. (It removes dissolved salts, colloidal particles). It consists of the following methods,

- a) Removal of phosphate, by adding Ca(OH)₂.
- b) Suspended fine particles are removed by sedimentation and coagulation.
- c) Filtration: Water is passed through conventional sand filter beds.
- d) Degasification: Stripping of NH₃ and other gases done by degasification.
- e) Disinfection: Pathogenic bacteria are removed by disinfection by using disinfectants like chlorine or ozone or UV light through the water.

Some countries like Kuwait, Saudi which have no fresh water and have to depend inevitably on ocean. But high content of dissolved salt in sea water prohibits its use for consumption and for other uses. So, this sea water can"t be purified by conventional methods. So, we need process called "Desalination or Desalting". It is very expensive process.

Note: a) Fresh water with dissolved salts less than 1000 mg/L.

- b) Brackish water with dissolved salt between 1000-35000 mg/L.
- c) Sea water with dissolved salts greater than 35000 mg/L.

The process of removal of dissolved salts from sea water or brackish water to an extent, which becomes usable is described as "Desalination or Desalting".

The important methods of desalination are:

- i) Reverse osmosis
- ii) Electrodialysis

Reverse osmosis:

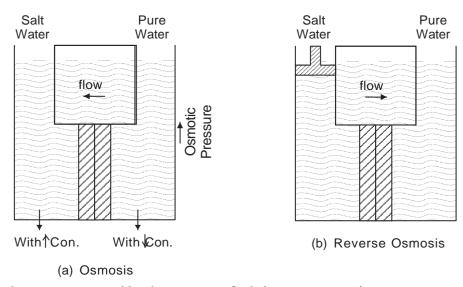
Principle:

In this process, the water is separated from dissolved salts by means of a membrane which permits the passage of water through it but not the salts.

If such a membrane is placed between brine and pure water as shown in Fig.a, water has a natural tendency to flow through the membrane into the brine side due to osmotic pressure.

This natural process may be reversed by applying a pressure on the brine side higher than that of osmotic pressure as shown in Fig. b. Then fresh water tends to flow from brine side into fresh water.

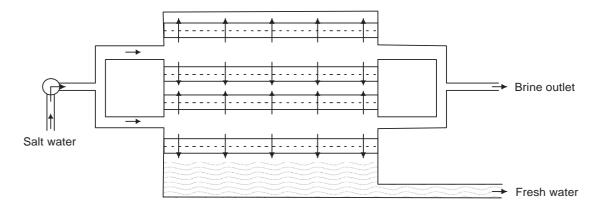
"The process which reverses the natural spontaneous osmosis is called Reverse osmosis".



During the osmosis, the pressure exerted by the mass transfer is known as osmotic pressure.

Process: A typical reverse osmosis unit is shown in figure below.

- 1. A series of tubes made up of porous material is lined inside with thin film of cellulose acetate semi-permeable membrane. These tubes are arranged in parallel array in fresh water.
- 2. Salt water or brackish water is pumped continuously at high pressure through these tubes.
- 3. Water flows through semi-permeable membrane from brackish water into fresh water.
- 4. The flow of water is proportional to the applied pressure.
- 5. Concentrated brine and fresh water are withdrawn through their respective outlets.



Advantages:

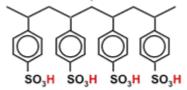
a) Process is simple and continuous b) It involves no phase changes c) The process needs extremely low energy

Softening method:

The process of removing hardness producing salts from water is known as Softening of water.

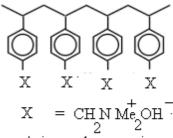
Ion exchange or de-ionization or de-mineralization: Ion exchange resins are insoluble, cross-linked, long chain organic polymers with a microporous structure and functional groups are capable of exchanging their ions with cations (Acidic functional groups -COOH, SO_3H) and anions(basic functional groups $-NH_2$, = NH).

There are two types of Ion exchange resins. i) Cation exchange resins (RH+) are mainly styrene divenyl benzene co-polymers, which on sulphonation or carboxylation, become capable to exchange their hydrogen ions with the cations in the water.



Cation exchange resm

i) Anion- exchange resins (R'OH-) are mainly styrene divenyl benzene co-polymers, which contains amino or quaternary ammonium or quaternary phosphonium or tertiary sulphonim groups as an integral part of the resin matrix. On treatment with dil. NaOH solution become capable to exchange their hydroxyl ions with the anions in the water.



Anion exchange resin

Process: The hard water is passed first through cation exchange column, which removes all the cations like Ca^{2+} , Mg^{2+} etc. from it and equivalent amount of H^+ ions are released to water.

$$2 \text{ RH}^+ + \text{Ca}^{2+} \rightarrow \text{R2Ca}^{2+} + 2\text{H}^+$$

$$RH^+ + Na^+ \rightarrow RNa^+ + H^+$$

Then hard water is passed through anion exchange column, which removes all the anions like SO $_4^{2-}$, Cl⁻ etc. from it and equivalent amount of OH⁻ ions are released to water.

$$R'OH^- + Cl^- \rightarrow R'Cl^- + OH^-$$

$$2R'OH^{-} + SO_{4}^{2-} \rightarrow R'_{2}SO_{4}^{2-} + 2OH^{-}$$

Now H⁺ and OH⁻ ions are combined to produce water molecule.

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

Water coming out from the exchanger is free from cations as well as anions and is known as deionized or demineralized water.

