Water Technology

1. Write a note on Hardness of water.

Hard water:

- Hard water does not form a white mass of bubbles (lather) easily with soap.
- Hard water forms a white curdy precipitate with soap. For example: Sea water.
- Hard water contains soluble salts like bicarbonates (HCO₃), Chlorides (Cl⁻) and Sulphates (SO₄²⁻) of calcium, magnesium and other heavy metals.

• Action of soap:

 \circ Soap is the sodium or potasium salt of fatty acid like stearic acid (C₁₇H₃₅COOH)

 $C_{17}H_{35}COONa + H_2O \rightarrow C_{17}H_{35}COOH + NaOH$ Sodium stearate Lather

o If soap is added to hard water

Causes of hardness of water:

 Hardness of water is due to the presence of bicarbonates, sulphates and chlorides of calcium, magnesium and other heavy metals.

• Types of hardness:

- It is of two types
 - 1. Temporary hardness
 - 2. Permanent hardness
- o **Temporary hardness**: (or carbonate hardness or alkaline hardness)
 - This is due to the presence of bicarbonates of calcium, magnesium and other heavy metals., i.e., Ca(HCO₃)₂ and Mg(HCO₃)₂
 - This can be removed by boiling the hard water
 - The soluble calcium bicarbonate is changed into insoluble calcium carbonate and magnesium bicarbonate is changed into insoluble magnesium hydroxide on boiling
- o **Permanent hardness:** (or non-carbonate hardness or non-alkaline hardness)
 - This is due to the presence of chlorides and sulphates of calcium, magnesium and other heavy metals. i.e., CaSO₄, MgSO₄, CaCl₂ and MgCl₂.
 - This can be removed by chemical treatment (or reactions) only.

• Disadvantages of hard water:

- When hard water is used in homes and industries, the following problems may come
 - A large amount of soap is required for washing and bathing
 - More fuel and time are required for cooking
 - Hard water forms stones in kidney or bladder
 - Affects the quality of the paper
 - Affects the crystallization of sugar
 - Affect the color of cloths during its make
 - Scale formation in boilers

• Degree of hardness:

- o It is the amount of hardness causing substance present in water
- o It is expressed in terms of CaCO₃ equivalent
- $\therefore \text{ The CaCO}_3 \text{ equivalent } = \frac{[\text{weight of hardness causing substance}] \times [\text{Molecular weight of CaCO}_3]}{[\text{molecular weight of hardness causing substance}]}$

Where, molecular weight of CaCO₃ is 100

• Units of Hardness:

- 1. Parts per million (ppm):
 - 1 ppm = 1 part of CaCO₃ equivalent hardness present in 10⁶ parts of water
- 2. Milligrams per liter (mg/L):
 - 1 mg/L = 1 mg of $CaCO_3$ equivalent hardness present in 1L of water

- 3. Clarke's degree of hardness (⁰ Cl):
 - 1° Cl = 1 part of CaCO₃ equivalent hardness present in 70,000 parts of water
- 4. French degree of hardness (⁰ Fr):
- 1^0 Fr = 1 part of CaCO₃ equivalent hardness present in 10^5 parts of water *** Relation among different units of hardness is

1 ppm = 1 mg/L =
$$0.1^0$$
 Fr = 0.07^0 Cl

2. Determine the Hardness of water by EDTA method.

Estimation of hardness of water by EDTA method:

Theory:

- The best method to determine water hardness is to conduct complexometric titration using a standard solution of disodium salt of Ethylene Diamine Tetra Aceticic acid (Na₂EDTA).
- Na₂EDTA, A weak acid forms a soluble complex with Ca²⁺ and Mg²⁺ ions in 1:1 molar ratio. Therefore,

Amount of EDTA consumed = Amount of Ca & Mg salts present in the hard water.

- The optimum pH for this experiment is 10.0 and is adjusted by using ammonia buffer solution.
- Eriochrome Black T is used as an indicator.
- When a small amount of the indicator solution is added to a hard water sample, the indicator reacts with Ca²⁺ and Mg²⁺ ions and produce wine red color.

Metal ions
$$+$$
 EBT \rightarrow [M - EBT] complex (Blue) Unstable & wine red

• As EDTA is added, all free Ca²⁺ and Mg²⁺ ions present in hard water sample are first complexed, as it forms stable complex.

• If an extra drop of EDTA is added, after all the free Ca²⁺ and Mg²⁺ ions have been complexed, EDTA takes up Ca²⁺ and Mg²⁺ ions from the weak M-EBT complex to form stable M-EDTA complex, simultaneously liberating indicator in the free form.

$$[M-EBT] + EDTA \rightarrow [M-EDTA] + EBT$$

Wine red Blue

• The color change from wine red to blue indicates the end point of the titration.

Estimation of hardness of water by EDTA method:

- Reagents:
 - 1. Standard disodium salt of ethylene diamine tetra acetic acid (Na₂EDTA) solution (0.01 M)
 - 2. Ammonia buffer solution (pH 10)
 - 3. Sodium hydroxide solution (1M)
 - 4. Erichrome black-T (EBT) indicator (1%)
 - 5. Murexide indicator (0.5%)

• Procedure:

- Determination of Total hardness:
 - 1. 20 ml hard water sample was taken in a 100 ml conical flask
 - 2. To this 2 ml of ammonia buffer and 2 drops of EBT indicator were added.
 - 3. It was titrated with standard EDTA solution slowly with continuous stirring till color changes from wine red to blue.

Total hardness =
$$\frac{V_1 M x 100 x 1000}{V}$$
 ppm
Where, V_1 = Volume of EDTA consumed in ml

Where, V_1 = Volume of EDTA consumed in ml

M = Concentration of EDTA = 0.01M
 V = Volume of the hard water sample in ml

Determination of calcium hardness:

- 1. 20 ml of hard water sample was taken in a 100 ml conical flask
- 2. To this, 2 ml of sodium hydroxide solution and a pinch of murexide indicator were added
- 3. It was titrated with standard EDTA solution slowly with continuous stirring till the color changes from red to blue-violet.

Calcium hardness =
$$\frac{V_2 M \times 40 \times 1000}{V}$$
 ppm

Where, V_2 = Volume of EDTA consumed in ml

M = concentration of EDTA = 0.01M

V = Volume of the hard water sample in ml

- O Determination of magnesium hardness:
 - Magnesium hardness = Total hardness Calcium hardness

3. What is potable water? And how does sterilization and disinfection carried out in drinking water?

Potable water:

- Clean and safe drinking water is called potable water
- The important qualities of potable water are
 - 1. It should be clear and smell-less.
 - 2. It should have good taste
 - 3. It should be cool
 - 4. Turbidity of water should be < 10 ppm
 - 5. It should be soft
 - 6. pH of water should be between 7 & 8
- 7. It should not have poisonous gases like H₂S and poisonous metals like mercury (Hg), arsenic (As), lead (Pb) etc.
- 8. The total dissolved solids (TDS) should be < 500 ppm
- 9. It should not have illness spreading micro organisms like bacteria, virus, fungus etc.

a. Removal of suspended impurities

Treatment	Done by	Purpose
Screening	Screening shutters with variable sized holes	Removes floating material like wood plastic, papers
Aeration	Mechanical aerator	Removes Oxygen, Carbon-dioxide , toxic gases, Fe, Mn salts
Sedimentation	Allowing the water to stand for 2 – 6 hrs in a tank	Removes 75% of suspended impurities
Coagulation	Adding alum, Al2(SO4)3 Al (OH)3	Removes 100% suspended and colloidal impurities, clay, silica
Filtration	Filter bed	Removes bacteria, colour, odour, small dust particles
Sterilization / Disinfection	Boiling, ozone, chlorine, UV radiation	Destroys bacteria

Sterilization and disinfection:

• These are used to kill illness spreading microorganisms present in drinking water

• Sterilization:

- o In this, water is boiled at 110-115°C for 15 minutes to kill all microorganisms
- o The water gotten from this is very safe.

Disadvantages of sterilization:

- 1. This can kill the present microorganisms in water at the time of boiling only
- 2. It is very costly
- 3. It can be used in some cases only when illness is spreading very fast
- 4. It cannot be used in municipal drinking water cleaning.

• Disinfection:

- o In this some chemicals are added to water for killing all microorganisms
- These chemicals are called disinfectants
- o The commonly used disinfectants are
 - 1. Bleaching powder
 - 2. Chlorine

- 3. Chloramine (ClNH₂)
- 4. Ozone

Chlorination:

- This can be done by adding calculated amount of bleaching powder (CaOCl₂) or by passing chlorine (Cl₂) gas directly into water.
- Bleaching powder releases Cl₂ gas into water. The Cl₂ reacts with water to form hypochlorous acid

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

 $Cl_2 + H_2O \rightarrow HCl + HOCl$

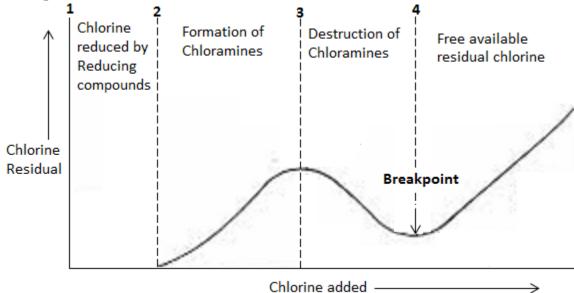
Microorganisms (Germs) + HOCl → Germs are killed

- About 1 kg of bleaching powder per 1000 KL of water is used.
- Disadvantages of bleaching powder:
 - 1. It adds calcium into water and it is not stable
 - 2. Excess of it gives bad taste to water
- Advantages of Chlorine:
 - 1. It is good disinfectant and not costly
 - 2. It is stable and it can be used at both low and high temperatures
 - 3. It does not add salt into water

Disadvantages of Chlorine:

- 1. Excess of it gives bad taste and smell
- 2. The quantity of free Cl₂ in drinking water should be less than 0.2 ppm

o Breakpoint Chlorination:



Between Points 1&2:

All the chlorine reacts with reducing compounds like H₂S & organic matter present in water until they are destroyed, there is no chlorine residual.

Between Points 2&3:

Chorine reacts with amino acids, urea and ammonia which come from proteins or from urine, which is naturally found in pool water.

The products of these reactions are called chloramines and there are 3 types of chloramines.

- 1. Monochloramines $NH_3 + HOCl \rightarrow NH_2Cl + H_2O$
- 2. Dichloramines $NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O$
- 3. Trichloramines $NH_2Cl + HOCl \rightarrow NCl_3 + H_2O$

Between Points 3&4:

Most of the chloramines are themselves got destroyed until there is nothing left to react and chlorine residual decreases.

After point 4:

The water reaches **Breakpoint**; Shown at point 4 in the above diagram, and at this point Chlorine begins to appear as "Free available Chlorine".

Definition of Breakpoint:

The Breakpoint is the point at which the chlorine demand has been totally satisfied. ie., the chlorine has reacted with all reducing agents, organic compounds and ammonia in the water.

Disinfection by chloramines:

• When chlorine and ammonia are mixed in 2:1 ratio by volume, chloramine is formed

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

Chloramine is good disinfectant than chlorine

$$ClNH_2 + H_2O \rightarrow HOCl + NH_3$$

o Ozonization:

- This can be done by passing ozone (O_3) gas into water and O_3 is a good disinfectant
- O₃ is formed by "silent electric discharge" in O₂ gas

$$3 O_2 \xrightarrow{\text{Silentelectric discharge}} 2 O_3$$

• O₃ is highly unstable and release nascent oxygen [O]

$$O_3 \rightarrow O_2 + [O]$$

• This [O] kills all the microorganisms by oxidation

Advantages of Ozonization:

- 1. Disinfection by ozone is costly than chlorine, but it removes color, smell and taste without adding any salt to water.
- 2. O_3 can be used in excess. Since it is unstable.

Disadvantages:

1. This method is very costly

4. What is softening of water? Describe the lime soda process.

Soft water:

- Soft water only forms a white mass of bubbles (lather) easily with soap
- Soft water should be used in industries
- Softening of water it the removal of hardness causing salts from water
- The following methods used for softening of water in industry
 - 1. Zeolite process
 - 2. Ion-exchange process

Lime-Soda process:

- In this, the soluble calcium and magnesium in water are changed into insoluble salts like Calcium carbonate (CaCO₃) and Magnesium hydroxide [Mg(OH)₂] by adding calculated amounts of lime [Ca(OH)₂] and Soda (Na₂CO₃).
- CaCO₃ and Mg(OH)₂ so precipitated are filtered off.
- Lime and soda needed for softening are calculated as follows
 - : Lime requirement for softening V liters of hard water

$$= \frac{74}{100} \begin{bmatrix} \text{Temp. Ca}^{2+} + (2 \text{ x Temp. Mg}^{2+}) + \text{perm. Mg}^{2+} + \text{Fe}^{2+} + \text{Al}^{3+} + \text{CO}_2 \\ + \text{H}^+ (\text{HCl or H}_2\text{SO}_4) + \text{HCO}_3^- - \text{NaAlO}_2 & \text{All in terms of CaCO}_3 \text{ equivalent} \end{bmatrix} x \text{ V}$$

... Soda requirement for softening V liters of hard water

$$= \frac{106}{100} \begin{bmatrix} \text{Perm.} (\text{Ca}^{2+} + \text{Mg}^{2+}) + \text{Fe}^{2+} + \text{Al}^{3+} + \text{H}^{+} (\text{HCl or H}_{2}\text{SO}_{4}) - \text{HCO}_{3}^{-} \\ \text{All in terms of CaCO}_{3} \text{ equivalent} \end{bmatrix} \times V$$

Where, Molecular weight of $Ca(OH)_2 = 74$

Molecular weight of $Na_2CO_3 = 106$

Molecular weight of $CaCO_3 = 100$

Fe²⁺, Al³⁺ comes from coagulants FeSO₄, Al₂(SO₄)₃ and NaAlO₂ (sodium alumiate)

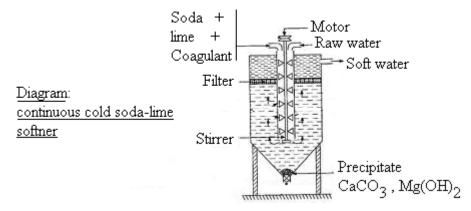
- There are two types of lime-soda process
 - 1. Cold lime-soda process
 - 2. Hot lime-soda process

• Cold lime-soda process:

- o In this, calculated quantity of lime and soda are mixed with water at room temperature
- A small amount of coagulants are added to bring down non filterable precipitate of CaCO₃ and Mg(OH)₂ along with the sticky precipitate of Al(OH)₃.

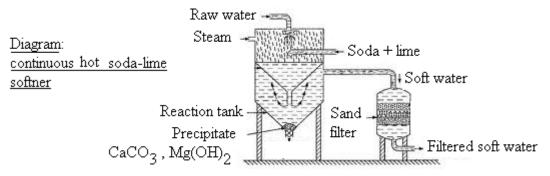
$$NaAlO_2 + 2H_2O \rightarrow NaOH + Al(OH)_3 \downarrow$$

- o In this process, the hard water can be softened till 50-60 ppm
- Raw water, soda, lime and coagulant are put in from the top into inner circular vessel as shown in the diagram.
- o The water mixture is mixed very fast with stirrer.
- o The solid precipitate comes down at bottom of the vessel as water is softened.
- The soft water moves up to the top of the outer vessel through filter then outside as shown in the diagram
- The precipitate is taken out some times only and this is a continuous process.



• Hot lime-soda process:

- o In this method, raw water, soda and lime are put in from the top into reaction tank.
- The water mixture is heated to the temperature of 80-150°C with steam
- o The solid precipitate comes down at the bottom of the tank as the water is softened.
- The soft water moves up to the top of the tank and it is passed through a sand filter to remove precipitate particles completely.
- o In this process the hard water can be softened till 15-30 ppm



Advantages:

- 1. It is not costly and this process increases the pH of water.
- 2. Amount of minerals, Iron and manganese are decreased.
- 3. Illness spreading microorganisms also decreased.

O Disadvantages:

- 1. Skilled people must be needed
- 2. Pollution problem with solid precipitate
- 3. This can remove hardness only up to 15 ppm, so this water should not be used in boilers

5. How does hard water softened with Zeolite or Permutit process

Zeolite or Permutit process:

- In this process, hardness causing salts are removed by using natural or artificial Zeolite.
- Zeolite is also called as permutit and chemical structure of zeolite is Na₂Al₂Si₂O₈.xH₂O
- Zeolite can exchange its sodium ions with hardness causing ions.

• Process:

- o Zeolite is placed in a cylinder as shown in the diagram
- o Hard water is put in from the top into the cylinder and it is allowed to pass through the Zeolite
- Sodium present in the Zeolite is replaced by Ca²⁺ and Mg²⁺ ions present in hard water as CaZe and MgZe.
- o The different reactions taking place are

$$\begin{array}{lll} Na_2Ze & + & Ca(HCO_3)_2 & \longrightarrow & CaZe + 2 \ NaHCO_3 \\ Na_2Ze & + & Mg(HCO_3)_2 & \longrightarrow & MgZe + 2 \ NaHCO_3 \\ Na_2Ze & + & CaCl_2 \ (or \ CaSO_4) & \longrightarrow & CaZe + 2 \ NaCl \ (or \ Na_2SO_4) \\ Na_2Ze & + & MgCl_2 \ (or \ MgSO_4) & \longrightarrow & MgZe + 2 \ NaCl \ (or \ Na_2SO_4) \end{array}$$

o Regeneration:

- After some time, Na₂Ze is completely changed into CaZe or MgZe.
- This can be gotten back by passing 10% NaCl solution.
 CaZe (or MgZe) + 2 NaCl → Na₂Ze + CaCl₂ (or MgCl₂)
 Wash

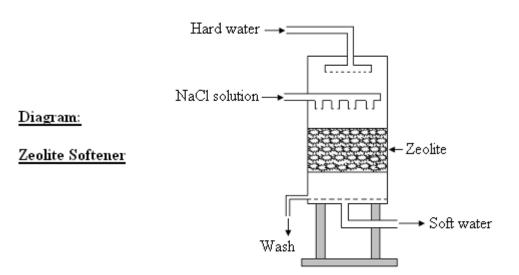
The washing is thrown away and the regenerated zeolite is used again.

Advantages:

- 1. It removes the hardness till 10 ppm and It needs less time for softening
- 2. No pollution problem as there is no precipitate formation and It needs less skilled people

• Disadvantages:

- 1. Turbid water cannot be used and the water having more Mn²⁺ and Fe²⁺ cannot be used.
- 2. The water having mineral acids must be neutralized.



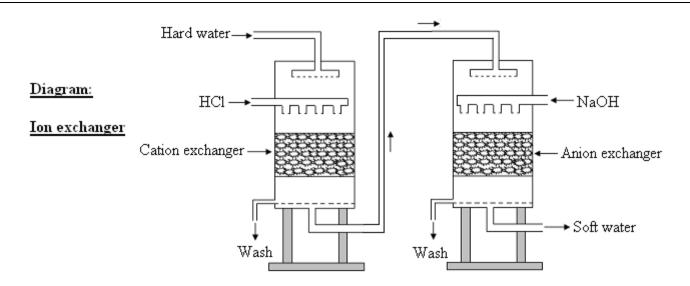
6. Describe ion-exchange process for softening water.

Ion-exchange process:

- It is also called as **demineralization** or **deionization**
- Ion exchange polymers having acidic functional groups like –COOH and –SO₃H can replace their H⁺ ions with other cations in hard water.
- Ion exchange polymers having basic functional groups like $-N^{\oplus}$ (CH_3)₂ OH^{\ominus} can replace their OHions with other anions in hard water.
- There are two types of ion exchange polymers
 - 1. Cation exchange polymers (RH⁺)
 - 2. Anion exchange polymers (R¹OH⁻)
 - o The chemical structure of above two ion exchange polymers are

Anion exchange polymer

o Process:



 \circ The hard water is first passed through Cation exchanger to remove the hardness causing Ca²⁺ and Mg²⁺ ions.

$$2 \text{ RH}^+ + \text{Ca}^{2+} (\text{or Mg}^{2+}) \rightarrow \text{R}_2 \text{Ca}^{2+} (\text{or R}_2 \text{Mg}^{2+}) + 2 \text{ H}^+$$

- The water coming out has H^+ , Cl^- , SO_4^{2-} and HCO_3^- ions.
- \circ The water is then passed through anion exchanger to remove hardness causing anions Cl⁻, SO $_4^{2-}$ and HCO $_3^{-}$ ions.

$$R^{1}OH^{-} + Cl^{-}(or HCO_{3}^{-}) \rightarrow R^{1}Cl(or R^{1}HCO_{3}) + OH^{-}$$

2 $R^{1}OH^{-} + SO_{4}^{2-} \rightarrow R_{2}^{1}SO_{4} + 2 OH^{-}$

 \circ $\;$ The $H^{\scriptscriptstyle +}$ ions formed in the cation exchanger reacts with $OH^{\scriptscriptstyle -}$ ions formed in anion exchanger.

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

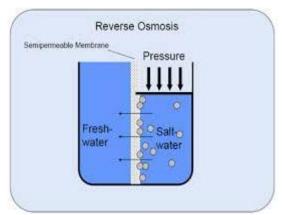
- o Regeneration:
 - The saturated cation exchanger is gotten back by passing dilute HCl solution. R_2Ca^{2+} (or R_2Mg^{2+}) + 2 HCl \rightarrow 2 RH⁺ + CaCl₂ (or MgCl₂)
 - CaCl₂ and MgCl₂ are removed as wash
 - The saturated anion exchanger is gotten back by passing dilute NaOH solution $R^{1}Cl$ (or $R^{1}HCO_{3}$) + NaOH \rightarrow $R^{1}OH^{-}$ + NaCl (or NaHCO₃) $R_{2}^{1}SO_{4}$ + 2 NaOH \rightarrow 2 $R^{1}OH^{-}$ + Na₂SO₄
 - NaCl, Na₂SO₄ and NaHCO₃ are removed as wash
 - The washings are thrown away and the regenerated ion exchanger used again.
- Advantages:
 - 1. It removes the hardness till 2 ppm. Hence this water can be used in boilers.
- o **Disadvantages**:
 - 1. The equipment and chemicals needed for making ion exchange polymers are costly.
 - 2. Turbid water should not be used.

7. What is reverse osmosis? And explain RO desalination process with a neat sketch.

Reverse osmosis:

- When two solutions of unequal concentrations are separated by a semi-permeable membrane, flow of solvent takes place from dilute side to concentrated side. This is called **osmosis**.
- The outside pressure applied on solution to stop the osmosis, is called **osmotic pressure**.
- A pressure more than osmotic pressure is applied on the concentrated side, solvent flow takes place from concentrated side to diluted side across the membrane. This is called **Reverse osmosis** (RO).
- In RO, water is separated from salt water. This is also called as super-filtration or hyper-filtration.

• RO is used to remove salt from sea water to get drinking water, so that it is also called RO desalination process.

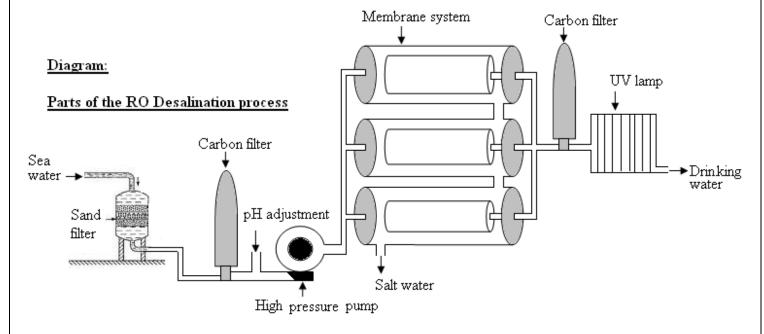


• RO desalination process:

- o In this, pressure of 15-40 Kg/Cm² is applied to sea water to move out pure water through semipermeable membrane.
- o The membrane is made up of very thin films of cellulose acetate fitted to a tube having holes.
- o The walls of cellulose acetate film acts as a semi-permeable membrane.
- o The fresh water is gotten from the inside of the tube.
- o **Advantages** of RO desalination:
 - 1. It removes ionic, non-ionic, colloidal and high molecular weight organic substances and colloidal silica.
 - 2. The life time of membrane is 2 years and it can be replaced in few minutes.
 - 3. Its running cost is low, very simple and more efficient.

Other uses of RO:

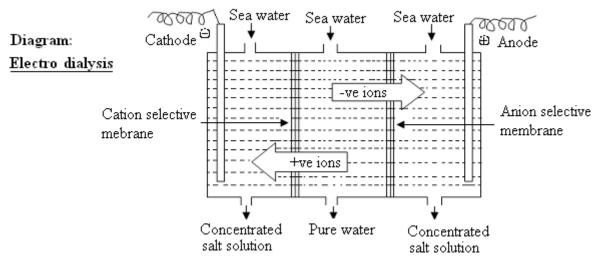
- 1. It is used
 - 1. to concentrated fruit juices, milk and wine.
 - 2. to remove waste material from kidney (Dialysis)
 - 3. in the make of deionized water
 - 4. to remove minerals from boiler water in thermal power plants



8. Explain how electro dialysis is used to remove salt from sea water.

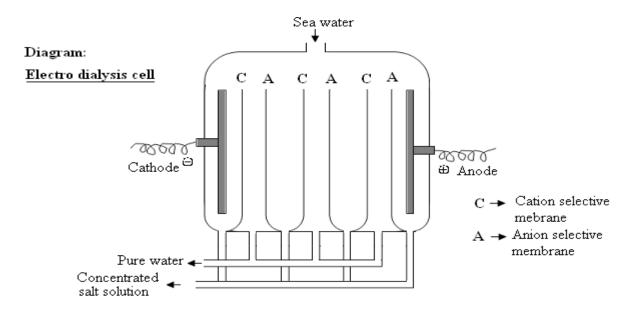
Electro dialysis:

- In this method, the ions of the salts present are moved out of the salt water by passing direct electric current, using electrodes and thin plastic membrane.
- When direct electric current is passed though salt water, the Na⁺ ions move towards cathode (-ve pole) and Cl⁻ ions move towards anode (+ve pole) through the plastic membrane at the same time as shown in the diagram.
- The concentration of NaCl decreases in central part and it increases in two side parts at the same time.
- Pure water and salt water are removed from the central part and the two side parts.
- An ion-selective membrane is used for good separation. There are two types of ion-selective membranes
 - 1. Cation selective membrane
 - 2. Anion selective membrane



• Electro dialysis cell:

- o It has a large number of plastic membrane pairs.
- o Salt water is passed under 5-6 Kg/Cm² pressure between membrane pairs.
- o Electric field is applied perpendicular to the direction of water flow.
- +ve ions move towards cathode and –ve ions move towards anode to decrease the concentration of salt in each membrane pair.
- o The concentration of salt in side parts is increased.
- o Thus, we get pure water and concentrated salt water as shown in diagram.



- Advantages of electro dialysis:
 - 1. Electro dialysis cell is very small in size
 - 2. It is not costly
 - 3. It can be used, where electricity is easily available.

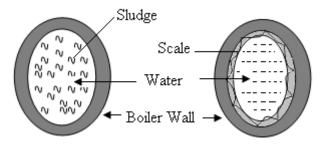
9. What is boiler feed water? Explain boiler trouble, Scale and Sludge formation.

Boiler feed water:

- Boiler is a closed vessel used to make steam by heating water.
- This steam is used to heat and dry materials in different industries and to get electricity by rotating a turbine in thermal power plants etc.
- Well softened water should be used in boilers.
- If the hard water is used in boilers, the following problems may be created in boilers
 - 1. Scale and sludge formation
 - 2. Corrosion
 - 3. Priming and foaming
 - 4. Caustic embrittlement

Scale and Sludge formation:

- In boilers, water changes into vapor continuously and the concentration of dissolved salts increases slowly.
- When their concentration reaches some point, they form solid on the inner walls of the boiler.
- If this solid moves easily in water, it is called **Sludge**.
- If this solid sticks very strongly on the inner wall of the boiler, it is called **Scale**.



• Sludge:

- o Sludge can be removed with wire net.
- o Sludge forms in low temperature areas and it is collected at bends.
- o Sludge is formed by salts like MgCO₃, MgCl₂, CaCl₂, MgSO₄ etc.

O Disadvantages of sludge formation:

- 1. Sludge wastes some amount of heat
- 2. Sludge also sticks very strongly on the inner walls of the boiler along with scale.
- 3. Sludge may be collected at the bends of the pipe and stops the flow of water and steam.
- o Sludge formation can be stopped by
 - Using well softened water
 - Using blow-down operation i.e. by removing some part of the concentrated water many times.

Scale:

- Scale cannot be removed even with hammer.
- o Scale is the main problem of boiler.
- o Formation of scale may be due to CaCO₃, CaSO₄, Mg(OH)₂, CaSiO₃ (calcium silicate) and MgSiO₃ (magnesium silicate).
- **O Disadvantages of Scale formation:**

- 1. Fuel will be wasted to give a constant heat to the boiler
- 2. Boiler may not be safe.
- 3. Boiler may not work correctly
- 4. When thick scales break, boiler may burst due to high pressure.
- Scales can be removed by
 - Adding 5-10% HCl for CaCO₃ scales
 - Adding EDTA for CaSO₄ scales
- Scales formation can be stopped by
 - Using well softened water.
 - Removing some part of the concentrated water.

10. Explain the following boiler troubles:

1) caustic embrittlement

2) boiler corrosion

3) Priming and foaming.

Caustic embrittlement:

- Caustic is a strong base like NaOH that makes the inner surface of the boiler very hard and easily broken to damage boiler.
- Caustic embrittlement is a type of chemical damage of boiler.
- It is due to the usage of highly basic water in the boiler.
- This is noticed in high pressure boilers, when softened water having small amount of Na₂CO₃ is used.
- In high pressure boilers, Na₂CO₃ reacts with water to form NaOH and CO₂.

$$Na_2CO_3 + H_2O \rightarrow 2 NaOH + CO_2$$

- The water having NaOH move into very small holes (cracks) present in the inner surface of boiler, bends, joints etc.
- Here water vaporizes and concentration of NaOH increases slowly.
- This NaOH dissolve iron of the boiler to form sodium ferrate and it damages boiler and stops it from working correctly.
- Caustic embrittlement can be stopped by
 - o Using sodium phosphate as softening agent in place of Na₂CO₃.
 - o Adding tannin or lignin to boiler water and it fills the small holes (cracks) of inner surface of the boiler, bends, joints etc.
 - Adding Na₂SO₄ to boiler water and it also fills the small holes (cracks) of inner surface of the boiler, bends, joints etc.
 - The following ratio of $\frac{[Na_2SO_4]}{[NaOH]}$ at different pressures can be added.
 - 1:1 ratio at 10 atm pressure
 - 2:1 ratio at 20 atm pressure
 - 3:1 ratio at >20 atm pressure

Boiler corrosion:

- It is the destruction of boiler material by chemical action over a period of time.
- The reasons for boiler corrosion are
 - Dissolved oxygen (DO)
 - Dissolved CO₂
 - Acids from dissolved salts
- Dissolved oxygen (DO):

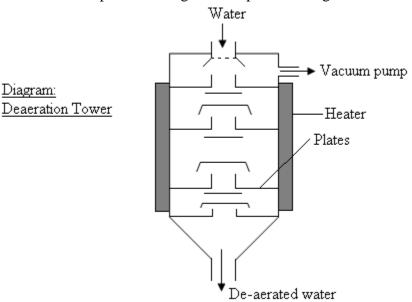
o DO present in water reacts with boiler material as shown to form Rust.

o DO can be removed by:

1. Adding calculated quantity of sodium sulphite or hydrazine or sodium sulphide

2. Mechanical de-aeration:

- In this, water is sprayed through a de-aeration tower
- This tower has the following thing as shown in the diagram
 - 1. Plates having holes
 - 2. Heater
 - 3. Vacuum pump
- The tower is heated to high temperature under vacuum.
- The water is passed through heated plates having holes to decrease DO.



• Dissolved CO₂:

• When CO₂ is dissolved in water, it forms carbonic acid

$$CO_2 + H_2O \rightarrow H_2CO_3$$

- o This carbonic acid destroys boiler material slowly.
- o CO₂ is also formed inside the boiler, if boiler water has bicarbonates.

$$Mg(HCO_3)_2 \xrightarrow{\Delta} MgCO_3 + H_2O + CO_2$$

- o CO₂ can be removed by:
 - Adding calculated quantity of liquor ammonia (NH₄OH)

$$2 \text{ NH}_4\text{OH} + \text{CO}_2 \rightarrow (\text{NH}_4)_2\text{CO}_3 + \text{H}_2\text{O}$$

Mechanical de-aeration along with DO

Acids from dissolved salts:

o Water having dissolved magnesium salts can form acid on hydrolysis.

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

o This acid reacts with iron of the boiler again and again.

Fe + 2 HCl
$$\rightarrow$$
 FeCl₂ + H₂ \uparrow
FeCl₂ + H₂O \rightarrow Fe(OH)₂ \downarrow + 2 HCl

- Hence a small amount of MgCl₂ can destroy the boiler material completely.
- o Removal of MgCl₂:
 - HCl so formed can be removed by adding alkali to the boiler water.
 - Well softened water must be used.
 - Addition of inhibitors like sodium silicate, sodium phosphate and sodium chromate.

Priming and foaming:

- When boiler is forming steam very fast, steam takes some liquid water along with it. This wet steam formation is called **priming**.
- Priming is due to
 - o The presence of more dissolved solids
 - High steam speed
 - Sudden boiling
 - o Sudden increase in steam formation rate

• Foaming:

- o It the formation of foam or bubbles continuously in boilers
- o It is due to the presence of oils and oil decreases surface tension of water.
- Priming and foaming forms at the same time.
- The following problems may come due to priming and foaming
 - o Dissolved salts are gathered on the blades of the turbine and it decreases the working of turbine.
 - o Dissolved salts are gathered on the inner parts of the machine and it decreases the life time of it.
 - o The level of boiler cannot be seen correctly.

Priming can be stopped by

- Using mechanical steam purifiers
- o Avoiding sudden change in steam formation rate.
- Keeping low water level in boiler
- o Using well softened water.

Foaming can be stopped by

- Adding castor oil
- o Adding sodium aluminate (NaAlO₂) to remove oil from boiler water.
- 11. Explain the functions of lime and Soda in removal of temporary and permanent hardness with proper reactions.

Chemical reactions that take place in Lime-Soda process: (or Functions of Lime and Soda)

• As lime is added to water, it will react with any carbon dioxide present as follows:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \downarrow + H_2O$$
 ----- (1)

• The lime will react with carbonate hardness as follows:

$$Ca(OH)_2 + Ca(HCO_3)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O$$
 ----- (2)
 $Ca(OH)_2 + Mg(HCO_3)_2 \rightarrow MgCO_3 + CaCO_3 \downarrow + 2H_2O$ ----- (3)

• The product magnesium carbonate in equation 3 is soluble. To remove it, more lime is added:

$$Ca(OH)_2 + MgCO_3 \rightarrow CaCO_3 \downarrow + Mg(OH)_2 \downarrow$$
 -----(4)

• Also, magnesium non-carbonate hardness, such as magnesium sulfate, is removed:

$$Ca(OH)_2 + MgSO_4 \rightarrow CaSO_4 + Mg(OH)_2 \downarrow \qquad ----- (5)$$

- Lime addition removes only magnesium hardness and calcium carbonate hardness.
- In equation 5 magnesium is precipitated, however, an equivalent amount of calcium is added.
- The water now contains the original calcium non-carbonate hardness and the calcium non-carbonate hardness produced in equation 5.
- Soda is added to remove calcium non-carbonate hardness:

$$Na_2CO_3 + CaSO_4 \rightarrow Na_2SO_4 + CaCO_3 \downarrow$$
 ----- (6)

- To precipitate CaCO₃ requires a pH of about 9.5; and to precipitate Mg(OH)₂ requires a pH of about 10.8, therefore, an excess lime of about 1.25 meq/l is required to raise the pH.
- The amount of lime required: lime (meq/l) = carbon dioxide (meq/l) + carbonate hardness (meq/l) + magnesium ion (meq/l) + 1.25 (meq/l).
- The amount of soda required: soda (meq/l) = non-carbonate hardness (meq/l)
- After softening, the water will have high pH and contain the excess lime and the magnesium hydroxide and the calcium carbonate that did not precipitate.
- Re-carbonation (adding carbon dioxide) is used to stabilize the water. The excess lime and magnesium hydroxide are stabilized by adding carbon dioxide, which also reduces pH from 10.8 to 9.5 as the following:

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

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

• Further re-carbonation, will bring the pH to about 8.5 and stabilize the calcium carbonate as the following:

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

• It is not possible to remove all of the hardness from water. In actual practice, about 50 to 80 mg/l will remain as a residual hardness.

THE END