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SCAN ME



Unit 1: Water Technology

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* Introduction:

Water is essential for survival of life on the earth. Water acts as a Solvent and medium for all living body reactions. Water is also essential for development of human civilization. All the ancient civilizations developed on the banks of rivers.

The Earth's 71% surface area is occupied by water and the remaining 29% by land. The Oceans contain nearly 97% of water as compared to that available on earth's surface. But ocean water, being saline, can not be used directly for drinking, agriculture and industrial purpose. So only small quantity present in lakes, rivers and as a underground water is useful.

The industrial revolution in Europe started with the invention of the Steam engine by James Watt. The steam is generated from water. It is an important component of the infrastructure essential for industrial development. It plays significant role in various industries such as boiler industry for steam generation, textile, paper, food processing, pharmaceutical industry etc. in addition to that of agriculture.

The Scientist Henry Cavendish prepared water in 1781 by igniting a mixture of two volumes of hydrogen and one volume of oxygen. So, water is a chemical compound of hydrogen and oxygen.

• Natural Sources of water-

- i) Surface water - Rivers water, Sea water, Lake water.
- ii) Rain water
- iii) Underground water - Tube well, Well, Spring water.

- Impurities in Water-

Water contains following type of impurities:

1. Suspended Impurities.
2. Colloidal Impurities.
3. Dissolved Impurities.
4. Biological Impurities.

1. Suspended Impurities - The impurities due to which water appears turbid & which are seen by eyes are known as suspended impurities. These impurities are removed by the process of filtration. The commonly occurring suspended impurities are clay particles, precipitates of iron hydroxides, calcium carbonates, bicarbonates & silicates. In addition to this, water may contain some organic impurities such as from decay of living matter, pesticides etc.

2. Colloidal Impurities - The impurities which are not seen by eyes and having size between 10 to 1000 A° or 10^{-5} to 10^{-7} cm . These impurities are evenly distributed in water & do not get settle down. These are removed by the processes of coagulation, sedimentation & filtration. The commonly used coagulants are FeSO_4 , alum, NaAlO_2 etc.

3. Dissolved Impurities - Rain water gets impure due to the dissolution of the gases such as O_2 , SO_2 , NH_3 , H_2S , CO_2 etc. present in the atmosphere. Underground & surface waters, due to contact with soil, rocks containing some inorganic impurities (cations/anions) such as Ca^{++} , Mg^{++} , Fe^{++} , Mn^{++} , Al^{+3} , Na^+ , K^+ , Cl^- , NO_3^- , HCO_3^- , SO_4^{--} . In specifically industries such as sugar, pesticides, agrochemicals,

fertilizes the effluent water containing dissolved organic impurities like Sugars, alcohols etc. Hence these dissolved gaseous, inorganic and organic impurities present in water are removed by the processes of Filtration, boiling, chemical treatment etc.

4 Biological Impurities - The impurities which are present in the form of algae, fungi and other small sized aquatic animals are known as Biological Impurities. These impurities are removed by the process of sterilization or by the use of bleaching powder, chlorine drops, ozone, U.V. light etc.

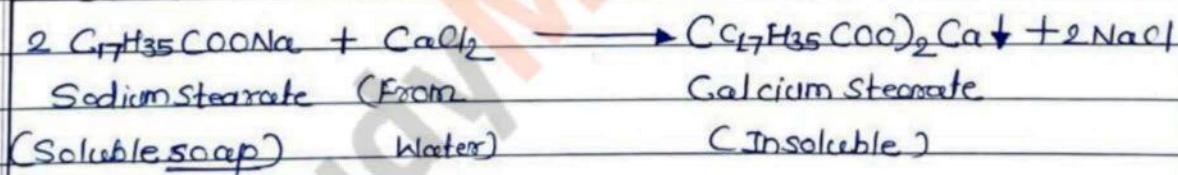
* Hard and Soft water :

- Soft water - Water which forms lather (foam) with soap easily is called as soft water.
The soft water does not contain dissolved calcium and magnesium salts in it.
- Hard water - Water which does not form lather with soap easily is called as hard water. i.e. when soap is dissolved in hard water then lather is not formed, instead of this Scum is formed.
Thus, this property or tendency of water is called as "Hardness of water".

* Hardness of Water:

- Hardness is the characteristic of water, which prevents the lathering of soap. It was originally defined as, "the soap consuming capacity of a water sample".
 - Soap is a mixture of sodium (or potassium) salts of higher fatty acids such as Palmitic acid, Oleic acid and Stearic acid. The soap consuming capacity of water gets reduced due to the presence of certain salts of Calcium, magnesium and other heavy metals dissolved in it.
 - When soap is added to hard water sample containing salts of Ca & Mg, then insoluble salts of Calcium and Magnesium are obtained, called as scum or curd.

Reaction:



- Hardness character to water, is due to presence of dissolved salts of heavy metals. Therefore, the water containing Ca^{++} , Mg^{++} , Fe^{++} , Mn^{++} , Al^{+3} etc. is hard water and among the hardness causing salts in water, calcium & magnesium salts are major.

• Types of Hardness -

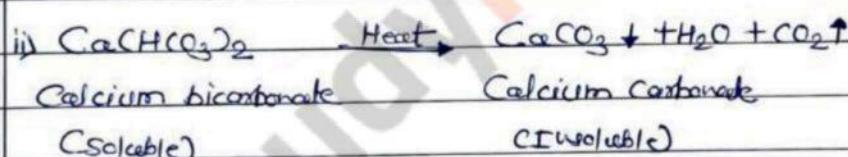
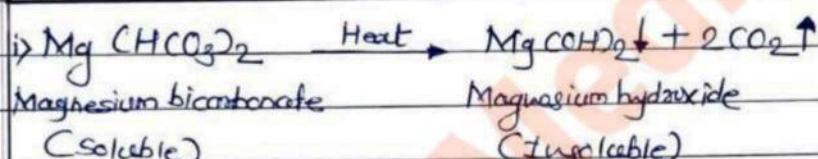
On the basis of salts present in water, there are two types of hardness - a) Temporary Hardness b) Permanent Hardness

a) Temporary Hardness (Carbonate / Alkaline Hardness)

If hardness of water is due to presence of Carbonates & bicarbonates of Calcium, magnesium and other metals such as CaCO_3 , MgCO_3 , $\text{Ca}(\text{HCO}_3)_2$, $\text{Mg}(\text{HCO}_3)_2$, $\text{Fe}(\text{CO}_3)_2$ etc., then it is called as temporary or carbonate hardness.

This type of hardness can be removed easily by simply boiling the water. During boiling, Carbonates & bicarbonates are converted into the form that is insoluble in water and these insoluble precipitate formed can be removed by filtration.

Reactions:



b) Permanent Hardness (Non-carbonate / Non-alkaline Hardness).

Hardness due to presence of dissolved salts other than carbonates and bicarbonates of Calcium, Magnesium and other metals. It is due to the presence of dissolved chlorides, sulphates and nitrates of calcium, magnesium, iron & other heavy metals.

The commonly occurring salts that causes the permanent hardness of water are CaCl_2 , MgCl_2 , CaSO_4 , MgSO_4 , $\text{Ca}(\text{NC}_3)_2$, $\text{Mg}(\text{NC}_3)_2$, FeCl_2 , CuCl_2 etc.

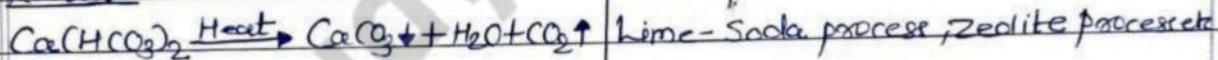
This type of hardness can not be removed by simply boiling but needs special chemical treatments.

Temporary Hardness

i) This type of hardness is due to the presence of dissolved bicarbonates & carbonates of calcium, magnesium and other heavy metals.

ii) Temporary hardness can be removed by simply boiling.

Reaction:



Permanent Hardness

i) This type of hardness is due to presence of dissolved chlorides and sulphates of calcium, magnesium, iron and other heavy metals.

ii) Permanent hardness can not be removed by simply boiling but needs some special treatments like Lime-Soda process, Zeolite process etc.

iii) It is called as Carbonate hardness.

iii) It is called as Non-Carbonate hardness.

iv) It is also known as Alkaline hardness.

iv) It is also known as Non-Alkaline hardness.

v) Temporary hardness leads to the formation of loose deposits of carbonates & hydroxides of Ca^{+2} , Mg^{+2} etc. if used in boilers.

v) Permanent hardness leads to the formation of adherent scales & sludges in boilers.

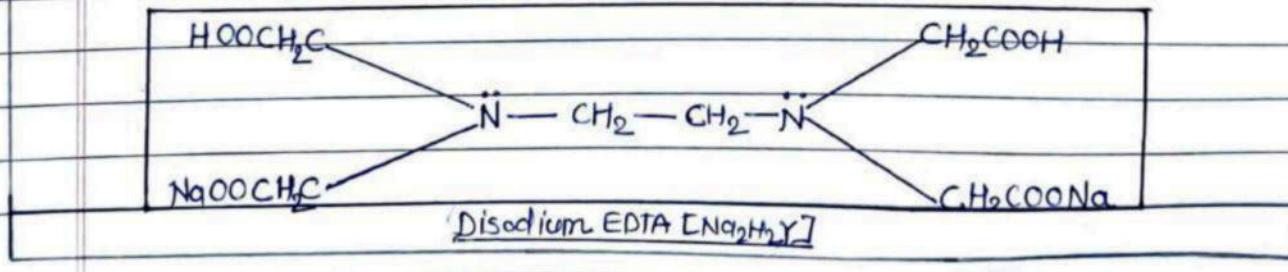
* Determination of Hardness of Water By EDTA Method:

- Hardness is the characteristic of water, which prevents the lathering of soap. The water sample containing Ca^{2+} , Mg^{2+} , Fe^{2+} , Mn^{2+} , Al^{3+} etc. is hard water and among the hardness causing salts in water, Ca^{2+} & Mg^{2+} salts are major.
- The hardness of water can be determined by following methods;
 - i) EDTA method - Used most widely
 - ii) O' Henners method - Not used commonly
 - iii) Soap titration method - Not used commonly.

* Determination of Hardness of Water EDTA method:

* Theory:

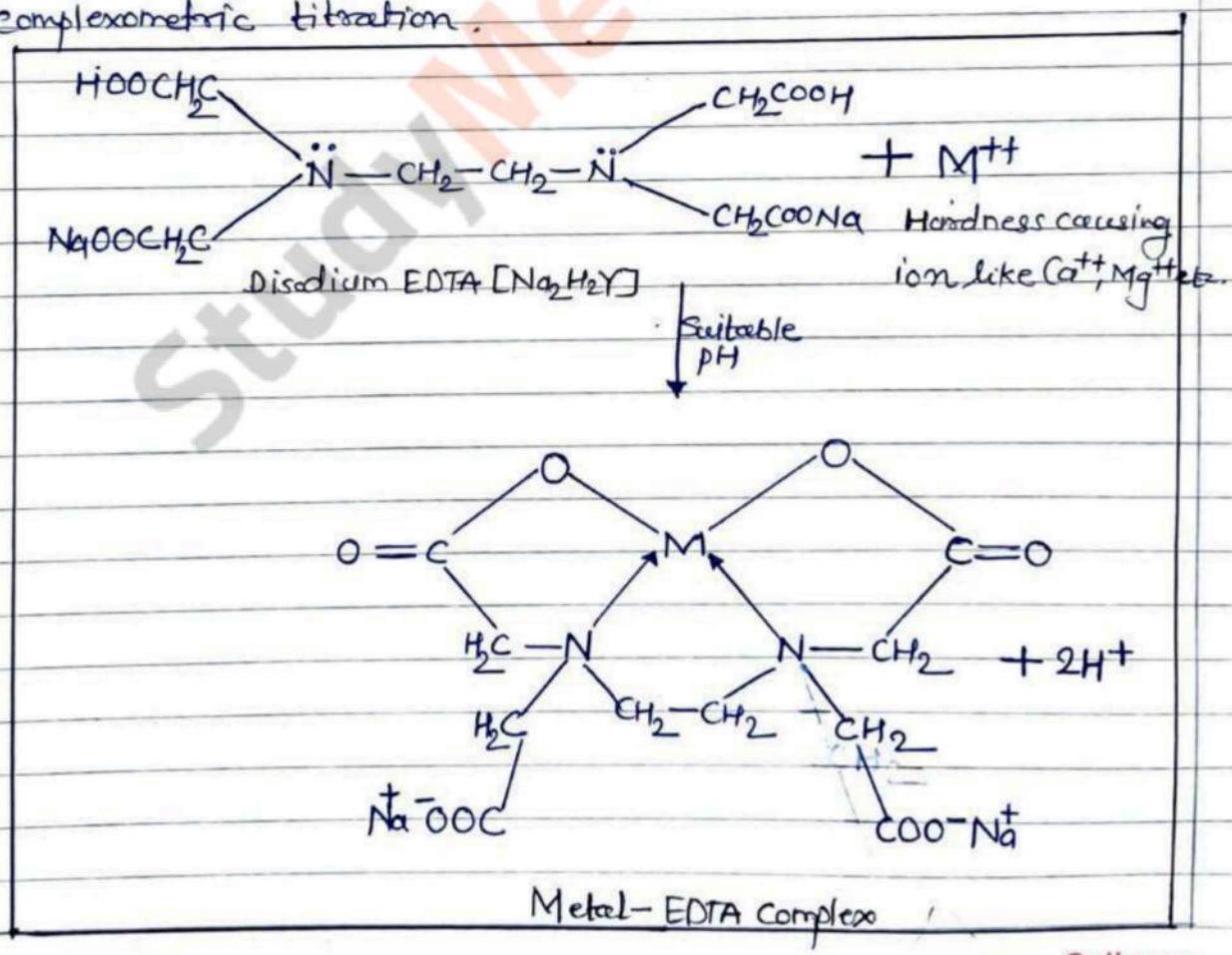
- i) This is the most commonly used experimental method to determine the total hardness of water.
- ii) The total hardness of a water sample is determined accurately by titrating the water sample with Ethylenediaminetetraacetic acid (EDTA). During this titration, EDTA forms complex with Ca^{2+} & Mg^{2+} ions present in water sample hence this titration is also known as Complexometric titration and the method is called as Complexometric method.
- iii) EDTA is insoluble in water or dissolves in water with great difficulty but the disodium salt of EDTA dissolves in water quickly & completely. Hence, for experimental purpose, instead of EDTA, disodium salt of EDTA is used.



iv) EDTA molecule has four carboxylic acid groups and two nitrogen atoms with lone pair of electrons, hence there are total six sites to form the co-ordinate bonds hence it is called as hexadentate ligand.

v) A suitable pH is required for the reaction between the metal ions of water and disodium EDTA, otherwise the reaction will be reversible and cannot go to completion in forward direction. Hence, a buffer solution of pH 10 is used to maintain the pH of solution during titration.

vi) The reaction between disodium EDTA & the heavy metal ions, results in the formation of cyclic co-ordination complex (Chelate) and hence the titration is known as complexometric titration.



* Principle:

The hardness causing ions like Ca^{++} & Mg^{++} present in water forms stable chelate complexes with disodium EDTA, at suitable pH., and certain organic dye indicators like EBT gives the sharp end point.

* Reactions:

i>	$\text{M}^{++} + \text{EBT} \xrightarrow{\text{pH}=10} \text{M-EBT} + 2\text{H}^{+}$	Wine red complex. (Unstable complex)
ii>	$\text{M}^{++} + \text{EDTA} \xrightarrow{\text{pH}=10} \text{M-EDTA} + 2\text{H}^{+}$	Colourless complex (Stable complex)
iii>	$\text{M-EBT} + \text{EDTA} \xrightarrow{\text{pH}=10} \text{M-EDTA} + \text{EBT}$	Wine red Colourless Blue complex

* Procedure:

- The titration is carried out in two parts.
- Titration part I:- Standardization of EDTA solution:
 - Prepare standard solution of $\text{MgSO}_4/\text{ZnSO}_4/\text{ZnCl}_2$ etc.
 - Fill a burette with disodium EDTA solution and pipette out 25 ml of std. prepared solution in a conical flask.
 - Add about 10-15 ml of buffer solution of pH=10 & 4-5 drops of EBT indicator to it.
 - Titrate this wine red coloured mixture against the EDTA solution till it changes to blue.
 - Let the titration reading be V_1 ml.

- Titration Part II :- Total Hardness of Water sample determination.
 - i) Take 25 ml of the water sample in a conical flask.
 - ii) Add about 10-15 ml of the buffer solution of pH=10 & 4-5 drops of EBT indicator solution in it.
 - iii) Titrate this wine red coloured solution against the EDTA till the colour changes to end point colour i.e. blue.
 - iv) Let the titration reading be 'y' ml.

* Calculations:

(1) Standardization of EDTA.

Molarity of EDTA solution is calculated by using formula;

$$M_1 V_1 = M_2 V_2$$



where,

M_2 = Mol. of MgSO_4 .

V_2 = Vol. of MgSO_4 taken in conical flask.

V_1 = Burette Reading.

$$M_1 = \frac{M_2 \times V_2}{V_1}$$

(2) Estimation of Total Hardness of water sample.

$$\boxed{\text{Total Hardness} = \frac{Y}{V} \times Z \times 100 \times 1000 \text{ ppm } \text{CaCO}_3 \text{ equivalent.}}$$

where,

V = Vol. of water sample titrated.

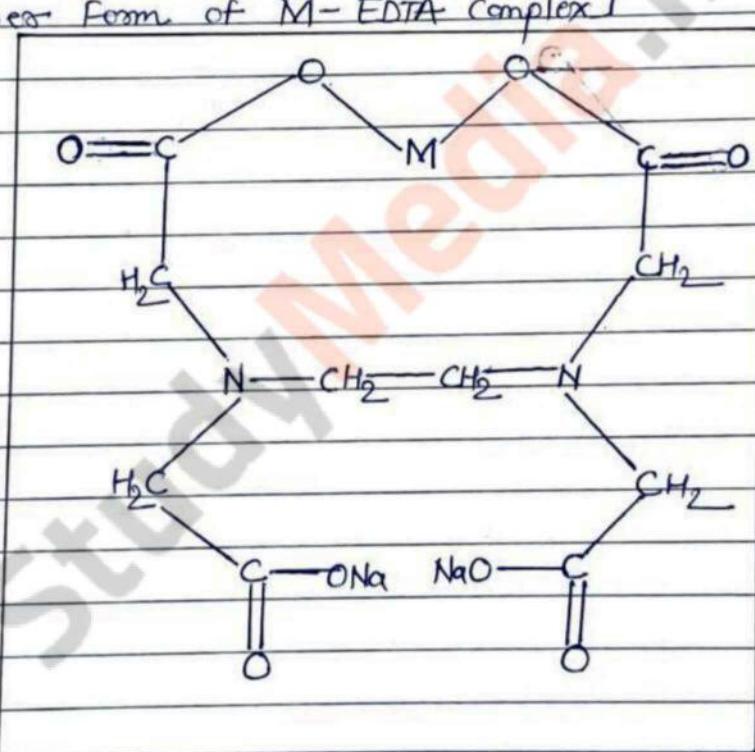
Y = Vol. of EDTA solution (Burette Reading).

Z = Molarity of disodium EDTA solution.

* Advantages of EDTA method over other methods:

- i) The EDTA titration method is convenient, fast and easy.
- ii) Gives sharp colour change at the end point of titration.
- iii) Gives accurate hardness as EDTA reacts with hardness causing metal ions in water even at very low concentrations.
- iv) Suitable indicators available for accurate reading.

* [Another form of M-EDTA complex]



* Numerical:

Ex. 50 ml of cooker sample requires 18 ml of 0.05 M EDTA during titration. Whereas 50 ml of boiled cooker sample requires 12.5 ml of same EDTA in the titration. Calculate total, temporary and permanent hardness of the water sample.

Soln. Given: Molarity of EDTA = $Z = 0.05 \text{ M}$.

Volume of water taken for titration = $V = 50 \text{ ml}$.

Burette reading for titration with W.S. = $Y = 18 \text{ ml}$.

Burette reading for titration with boiled W.S. = 12.5 ml .

$$\therefore \text{Total hardness of cooker sample} = \frac{Y \times Z \times 100 \times 1000 \text{ ppm CaCO}_3}{V} \text{ equivalent}$$

$$= \frac{18 \times 0.05 \times 100 \times 1000}{50}$$

$$= 1800 \text{ ppm CaCO}_3 \text{ equivalent.}$$

- After boiling, temporary hardness gets removed and the boiled water contains only permanent hardness.

Boiled water titration : $Y = 12.5 \text{ ml}$, $V = 50 \text{ ml}$ and $Z = 0.05 \text{ M}$.

$$\text{Hence, Permanent hardness of boiled W.S.} = \frac{Y \times Z \times 100 \times 1000 \text{ ppm CaCO}_3}{V} \text{ equivalent}$$

$$= \frac{12.5 \times 0.05 \times 100 \times 1000}{50}$$

$$= 1250 \text{ ppm CaCO}_3 \text{ equivalent.}$$

$$\therefore \text{Temporary hardness} = \text{Total hardness} - \text{permanent hardness}$$

$$= 1800 - 1250$$

$$= 550 \text{ ppm CaCO}_3 \text{ equivalent.}$$

* Determination of Alkalinity of Water:

- Alkalinity of water is the ability of water to neutralize acids.
- A natural water may be alkaline due to presence of hydroxides, bicarbonates and carbonates compounds dissolved in water.
- The commonly occurring alkaline substances in water are:

Hydroxides : NH_4OH , $\text{Ca}(\text{OH})_2$

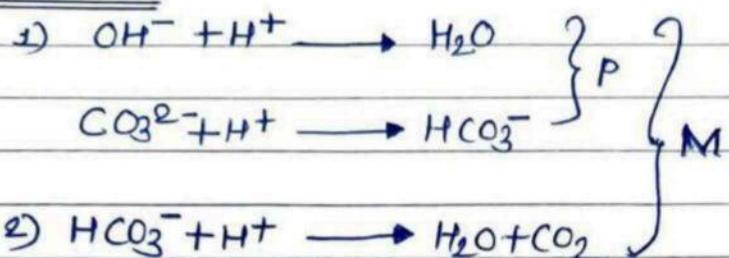
Carbonates : MgCO_3 , FeCO_3

Bicarbonates : $\text{Ca}(\text{HCO}_3)_2$, $\text{Mg}(\text{HCO}_3)_2$, $\text{Fe}(\text{HCO}_3)_2$

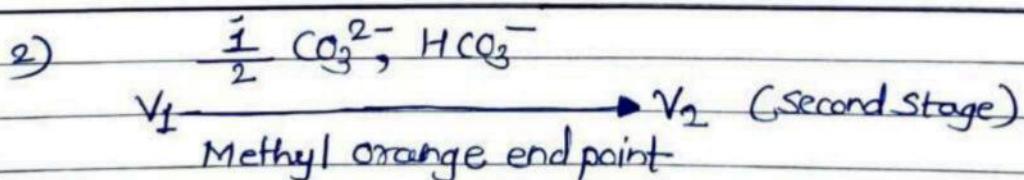
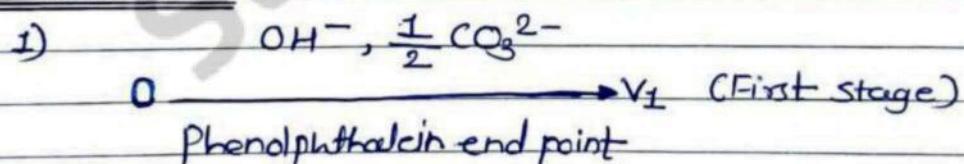
- Basic strength of alkaline substances is,
- Hydroxides > Carbonates > Bicarbonates.

Theory :

- When an alkaline water is titrated with a strong acid, first all OH^- get neutralized completely, then all the CO_3^{2-} get half neutralized to HCO_3^- up to the phenolphthalein end point.
- This is the first step of titration in which pH of solution decreases due to neutralization of OH^- completely and CO_3^{2-} half. Completion of this stage is indicated by change in pink colour to colourless.
- On continued addition of acid during titration, all the HCO_3^- in the titration mixture (produced by half neutralization of CO_3^{2-} and present from beginning) get neutralized and completion of this stage, is indicated by change in yellow colour to orange at about pH 4.

Reactions:Procedure:

- Fill the burette with standard strong acid HCl or H₂SO₄.
- Take V ml (generally 25 ml) of the alkaline water sample in a conical flask, and add 2-3 drops of phenolphthalein indicator in it.
- Titrate this sample against standard strong acid from burette, till pink colour changes to colourless.
Note burette reading as V₁ ml.
- Add few drops of methyl orange indicator into the same titrating mixture and continue the titration till the yellow colour changes to orange.
Note burette reading as V₂ ml.

Calculations:

(15)

P = Phenolphthalein alkalinity

$$= \frac{V_1 \times Z \times 50 \times 1000}{V} \text{ ppm } \text{CaCO}_3 \text{ equivalent}$$

M = Methyl orange alkalinity = total alkalinity

$$= \frac{V_2 \times Z \times 50 \times 1000}{V} \text{ ppm } \text{CaCO}_3 \text{ equivalent}$$

Where, Z = Conc. of acid = Normality.

V = Volume of water sample

50 = Equivalent weight of CaCO_3

Types of Alkalinities:

The possible combinations of alkalinities in water are;

i) Only OH^- , ii) Only CO_3^{2-} , iii) Only HCO_3^- , iv) OH^- and CO_3^{2-} together, v) CO_3^{2-} and HCO_3^- together.

- HCO_3^- and OH^- cannot remain together as they react to form carbonate.



- The amount of alkalinities due to the OH^- , CO_3^{2-} , HCO_3^- types are calculated from the relation between values of P and M .

Sr. No.	Relation between P and M	Hydroxide alkalinity (OH^-)	Carbonate alkalinity (CO_3^{2-})	Bicarbonate alkalinity (HCO_3^-)
1.	$P = 0$	0	0	M
2.	$P = M$	P or M	0	0
3.	$P = \frac{1}{2}M$	0	$2P$	0
4.	$P > \frac{1}{2}M$	$2P - M$	$2(M - P)$	0
5.	$P < \frac{1}{2}M$	0	$2P$	$M - 2P$

FOR EDUCATIONAL USE

(16)

Numerical:

Ex 50 ml of water requires 3.7 ml of 0.025 N H_2SO_4 upto phenolphthalein end point and further 4.8 ml upto the methyl orange end point. Calculate the types and amounts of alkalinities in the water sample.

Soln: Given:

$$\text{Volume of water sample titrated} = V = 50 \text{ ml.}$$

$$\text{Normality of acid} = z = 0.025 \text{ N.}$$

$$\text{Phenolphthalein end point reading, } V_1 = 3.7 \text{ ml}$$

$$\text{Methyl orange end point reading from initial} = V_2 = 3.7 + 4.8 \\ = 8.5 \text{ ml.}$$

$$1. \text{ Phenolphthalein alkalinity} = P = \frac{V_1 \times z \times 50 \times 1000}{V} \\ = \frac{3.7 \times 0.025 \times 50 \times 1000}{50} \\ = 92.5 \text{ ppm CaCO}_3 \text{ equivalent.}$$

$$2. \text{ Methyl orange alkalinity} = M = \frac{V_2 \times z \times 50 \times 1000}{V} \\ = \frac{8.5 \times 0.025 \times 50 \times 1000}{50} \\ = 212.5 \text{ ppm CaCO}_3 \text{ equivalent}$$

- From the values of P and M, it is observed that,

$$P < M.$$

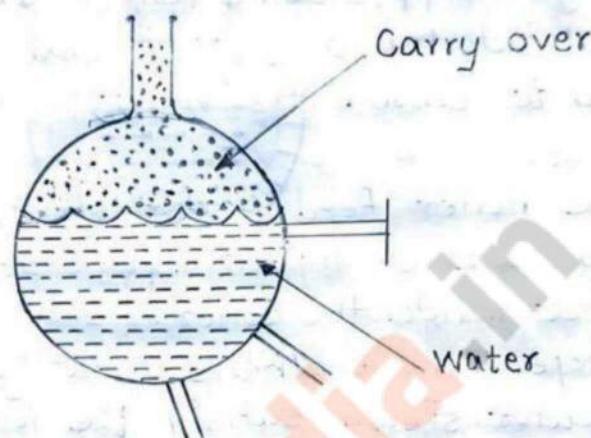
Hence, the alkaline water sample contains CO_3^{2-} and HCO_3^- alkalinities.

* III effects of hard water in Boilers:

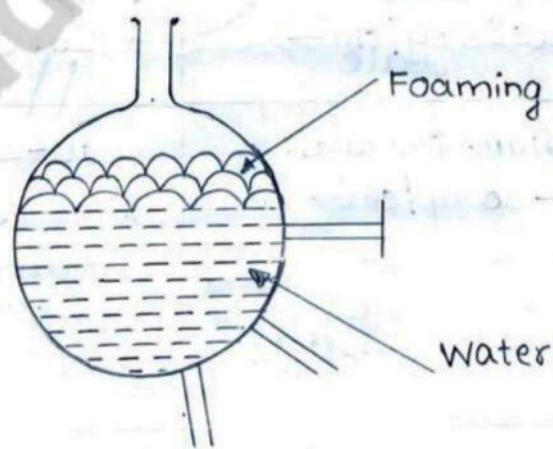
- The most important use of water in industry is for steam generation using boilers. It is also used in chemical industry as solvent and coolant where it can be used to absorb the heat produced during exothermic reactions.
- The boiler feed water should be free from hardness causing salts or impurities in order to avoid bad effects of water inside the boiler.
- Depending upon the operating pressure of boiler, the feed water should satisfy the following requirements of hardness:

Type of boiler, steam pressure	Permitted hardness of feed water
Low pressure: Below 15 kg/cm ²	25-50 ppm CaCO_3 equivalent
Medium pressure: 15-30 kg/cm ²	10-25 ppm CaCO_3 equivalent
High pressure: Greater than 30 kg/cm ²	0-10 ppm CaCO_3 equivalent

- If the boiler feed water is not upto the standard limit, it gives rise to number of problems in boiler like;
- A) Corrosion C) Scales and Sludges formation
 B) Priming and foaming D) Caustic embrittlement



PRIMING



FOAMING

- Priming and Foaming:

- 1) Definitions:

Priming - The process of 'wet' steam formation is called as priming.

Foaming - Formation of continuous foam or bubbles on the surface of water, is called as foaming.

- The priming and foaming processes usually occur together.

- 2) Causes:

- Priming is caused due to;

- i) Very high level of boiler-feed water.

- ii) High speed of steam generation.

- iii) Faulty boiler design.

- iv) presence of large amount of dissolved salts.

- v) High transfer rate of steam due to sudden boiling or increase in temperature.

- Foaming is caused due to;

- i) Presence of high concentration of dissolved salts in boiler-Feed water.

- ii) Presence of oil droplets and alkali in boiler-feed water.

- iii) Presence of finely dispersed suspended materials.

- iv) Violent agitation of boiler-feed water.

- 5) Disadvantages:

- i) Because of foaming actual height of water column cannot be judged well.

- ii) Because of priming, the salts present in the water droplets enter in the parts of machinery where steam is being used, thereby decreasing life of machinery.

iii) The dissolved salts in droplets of wet steam get deposited on evaporation of water. This causes reduced efficiency of machine parts and to some extent their corrosion.

iv) Foaming disturbs the working of boiler.

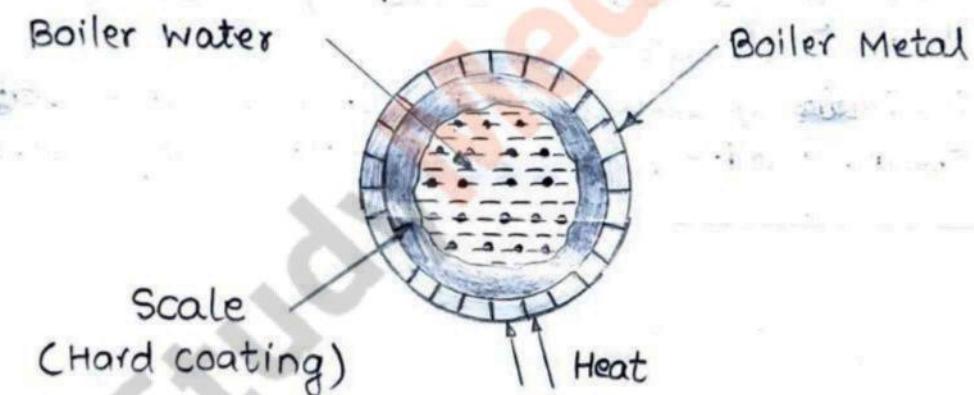
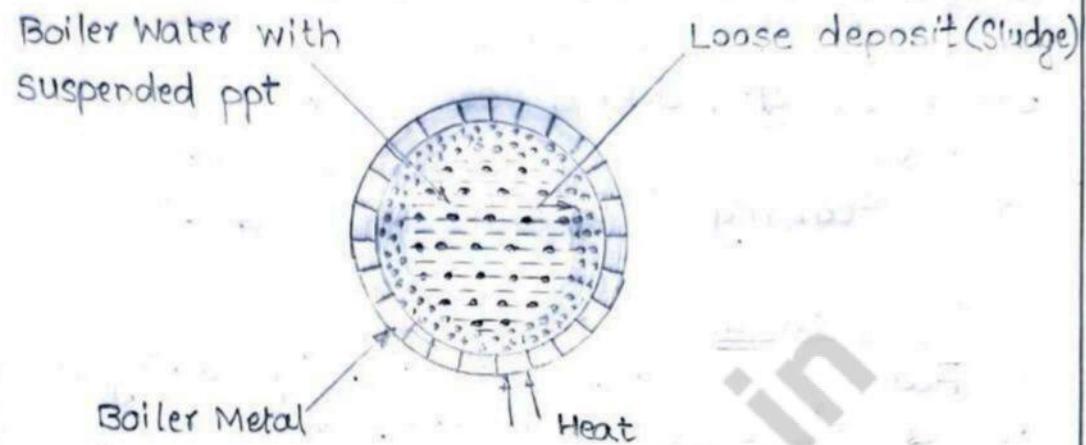
4) Prevention:

i) Foaming can be prevented by adding antifoaming agents like alcohol, castor oil or removing oil from boiler water by adding chemicals like sodium aluminate and blow-down operations at appropriate time.

ii) Priming can be prevented by use of well softened and filtered water.

iii) Maintaining close water level in boiler, prevents priming.

iv) Steam purifiers can be used if priming happens.



SECTION OF BOILER TUBE
SHOWING SLUDGE AND SCALE

- Scales and Sludges formation:

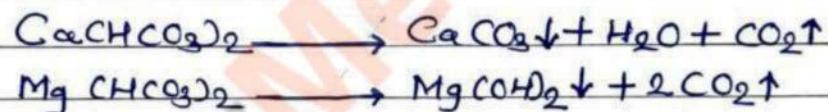
- * Scales :-

i) Definition: The hard and strong coating formed inside the boiler by chemical reactions, is known as scale.

Causes of scale formation:

i] Decomposition of Bicarbonates -

At high temperature, bicarbonates in water undergo decomposition and produces sticky hard insoluble materials, which strongly stick to the inner side of boilers as scales



ii] Hydrolysis of Magnesium salts -

At higher temperature, magnesium salts undergo hydrolysis to form sticky magnesium hydroxide solid particles.



iii] Presence of Silica -

If SiO_2 present in water, it reacts with calcium or magnesium salts and produces insoluble calcium or magnesium silicates which gets deposited to the inner side of boiler as scales.

iv] Decreased solubility of CaSO_4 -

CaSO_4 has lesser solubility at higher temperatures. Hence at high temp. CaSO_4 present in boiler feed water, will precipitate as hard scale forming material.

Thus the scale is composed of CaCO_3 , MgCO_3D_2 , silica, CaSO_4 solids as coat.

3) Disadvantages of scale formation:

i) Wastage of fuel-

The scales are bad conductors of heat. If boiler contains scales then complete transfer of heat to the boiler water is not possible. As thickness of scales inside the boiler increases the wastage of fuel increases because maximum heat gets absorbed by the thick scales.

ii) Over Heating of Boiler-

Scale being poor conductor of heat, it reduces transfer of heat from boiler to boiler water. To keep the required steam pressure, we need to overheat the boiler.

iii) Boiler Safety -

Due to overheating of boiler, boiler metal becomes soft and weak leading to decrease in its life and become unsafe to use.

iv) Danger of Explosion-

The produced layer of scale inside the boiler is not even i.e. in different parts of boiler, the thickness of scale is different. Boiler water will experience more heat where thickness is less as compared to water where scale

thickness is more. This will give rise to uneven pressures inside the boiler and may lead to the explosion.

4) Removal of scales:

Scales are removed from time to time by different ways;

- i) By use of suitable chemicals, the scales can be dissolved and removed, by blow down operation e.g. EDTA, sodium phosphate, calgon etc. chemicals used for dissolving or loosening the scale and then removal.
- ii) Use of scrapers or wire brush for thin scales removal
- iii) Thick scales can be removed by hammer and chisel.
- iv) Thermal shock technique is used to remove hard-brittle scale. In this method empty boiler is heated and cooled by cold water suddenly. While sudden cooling, the contracting boiler metal exerts pressure on scales to crack them.

5) Prevention of Scales:

- i) Use of softened water of enough low hardness.
- ii) Adding organic chemicals like tannin, lignin which forms coating on the scale forming particles. This matter becomes easily removable by blow down operation.
- iii) Frequent blow down operation should be carried out to avoid deposition of insoluble sticky materials as scale to the inner side of boiler.
- iv) Trapping of scale forming materials and not allowing to deposit in the inner side of boiler by adding sodium aluminate chemical.

* Sludges:-

i) Definition: The slimy and loose deposit of precipitated salts inside the boilers, depositing at the bends and valves, affecting free flow of water, is known as sludge.

2) Causes of Sludge Formation:

i) In boiler, water evaporates continuously and the concentration of salts left behind, goes on increasing. After the saturation point they get precipitated to form sludge.

ii) Sludges are formed by the substances which have greater solubility in hot water than cold water.
e.g. $MgCO_3$, $MgCl_2$, $MgSO_4$, $CaCO_3$.

3) Disadvantage of Sludges:

- They tend to waste some portion of heat.
- Excessive sludge formation disturbs working of boiler and sometimes may choke up the pipe.
- Sludge reduces water flow rate in boiler.

4) Prevention of Sludges:

- Use of water containing very low quantity of total dissolved solids.
- Frequently making blow down operation i.e. Replacing salts rich water with fresh water.

5) Removal of Sludges:

Sludges are easy to remove by using brushes, detergent solutions, blow down operation, etc.

* Softening of Water/Water Treatment:

- "The process of removing hardness causing salts from water is called as Softening of water".
- During the process of softening of hard water, the Soluble salts are converted into insoluble salts.
- These insoluble salts are in the form of precipitates which can be removed by filtration and soft water can be obtained.
- The hardness of water is due to presence of carbonates, chlorides and sulphates of calcium, magnesium and other metal ions which can be removed by the following methods:
 - 1) Zeolite Process (Permutit process).
 - 2) Ion Exchange process (Demineralization/Deionization process)
 - 3) Lime-Soda process → Hot lime-soda process
Cold lime-soda process

* Softening of Water : (Water Treatment)

i) Zeolite Process (Fermitit Process)

- Zeolites are the complex mixture of metal aluminosilicates. The name zeolite (Greek: zein-boiling, lithos-stone) means boiling stone. Sodium aluminosilicates show the property of exchanging heavy metal ions in water, with their loosely held Na⁺ ions.
- The chemical formula of sodium zeolite may be represented as,



sodium zeolite is actually the hydrated sodium aluminosilicate. For convenience the chemical formula of sodium zeolite can be simplified as; Na_2Ze

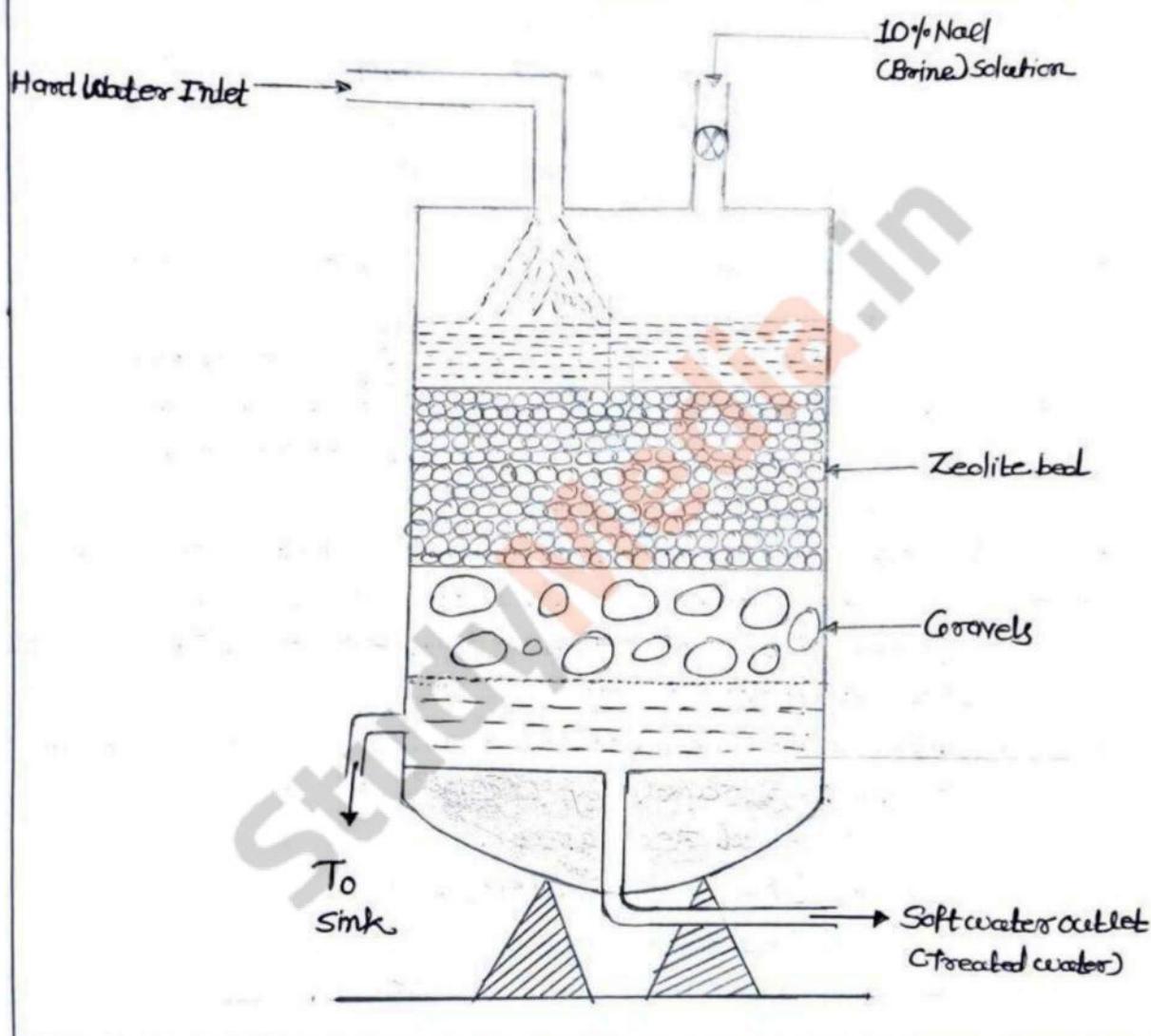
- Zeolites are naturally occurring complex compounds of Na, Al & Si, which when prepared artificially, are called as fermitits. Zeolites are of two types - Natural zeolites and Synthetic zeolites.

i) Natural zeolites - They are amorphous & non-porous. They are derived from green sandal by washing, heating and treating with NaOH. Natural zeolites are more durable.

e.g. Natrolite [$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$]

ii) Synthetic zeolites - They are porous and possess gel structure. They are prepared by heating together China clay, Feldspar and Soda ash and granulating the resultant mass after cooling or Solutions of sodium silicate, aluminium sulphate and sodium aluminate or Solutions of sodium silicate and aluminium sulphate etc. They have higher exchange capacity per unit weight.

Diagram: Zeolite Softener



* Principle:

When hard water is passed over a sodium zeolite bed, the heavy metal ions (Ca^{++} , Mg^{++} etc) are displaced by Na^{+} ions. Due to removal of heavy metal ions from water, the hard water is converted into soft water, by zeolite.

Reactions:



* Process:

The zeolite softener consists of cylindrical pot in which a coarse powder of sodium zeolite is placed over a layer of gravels. There is an inlet on the top for hard water which passes through zeolite column. Ca^{+} , Mg^{+} ions are taken by zeolite and instead sodium ions are released in water. Also there is an outlet at the bottom to collect soft water. There is another inlet at the top for adding 10% NaCl soln. to regenerate the exhausted zeolite bed.

The soft water obtained, however, contains equivalent quantity of sodium salts.

* Regeneration:

When a large quantity of hard water is passed through the zeolite bed, the sodium zeolite bed completely changes to Ca & Mg zeolite beds and there is no exchangeable Na^{+} ions in it. Such zeolite bed is said to be exhausted and needs regeneration.

The regeneration can be done by passing suitable volume of 10% NaCl solution.

Reactions:



The washing containing CaCl_2 , MgCl_2 etc. are led to drain and the regenerated zeolite bed thus obtained is reused for softening hard water again.

* Advantages:

- i) It removes the hardness almost completely and water of about $< 10 \text{ ppm}$ hardness is produced.
- ii) The process automatically adjusts itself for different hardness of incoming water.
- iii) Operating & Maintenance cost is very less.
- iv) This is the easy process & equipment is compact.
- v) If this water is used as Boiler feed water then boiler will be free from problems such as corrosion, caustic embrittlement, scales & sludges formation thereby increasing its efficiency of steam generation.

* Disadvantages:

- i) Only cations can be removed from water whereas anion impurities remain in softened water.
- ii) Water turbidity can not be removed using zeolite treatment.
- iii) Although running cost is low, installation cost is high.
- iv) Natural zeolites are rare & synthesis of zeolite is difficult.
- v) Can not remove the dissolved gases such as O_2 , CO_2 etc.
- vi) The treated water contains more sodium salts.

* Applications:

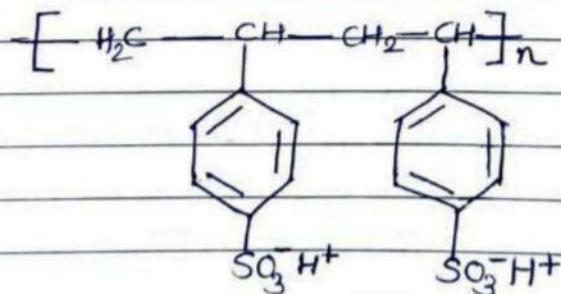
- i) It is used to remove toxic metal ions and dye cations from the polluted water.
- ii) It can be used to recover valuable trace metals from the industrial waste water e.g. Ni, Cr, Pb, Cu, Ag, etc.
- iii) The method is simple, convenient for treatment of hard water or polluted water containing toxic cation impurities and it is a low operation cost process.

2] Ion Exchange Process (Demineralization process/ Deionization process)

- In Ion-Exchange process, cation as well as anion impurities can be removed from hard water. This process is commonly used for obtaining pure water from an ordinary water.
- This process involves use of synthetic polymers/ Resins as the ion exchangers. There are two synthetic resins used i.e. a cation exchanger resin and an anion exchanger resin.

i) Cation exchanger resin -

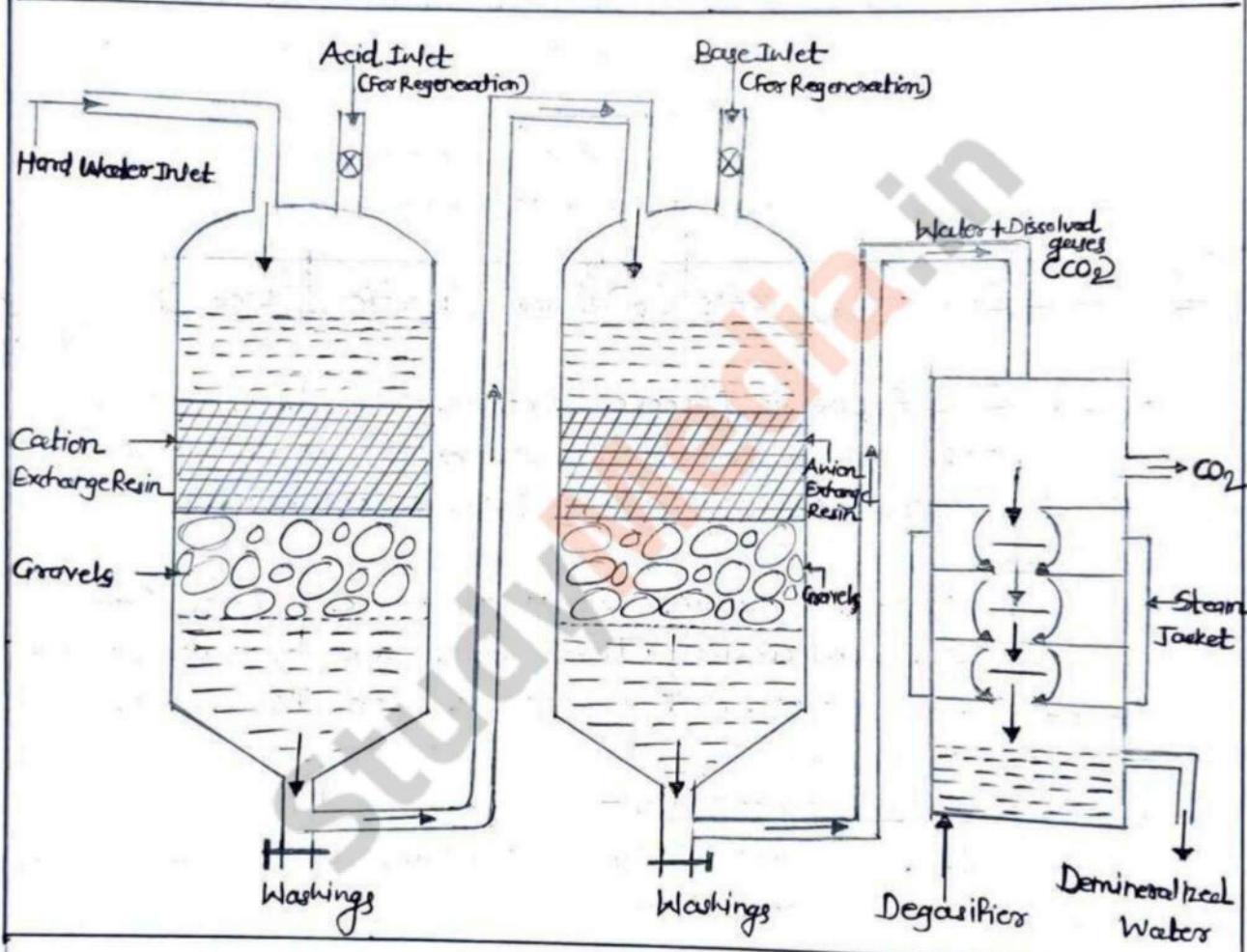
This polymer having carboxylated / sulfonated aromatic rings attached to the chain.



The H^+ ions are loosely held on SO_3^- or COO^- groups and easily exchanged with cations from water.

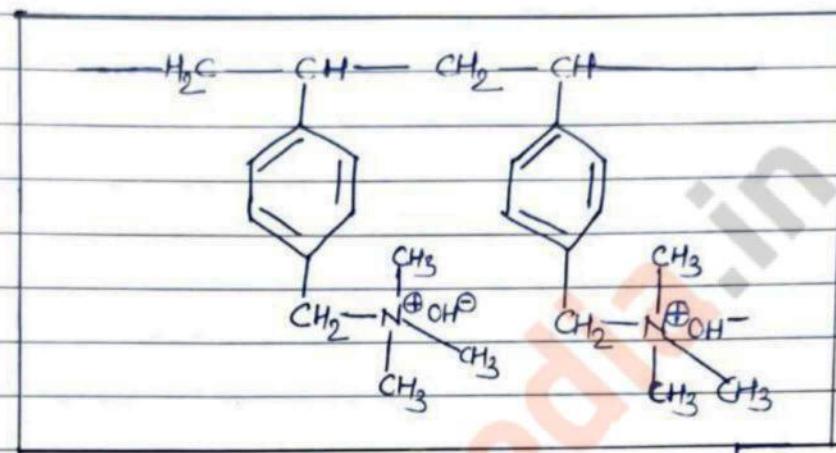
For simplicity, it can be written as; RH^+

Diagram: Demineralization of Water by Ion-Exchangers.



ii) Anion exchanger resin-

This is a polymer having aromatic rings linked to the polymer chain and the rings are with quaternary ammonium group.

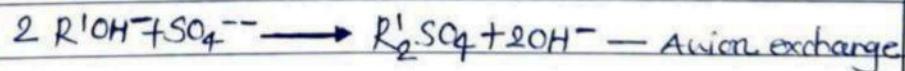
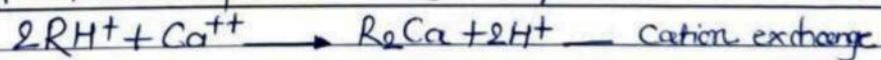


For Simplicity, it can be written as; $\text{R}'\text{OH}^-$

* Principle:

When water containing cations and anions, is passed through the resins, cation exchanger resin captures all cations (in exchange of H^+) and anion exchanger resin captures all anions (in exchange of OH^-), to give pure and all ion-free water.

Reactions: (If water sample containing CaSO_4 salt)



* Process:

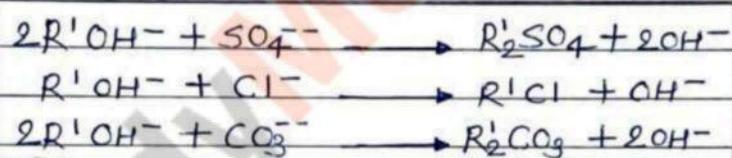
- In this process, there are two cylindrical towers, containing exchangers, where, in first tower, cation exchange resin is placed and in second tower, anion exchange resin is placed.

- The Hard water (water to be treated) is first passed through a tower containing cation exchange resin, which removes all the cations such as Ca^{+2} , Mg^{+2} , Fe^{+2} , Mn^{+2} etc. from it and equivalent amount of H^+ ions are released from resin.

Reactions:



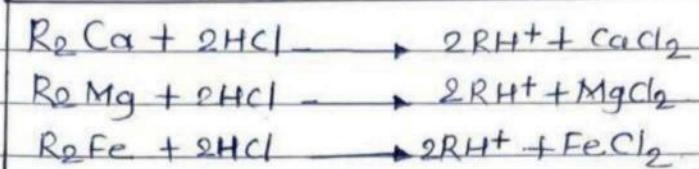
- This water sample is then passed through anion exchange resin where all the anions like SO_4^{2-} , Cl^- , NO_3^- are replaced by equivalent quantity of OH^- ions (Resulting in the formation of water).



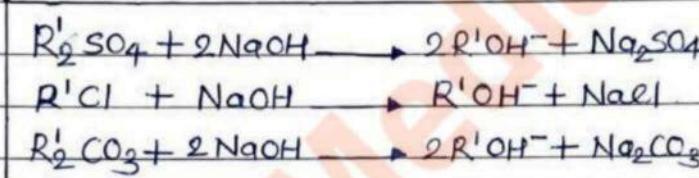
- Thus, the water coming out from anion exchange bed becomes free of cations as well as from anions. The resulting ion-free water is deionised water or demineralised water.
- The water is finally freed from dissolved gases by passing it through a degasifier, which is a tower heated from both sides and is connected to a vacuum pump. High temperature and low pressure reduces the quantity of dissolved gases.
- Water obtained by this process is very near to distilled water, which is the requirement of boiler feed water. This process is very good for high pressure boilers.

* Regeneration:

- i) The exhausted cation exchange resin is regenerated by washing with dil. HCl solution.



- ii) The exhausted anion exchange resin is regenerated by washing with dil. NaOH solution.



* Advantages:

- i) This process gives water of very low hardness ($<2\text{ ppm}$)
- ii) It is useful for purifying or treating acidic water & turbid alkaline water (Turbidity $<10\text{ ppm}$).
- iii) Equipment occupies small space.
- iv) Process is easy to operate with negligible running cost.

* Disadvantages:

- i) The equipment is costly / Initial investment is high.
- ii) If water contains turbidity, then the output of process is reduced. Turbidity should be below 10 ppm.

* Applications:

Ion exchange process is widely used for water treatment in both Industrial & Municipal water treatment systems.

* Purification of Water:

A brackish water contains high concentration of salts dissolved and has peculiar salty taste e.g. Sea water (containing about 35 g salts per litre), deep bore water from some areas. This water can be converted to fresh water or potable water after removing dissolved salts present in it.

The process of removing dissolved salts from sea water is known as Desalination. Commonly used membrane techniques for desalination are - Electrodialysis, Reverse Osmosis.

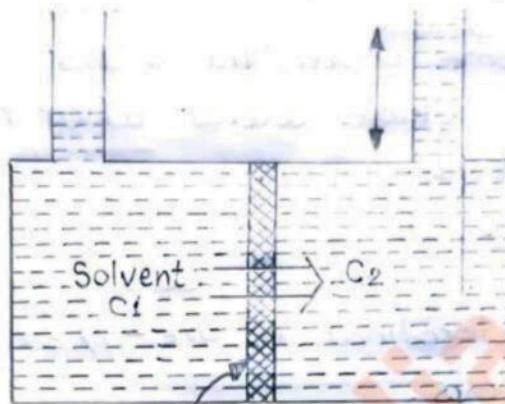
I] Reverse Osmosis:

a) Osmosis:- Flow of solvent from lower concentrated solution to higher concentrated solution through semipermeable membrane. Semipermeable membrane allows only small molecules of solvent to pass from one compartment to adjacent compartment.

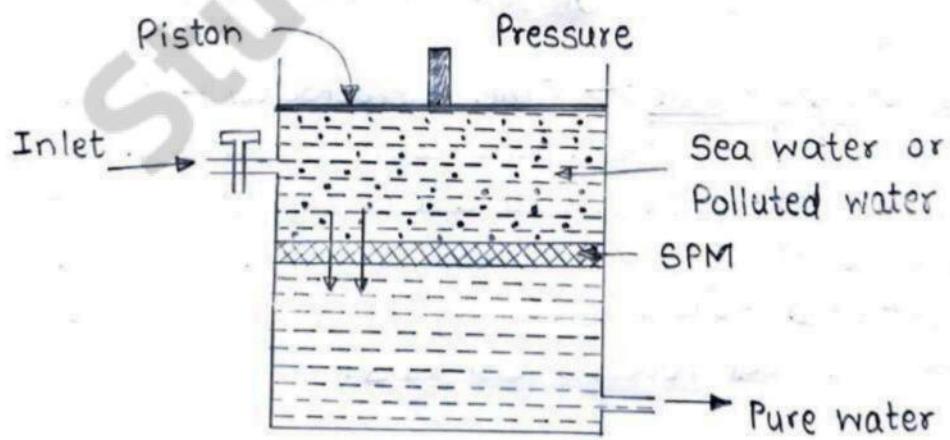
b) Reverse Osmosis:- The flow of solvent from higher concentrated solution to lower concentrated solution by applying external pressure on higher concentrated solution which is slightly higher than osmotic pressure of higher concentrated solution through semipermeable membrane, is known as reverse osmosis.

- Semipermeable membrane is made by using polymer film. Generally Polyamide, polymethyl acrylate polymers are used. porosity of membrane allows only small molecules of

OSMOSIS



REVERSE OSMOSIS CELL



water solvent to pass through it while large sized molecules are left behind.

- Process:-

Sea water or water polluted by ionic pollutants, is filled in reverse osmosis cell and external pressure is applied on it by using piston to force the solvent to pass through semipermeable membrane.

Applied pressure is higher than Osmotic pressure of sea water which lead to flow of water molecules only through semipermeable membrane to lower concentration solution.

- Advantages:-

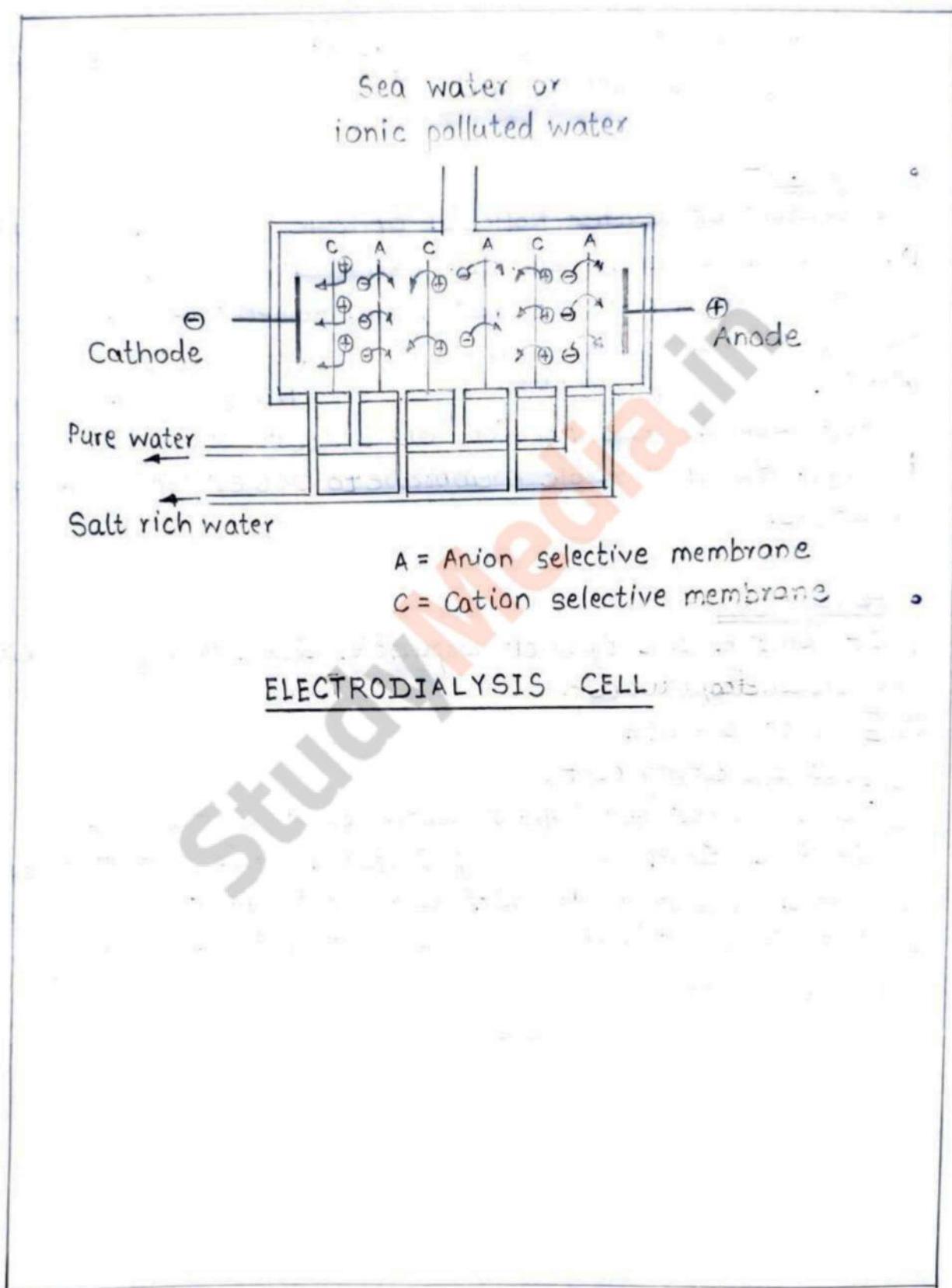
i) It removes all types of impurities like ionic, non-ionic, colloidal etc.

ii) Easy to operate

iii) Low operating cost.

iv) Pure water for high pressure boiler can be obtained.

v) If the SPM is specially prepared such that it allows limited quantity of salts to pass through it along with water, the RO technique is used to obtain drinking mineral water.



III Electrodialysis:

a) Definition:-The process of removing dissolved ionic impurities from water by using ion selective membranes and electric field.

b) Construction and Working:-

- An electrodialysis cell consists of a large number of paired sets of plastic membranes.
- The membranes are ions-selective.
e.g. A cation selective membrane will allow only cations to pass through it, as this membrane consists of negatively charged fixed groups which repel anions and do not allow to go through Cgroups on membrane, $-SO_3^{\ominus}$, $-(COO)^{\ominus}$ etc)
- The anion selective membrane allows only anions to pass through and the plastic membrane has cations repelling groups like $-NR_3^+$.
- When an electric field is applied, perpendicular to the direction of flow of water, the anions move towards positively charged electrode through the anion selective membrane in the neighbouring compartment but after that there is cation selective membrane and the movement stopped.
- Similarly cations move in the direction of negatively charged electrode and go in neighbouring compartment. They cannot move further because next is anion selective membrane.
- The result will be alternate compartments with very high concentration of electrolytes and neighbouring compartments to them with negligible conc. of ionic substance. Thus we get alternate streams of pure water from the electrodialysis cell.

c) Applications :-

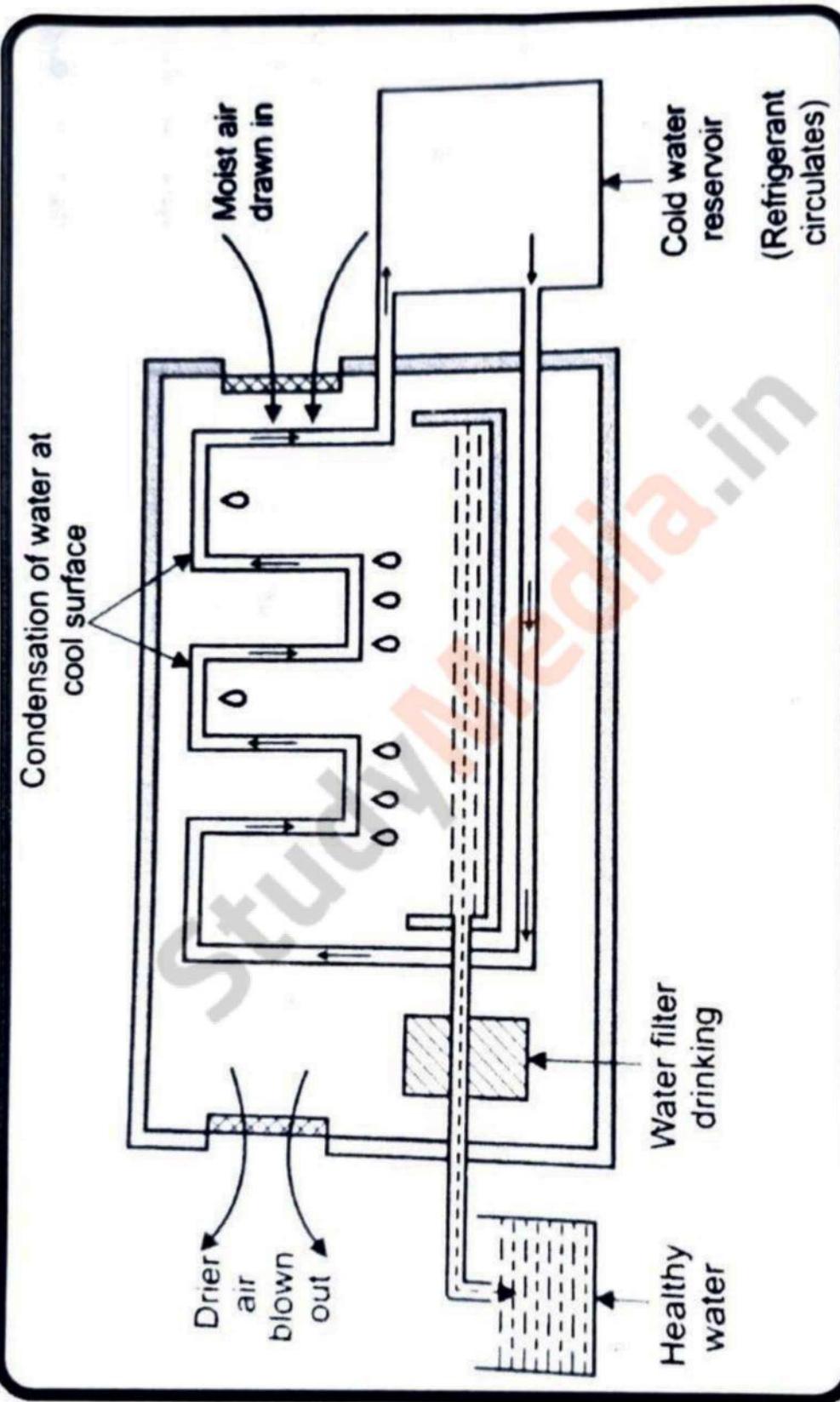
- i) Removal of ionic pollutants (toxic salts, ionic dyes, etc.) from treated industrial waste.
- ii) Removal of salts from sea water, to get pure water.
- iii) Salts rich outlet water can be used to recover salts.

d) Limitations:

- i) Does not remove dissolved organic matter.
- ii) Does not remove colloidal impurities.
- iii) Frequent maintenance or replacement of membranes required.

* Modern Technique for Atmospheric Water Generation:

- Half of the world population could be living in areas with water stress as early as 2025 according to a United Nations Report.
- In India, where ground water is critical for food security and drinking, is already grappling with water-table decline. This alarming trend highlights the urgent need for sustainable water solutions in India and around the world.
- Instead of digging deeper wells and transporting water over long distances, converting atmospheric water vapour to liquid water could be promising alternative solution. But practically to achieve this, there are many challenges.
- Some techniques are developed for trapping water from air which are based on an Atmospheric Water Generator (AWG). It is a device that extracts water from



* Atmospheric Water Generator *

humid ambient air, producing potable water.

Nowadays, AWA techniques used for trapping water from air are as follows;

1) Using the Dew point:-

- The most common method for harvesting moisture from the air is using the dew point. The dew point is the temperature at which air containing a certain amount of humidity becomes saturated with moisture, at this point, the moisture can condense out of the air.
e.g. When the air temp. is 25°C and the relative humidity is 35%, the dew point is 8.5°C . If the 25°C warm air has 65% relative humidity, the dew point is 18°C .

Formula to calculate dew point is;

$$T_d = T - \left[\frac{100 - RH}{5} \right]$$

where,

T_d = Dew point temperature ($^{\circ}\text{C}$)

T = Observed temperature ($^{\circ}\text{C}$)

RH = Relative humidity (%)

- Many organisms in nature have evolved to take advantage of this relationship by utilizing variations in temp. throughout the day to store moisture.

For instance, during the night, when the temp. drops in tropical Australia, tree frogs seek out cool, enclosed spaces where the humidity in the air is higher. Here, water vapour condenses and wets the frog by contacting its chilly skin.

Desert cactuses allow droplets to condense at the tips of their spines, where they are then directed via a channel system to the stem, taking advantage of physical forces such as capillaries.

2) Using Heat Exchange Technologies:-

- This technique can be used independent of the time of the day. It is electrically driven heat exchanger technique called as Atmospheric Water Generators (AWGs).
- An AWG device draws in atmospheric air usually using a fan and regulates it over cooled plates where water vapours from air condense into liquid water. This water is collected, filtered and sometimes supplemented with minerals to use as healthy drinking water.
- AWGs require energy to work, so it is always necessary to have a charged battery, a power socket or a solar panel nearby.

3) Using Brine - Base Solutions:-

- An entirely different way to harvest water from the atmosphere is the use of hygroscopic salts.
- Deliquescent salts, such as Calcium chloride, capture water molecules passively through the hydration process, which involves chemical and physical absorption. They form highly concentrated solutions that attract more moisture from the environment.

* Challenges to Air Water Extraction system:-

- i) Air water extraction device may not work in dry and cold climates.

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