

Engineering Chemistry

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Unit 1: Dissolved Mineral Matter in Water

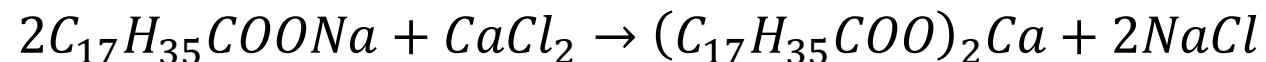
Most Important dissolved mineral matter in water

from **Industrial application** point of view): **Hardness & Alkalinity**

Hardness: Defined as **soap consuming capacity** of a water sample (mainly due to the presence of Ca & Mg ions)

What are Soaps?

Soaps are sodium salts of long chain fatty acids such as oleic acid, palmitic and stearic acid
Ca & Mg ions react with sodium salts of long chain fatty acids present in the soap to form insoluble scums of calcium and magnesium soaps which do not possess any detergent value
(*does not produce lather or foam*)



Water hardness is classified by the **U.S. Department of Interior and the Water Quality Association** as follows:

Classification mg/l or ppm

- Soft 0 - 17.1
- Slightly hard 17.1 - 60
- Moderately hard 60 - 120
- Hard 120 - 180
- Very hard 180 & over

S.No.

Parameters

**Drinking water
IS 10500 : 2012**

Permissible Limit

**Maximum
Limit**

1	Odor	Agreeable	Agreeable
2	Taste	Agreeable	Agreeable
3	pH	6.5 to 8.5	No relaxation
4	TDS (mg/l)	500	2000
5	Hardness (as CaCO ₃) (mg/l)	200	600
6	Alkalinity (as CaCO ₃) (mg/l)	200	600
7	Nitrate (mg/l)	45	No relaxation
8	Sulfate (mg/l)	200	400
9	Fluoride (mg/l)	1	1.5
10	Chloride (mg/l)	250	1000
11	Turbidity (NTU)	5	10
12	Arsenic (mg/l)	0.01	0.05
13	Copper (mg/l)	0.05	1.5
14	Cadmium (mg/l)	0.003	No relaxation
15	Chromium (mg/l)	0.05	No relaxation
16	Lead (mg/l)	0.01	No relaxation
17	Iron (mg/l)	0.3	No relaxation
18	Zinc (mg/l)	5	15
19	Fecal Coliform (cfu)	0	0
20	E. Coli (cfu)	0	0

Unit 1: Hardness of Water

Hard Water: Does not produce lather with soap solution, forms precipitate

Soft water: Lathers easily with soap solution

Types of Hardness:

1. Temporary Hardness (Carbonate Hardness or Alkaline Hardness)

Due to the presence of dissolved impurities in water like bicarbonates of Ca, Mg, Fe, Al, Mn that can be removed from water by merely boiling followed by filtration.

When natural water is boiled, the soluble bicarbonate ions present get decomposed and form insoluble carbonates or hydroxides.



Thus, temporary hardness causing impurities can be easily removed by boiling and filtration

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Unit 1: Hardness of Water



Types of Hardness:

2. Permanent Hardness (Non-Carbonate Hardness or Non-Alkaline Hardness)

Due to the presence of dissolved impurities in water like chlorides, sulphates and nitrates of Ca, Mg, Fe, Al, Mn etc.

These salts cannot be removed by merely boiling, needs special water softening methods to remove permanent hardness of water.

Temporary and permanent hardness together called as total hardness of water.

$$\text{Total Hardness} = \text{Temporary Hardness} + \text{Permanent Hardness}$$

Unit 1: Hardness of Water



Degree of Hardness:

- Total hardness present in water is because of different salts of calcium and magnesium with different molecular weights.
- Hence, **hardness of water** is conveniently **expressed in terms of calcium carbonate equivalence**.
- The weights of different salts causing hardness are converted to weight equivalent to that of calcium carbonate.
- If a water sample contains 2 or more salt their quantities are converted to calcium carbonate equivalence and the sum will give total hardness in terms of calcium carbonate equivalence.

Unit 1: Hardness of Water



Degree of Hardness:

- Degree of hardness is defined as the number of parts by weight of calcium carbonate hardness per particular number of parts of water, depending upon the unit employed.
- Though the hardness does not always arise due to calcium carbonate in water, it is a standard practice to express it in terms of **equivalents of CaCO_3** . **WHY ??????**
- Calcium carbonate is selected for expression of degree of hardness because:
 - its molecular weight is exactly 100 which makes calculation convenient
 - it is the most insoluble salt that can be precipitated out of water

Unit 1: Hardness of Water

Degree of Hardness:

The CaCO_3 equivalent for any dissolved salt in water can be calculated as:

$$\text{CaCO}_3 \text{ equivalent of any salt} = \text{Weight of salt present (mg/l)} \times \frac{\text{Equivalent weight of CaCO}_3}{\text{Equivalent weight of salt}}$$

$$\text{CaCO}_3 \text{ equivalent of bivalent salt} = \text{Weight of salt present (mg/l)} \times \frac{\text{Molecular weight of CaCO}_3}{\text{Molecular weight of salt}}$$

Unit 1: Hardness of Water

Units of Hardness:

1. Parts per Million (ppm): It is the number of equivalent parts of CaCO_3 present per million parts (10^6) parts of water by weight
 2. Milligram per liter (mg/l): It is the number of mg of CaCO_3 dissolved in 1 litre of water.
 3. Degree Clarke ($^\circ\text{Cl}$): It is the number of equivalent parts of CaCO_3 present per 70,000 parts of water or 1 gallon of water
 4. Degree French ($^\circ\text{Fr}$): It is the number of equivalent parts of CaCO_3 present per 10^5 parts of water
- 1 mg/l = 1 ppm (Prove)**

Numericals: Hardness of Water

↳ Conversion

$$\text{Mg}(\text{HCO}_3)_2 = \frac{7.3 \times 100}{146} = 5 \text{ mg/L}$$

$$\text{Ca}(\text{HCO}_3)_2 = \frac{16.2 \times 100}{162} = 10 \text{ mg/L}$$

$$\text{MgCl}_2 = \frac{9.5 \times 100}{95} = 10 \text{ mg/L}$$

$$\text{CaSO}_4 = \frac{13.6 \times 100}{136} = 10 \text{ mg/L}$$

$$\text{T.H} = \text{Ca}(\text{HCO}_3)_2 + \text{Mg}(\text{HCO}_3)_2$$
$$= 10 + 5$$

$$\boxed{\text{T.H} = 15 \text{ mg/L}}$$
 ✓

$$\text{P.H} = \text{MgCl}_2 + \text{CaSO}_4$$
$$= 10 + 10$$

$$\boxed{\text{P.H} = 20 \text{ mg/L}}$$
 ✓

NaCl does not contribute in hardness

A) Convert all salts into CaCO_3 eqvt

$$1) \text{Ca}(\text{HCO}_3)_2 = \frac{12.2 \times 100}{162} = 7.53 \text{ mg/l}$$

$$2) \text{Mg}(\text{HCO}_3)_2 = \frac{8.2 \times 100}{146} = 5.62 \text{ mg/l}$$

$$3) \text{MgSO}_4 = \frac{5.6 \times 100}{120} = 4.67 \text{ mg/l}$$

$$4) \text{MgCl}_2 : \frac{6.2 \times 100}{95} = 6.52 \text{ mg/l}$$

$$5) \text{CaSO}_4 = \frac{10.3 \times 100}{136} = 7.57 \text{ mg/l}$$

$$\begin{aligned} \text{B) T.H} &= \text{Ca}(\text{HCO}_3)_2 + \text{Mg}(\text{HCO}_3)_2 \\ &= 7.53 + 5.62 \\ &= 13.14 \text{ mg/l} \end{aligned}$$

$$\begin{aligned} \text{C) P.H.} &= \text{MgSO}_4 + \text{MgCl}_2 + \text{CaSO}_4 \\ &= 4.67 + 6.52 + 7.57 \\ &= 18.76 \text{ mg/l} \end{aligned}$$

$$\begin{aligned} \text{D) Total Hardness} &= \text{TH} + \text{PH} \\ &= 13.14 + 18.76 \\ &= 31.1 \text{ mg/l} \end{aligned}$$

Unit 1: Chemical analysis of water



Determination of Hardness of Water by EDTA Method:

The hardness of water can be determined by complexometric titration.

Complexometric titrations involve formation of a soluble complex between a metal ion and a complexing agent.

Metal ion is called the **central atom** and the **complexing agent** is called the **ligand**. The ligands can be unidentate, bidentate or polydentate having one, two and more than two donor atoms respectively which can form stable complexes.

The polydentate ligands form stable complexes with wide variety of metals as these ligands form ring structures called chelates.

EDTA is used as **complexing agent** in determination of **hardness** of water

Unit 1: Chemical analysis of water

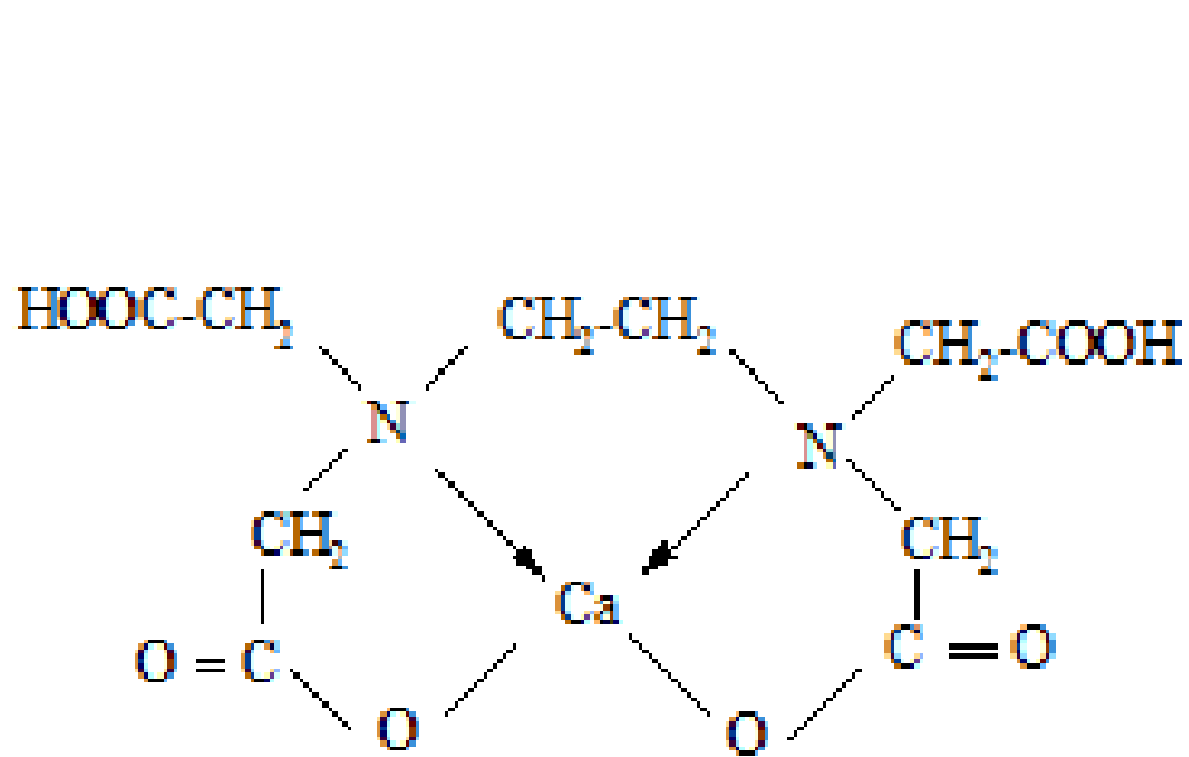
Determination of Hardness of Water by EDTA Method:

Ethylene Diamine Tetra Acetic acid (EDTA) is one of the notable ligands used as complexing reagent.

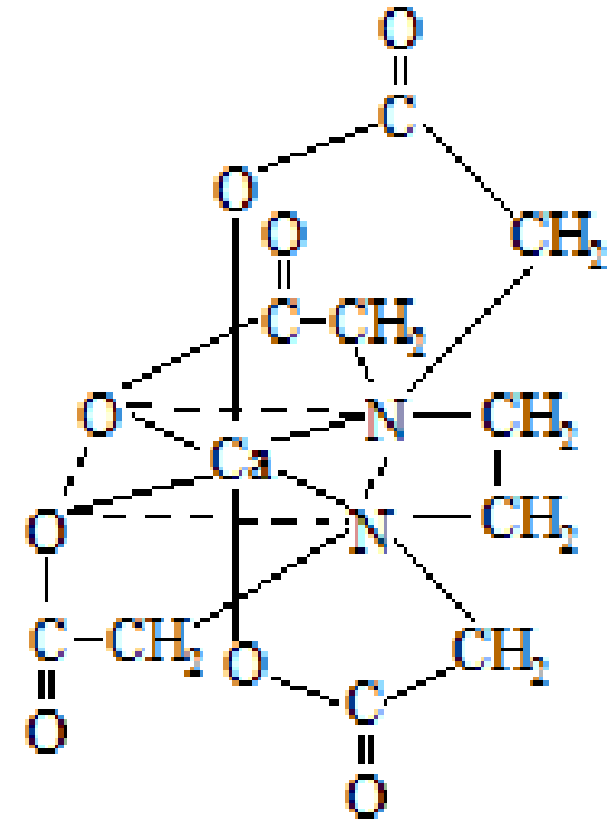
EDTA has six potential sites (hexadentate) for bonding a metal ion, the two amino groups and four carboxy group. When EDTA is dissolved in water, it forms zwitterion (an ion with a positive and a negative electrical charge at different locations within a molecule). The various EDTA species are abbreviated as H_4Y , H_3Y^- , H_2Y^{2-} , HY^{3-} and Y^{4-} . EDTA forms stable complexes (chelates) with the metal ions.

Because of limited solubility of EDTA, the disodium salt Na_2H_2Y is used for analytical work (high state of purity as the dihydrate)

Structure of EDTA & Ca-EDTA Chelate



A



B

Unit 1: Chemical analysis of water

Principle of EDTA Method:

- **EDTA** forms stable complexes (chelates) with the hardness causing metal (Ca or Mg) ions.
- **Hard water** titrated against Na_2EDTA in a complexometric titration.
- **Eriochrome Black-T (EBT) indicator** is used in complexometric titration. EBT is pH sensitive indicator and effective in alkaline condition (about pH 10).
- **Ammoniacal Buffer solution** ($\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$) is used to maintain pH of about 10 during a complexometric titration.
- EDTA a complexometric titration works as follows:

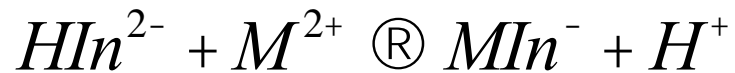
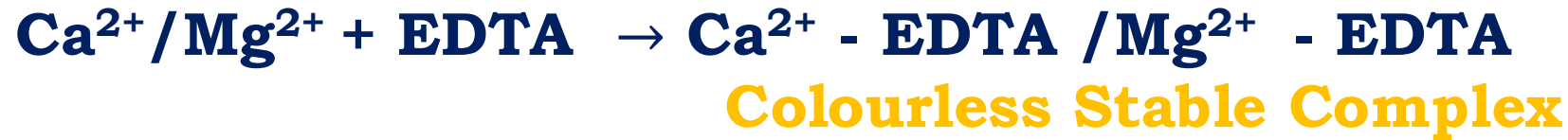
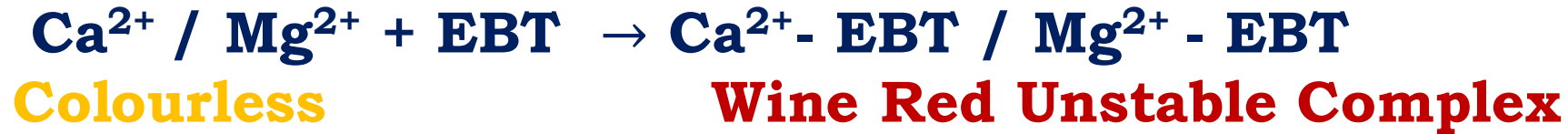
Unit 1: Chemical analysis of water

Principle of EDTA Method:

- EDTA solutions are used as Titrant in complexometric titration.
- Indicator EBT, which is a blue-coloured dye, forms an unstable & soluble wine-red color complex with Ca and Mg ions in hard water at a pH of 9 to 10.
- When unstable wine-red color complex is treated with EDTA solution, EDTA being more sensitive replaces Ca^{2+} and Mg^{2+} ions from the unstable indicator complex to form a stable complex, with the result, indicator is set free giving its original blue color.
- $[\text{Mg}^{2+} / \text{Ca}^{2+} - \text{EBT}] + \text{EDTA} \rightarrow [\text{Mg}^{2+} / \text{Ca}^{2+} - \text{EDTA}] + \text{EBT}$
(**Wine-red**) (Colourless) (Blue)
- Thus, in EDTA complexometric titration using EBT indicator, the **end point** is **wine-red turns blue**
- Thus, the amount of EDTA consumed in titration corresponds to the hardness of water.

Unit 1: Chemical analysis of water

Reactions:



Unit 1: Chemical analysis of water

Procedure to find Total Hardness of Water Volumetrically:

1. Standardisation of EDTA:

- Prepare standard ZnSO_4 solution (of exact M_1 molarity)
- Fill the burette with EDTA solution (of approximate M_2 molarity)
- Pipette out V_1 ml of standard ZnSO_4 solution in a conical flask
- Add one-third test tube of ammoniacal buffer solution and few drops of EBT indicator
- Wine red coloured solution is then titrated against EDTA solution from burette till colour changes to blue.
- Note down the end point as V_2 ml (EDTA consumed)

(Standardisation: To get the Exact molarity of EDTA solution using primary standard substance)

Unit 1: Chemical analysis of water

Procedure to find Total Hardness of Water Volumetrically:

2. Estimation of total hardness of water:

- Fill the burette with EDTA solution
- Pipette out V ml of hard water in a conical flask
- Add one-third test tube of ammoniacal buffer solution and few drops of EBT indicator
- Wine red coloured solution is then titrated against EDTA solution from burette till colour changes to blue.
- Note down the end point as 'Y' ml (volume of EDTA consumed)

Unit 1: Chemical analysis of water

Procedure to find Total Hardness of Water Volumetrically:

3. Calculations to find total hardness of water:

- For standardisation of EDTA: Using, $M_1V_1 = M_2V_2$ (ZnSO₄ vs EDTA)

Exact Molarity of EDTA can be found out.

- Calculation of total hardness of water: EDTA forms 1 : 1 complex with Ca and Mg ions
- 1 mole of EDTA = 1 mole of CaCO₃
- 1000 ml of 1 M EDTA = 100 g of CaCO₃
- 1 ml 1 M EDTA = 100 mg of CaCO₃
- 'CBR' ml M₂ EDTA = 100 x 'CBR' x M₂ mg of CaCO₃
- V ml water sample contains = mg of CaCO₃

$$\text{Hardness of water sample} = \frac{100 \times \text{Volume of EDTA consumed (ml)} \times \text{Molarity of EDTA} \times 1000}{\text{Volume of water sample (ml)}} \text{ ppm}$$

1 ml 1M EDTA \equiv 100 mg CaCO_3 eqvt.

Y ml ' M_2 ' M EDTA \equiv ? $=(100 \times Y \times M_2)$ mg CaCO_3 eqvt

' V ' ml Hard water \longrightarrow $(100 \times Y \times M_2)$ mg CaCO_3
 1000 ml \longrightarrow ?

$$\text{Hardness} = \frac{100 \times 1000 \times Y \times M_2}{V \text{ (ml)}} \quad \begin{array}{l} \text{mg/l} \\ \text{or} \\ \text{ppm} \end{array}$$

Numericals



1. 250 mL of a water sample on EDTA titration with Eriochrome Black –T consumed 13 mL of 0.022 N EDTA till end point is reached. Calculate the hardness of water.
2. (Hardness = 114.4 ppm)
3. 100 mL of a sample of water required 15 mL of 0.01 M EDTA for titration using Eriochrome Black –T as indicator. In another experiment, 100 mL of the same sample was boiled to remove the temporary hardness, the precipitate was removed and the cold solution required 8 mL of 0.01 M EDTA using Eriochrome Black –T as indicator. Calculate the total hardness, permanent hardness and temporary hardness in mg/L of CaCO_3 equivalent.
4. (Total Hardness = 150 ppm, PH=80 ppm & TH=70ppm)

3. 100 mL of the hard water sample required 35 mL of the same EDTA solution on titration. After boiling 100 mL of this water, cooling, filtering and then titration required 10 mL of EDTA solution. Calculate the temporary and permanent hardness of water.

(Total hardness = 350 ppm, Permanent Hardness = 100 ppm, Temporary Hardness = 250 ppm.)

Alkalinity of water



Alkalinity is a measure of the ability of water to neutralize the acids

- The alkalinity of water is normally due to the presence of **bicarbonates, carbonates** and **hydroxides** of sodium, potassium, calcium and magnesium.
- Some of the salts, which cause alkalinity, also cause hardness, but not all. (However, the presence of other bases such as borates, silicates, phosphates can also contribute to the total alkalinity, though to a small extent)

Alkalinity of water

Classification of Alkalinity: Alkalinity based on the anions present in the water is classified as:

1. Caustic Alkalinity (due to Hydroxide and Carbonate ions)
2. Bicarbonate Alkalinity (due to Bi-carbonate ions)

Alkalinity of a water sample due to different ions can be **determined by neutralization titration** using a **standard acid** and making selective use of indicators. The indicators used are **Phenolphthalein** and **Methyl orange**.

Alkalinity of water

Reactions: The determination is based on following reactions

- i. $\text{OH}^- + \text{H}^+ \rightarrow \text{H}_2\text{O}$
- ii. $\text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{HCO}_3^-$
- iii. $\text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{CO}_3$

- Reaction 1 and 2 corresponds to Phenolphthalein (P) end point i.e. complete neutralization of OH^- and half neutralization of CO_3^{2-}
- Reaction 1 to 3 corresponds to Methyl Orange (M) end point i.e. complete neutralization of OH^- , CO_3^{2-} and HCO_3^- ions.

Alkalinity of water

Alkalinity may be due to presence of following combinations:

- 1) Alkalinity due to HCO_3^- only
- 2) Alkalinity due to CO_3^{--} only
- 3) Alkalinity due to OH^- only
- 4) Alkalinity due to CO_3^{--} and HCO_3^- ions
- 5) Alkalinity due to OH^- and CO_3^{--}

The possibility of OH^- and HCO_3^- together is ruled out, they combine instantaneously to form CO_3^{--} ions, thus all ions cannot exist together.

Thus, on the basis of Phenolphthalein alkalinity and methyl orange alkalinity, the alkalinity in water due to different ions can be calculated.

Alkalinity of water

Procedure:

- Pipette out 100 mL of the water sample in a clean titration flask.
- Add 2–3 drops of phenolphthalein indicator.
- Run in N/50 H_2SO_4 or HCl (from a burette), till the pink color is just discharged. This is the first end point.
- Let the volume of acid used until phenolphthalein end point = V_1 mL.
- Then to the same solution, add 2 to 3 drops of methyl orange. Continue titration, till the yellow colour changes to orange/red. This is the second end point.
- Let *volume* of acid used to methyl orange end point = V_2 mL.

Alkalinity of water

OBSERVATIONS:

Volume of water sample (unknown alkalinity) selected = _ ml

For Phenolphthalein end point

- Burette: HCl solution of _____N
- Indicator: Phenolphthalein
- End point: Pink turns colourless
- Volume of titrant (HCl) consumed, V_1 = _____ml

For Methyl orange end point

- Burette: HCl solution of _____N
- Indicator: Methyl Orange
- End point: Yellow turns orange/red
- Volume of titrant (HCl) consumed, V_2 = _____ml

Alkalinity of water



CALCULATIONS:

$$\text{Phenolphthalein Alkalinity (P)} = \frac{50 \times \text{Volume of acid consumed (ml)} \times \text{Normality of acid} \times 1000}{\text{Volume of water sample (ml)}}$$

$$\text{Methyl Orange Alkalinity (M)} = \frac{50 \times \text{Volume of acid consumed (V2)} \times \text{Normality of acid} \times 1000}{\text{Volume of water sample}}$$

From the measurement of Phenolphthalein alkalinity and methyl orange alkalinity, it is possible to calculate the magnitude of various forms of alkalinity present in water sample,

Alkalinity of water



Sr. No.	Alkalinity	OH^- (ppm)	CO_3^{2-} (ppm)	HCO_3^- (ppm)
1	$P = 0$	NIL	NIL	M
2	$P = \frac{1}{2} M$	NIL	2P	NIL
3	$P < \frac{1}{2} M$	NIL	2P	(M - 2P)
4	$P > \frac{1}{2} M$	(2P - M)	2 (M - P)	NIL
5	$P = M$	P = M	NIL	NIL

Alkalinity of water

- (i) When **P = 0**, both OH^- and CO_3^{2-} are absent and alkalinity in that case is due to **HCO_3^-** alone.
- (ii) When **P = M** neither CO_3^{2-} nor HCO_3^- ions are present, only OH^- ions are present, Thus alkalinity due to **OH^-** = P = M.
- (iii) When **P = 1/2 M** or $V_1 = V_2/2$, only CO_3^{2-} is present, since half of carbonate neutralisation (ie $\text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{HCO}_3^-$) takes place with phenolphthalein, while complete carbonate neutralisation ($\text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{HCO}_3^-$; $\text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{O} + \text{CO}_2$) occurs when methyl orange indicator is used. Thus, alkalinity due to **CO_3^{2-}** = 2P.

Alkalinity of water

(iv) When **$P > 1/2 M$** or $V_1 > V_2/2$ In this case, besides CO_3^{2-} , OH^- ions are also present.

Now half of CO_3^{2-} (i.e., $\text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{O} + \text{CO}_2$) is equal to $(M - P)$, so alkalinity due to complete **$\text{CO}_3^{2-} = 2(M - P)$** and alkalinity due to **$\text{OH}^- = M - 2(M - P) = (2P - M)$** .

(v) When **$P < 1/2 M$** or $V_1 < V_2/2$, in this case, besides CO_3^{2-} , HCO_3^- ions are also present, now alkalinity due to **$\text{CO}_3^{2-} = 2P$** and alkalinity due to **$\text{HCO}_3^- = (M - 2P)$** .

Numericals on Alkalinity of water



1. 50 mL of a sample of water required 5 mL of N/50 H_2SO_4 using methyl orange as indicator but did not give any coloration with phenolphthalein. What type of alkalinity is present? Express the same in ppm. (**P=0, Only HCO_3^-**)
2. 200 mL of water sample on titration with N/50 H_2SO_4 using phenolphthalein as indicator gave the end point when 10 mL of acid were run down. Another lot of 200 mL of the sample also required 10 mL of the acid to obtain methyl orange end point. What type of alkalinity is present in the sample and what is its magnitude? (**P=M/2, Only CO_3^{--}**)
3. 500 mL of a water sample on titration with N/50 H_2SO_4 gave a titre value of 29 mL to phenolphthalein end point and another 500 mL sample on titration with same acid gave a titre value of 58 mL to methyl orange end point. Calculate the alkalinity of the water sample in terms of CaCO_3 and comment on the type of alkalinity present.

Numericals on Alkalinity of water

- A sample of water was alkaline to both phenolphthalein and methyl orange. 100 mL of this water sample required 30 mL of N/50 H_2SO_4 for phenolphthalein end point and another 20 mL for complete neutralisation. Determine the type and extent of alkalinity present.
- (**$P = 300 \text{ ppm}$, $M = 500 \text{ ppm}$** ; Since $P > M/2$, **$\text{OH}^- \text{ alkalinity} = 100 \text{ ppm}$ $\text{CO}_3^{2-} \text{ alkalinity} = 400 \text{ ppm}$**)
- A water sample is alkaline to both phenolphthalein as well as methyl orange. 200 mL of this water sample on titration with N/50 HCl required 9.4 mL of the acid to phenolphthalein end point. When a few drops of methyl orange are added to the same solution and titration is further continued, the yellow color of the solution just turned red after addition of another 21 mL of the acid solution. Elucidate on the type and extent of alkalinity present in the water sample.
- (**$P = 47 \text{ ppm}$, $M = 152 \text{ ppm}$** , $P < M/2$, **$\text{HCO}_3^- \text{ alk.} = 58 \text{ ppm}$ & $\text{CO}_3^{2-} \text{ alk.} = 94 \text{ ppm}$**)

Unit 1: Water Softening Techniques



Water Softening:

Process of converting hard water into soft water. Softening methods are of 2 types:

1) Internal Treatment

2) External Treatment Process: Based on following Principle

1) Precipitation 2) Ion-exchange

a) Zeolite Method or Permutit Process

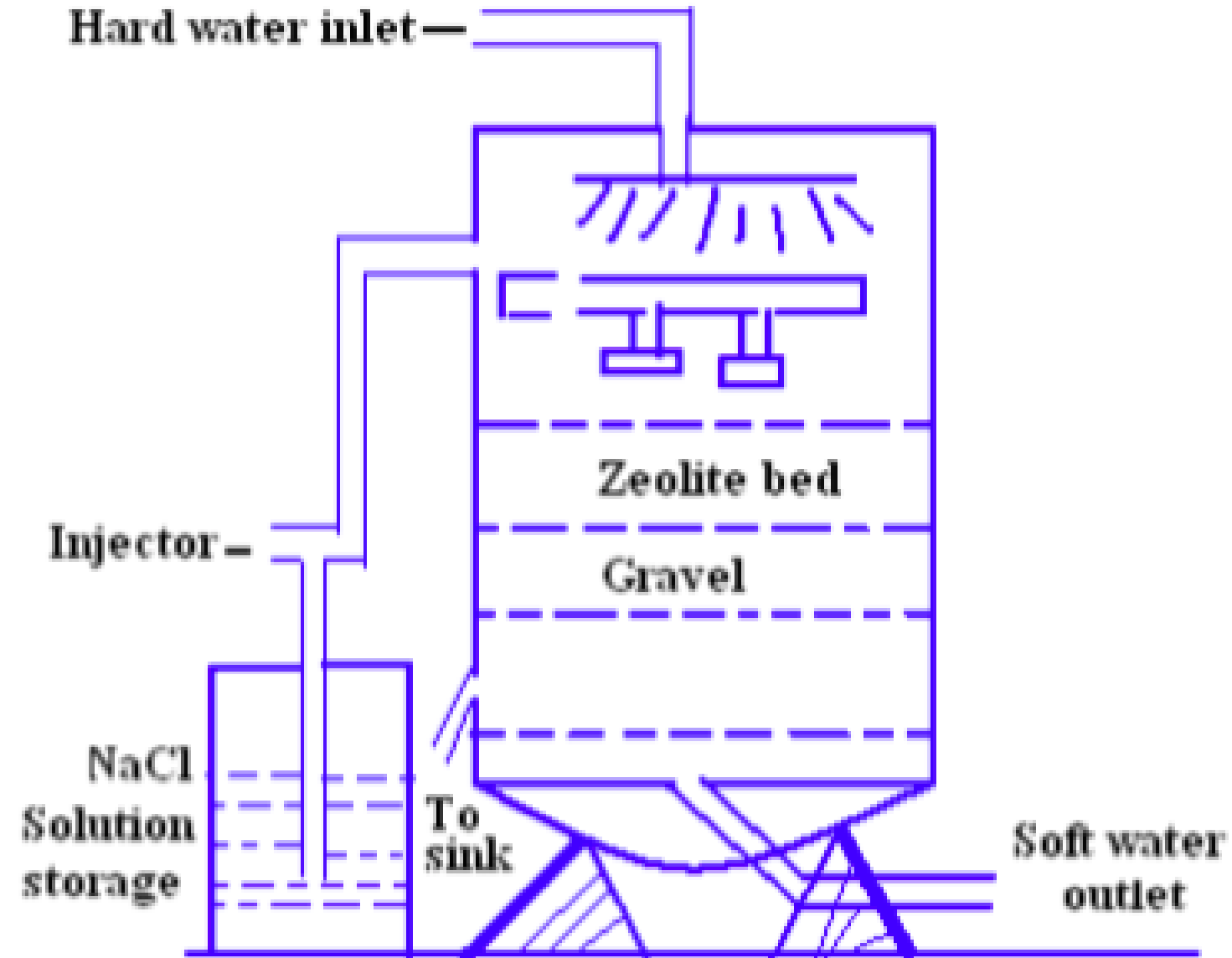
b) Demineralization or Deionization Method

c) Lime Soda Method (Hot/Cold)

Zeolite Method

- Zeolites are also known as permutit and in Greek it means 'boiling stone'. They occur naturally as hydrated alumino silicate minerals like **$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x \text{SiO}_2 \cdot y \text{H}_2\text{O}$**
- where $x = 2-10$ and y is $2-6$. They are capable of exchanging reversibly sodium ions for hardness producing ions in water.
- 1. *Natural Zeolites* Non porous, amorphous and durable, for example, Natrolite **$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$**
- 2. *Synthetic Zeolites* Porous with gel-like structure. They are prepared by heating sodium carbonate (Na_2CO_3), alumina (Al_2O_3) and silica (SiO_2).

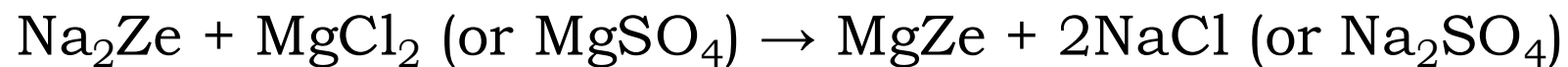
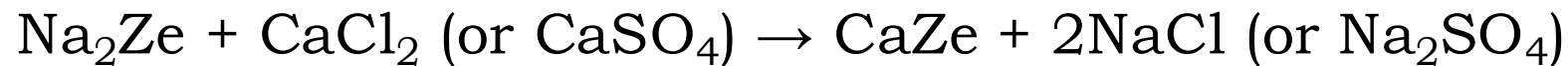
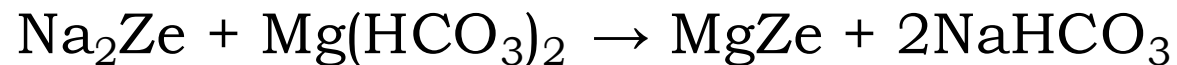
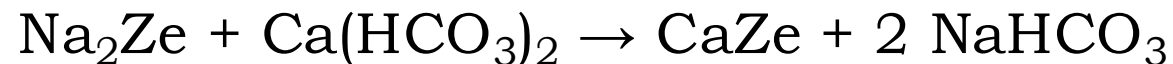
Zeolite Softener



Zeolite Method

- **Process** Hard water is percolated at a specified rate through a bed of zeolite stacked in a cylindrical unit. The hardness causing elements (Ca^{2+} , Mg^{2+} etc) are retained by zeolite as CaZe and MgZe , while the outgoing water contains sodium salts.

- The chemical reactions involved are



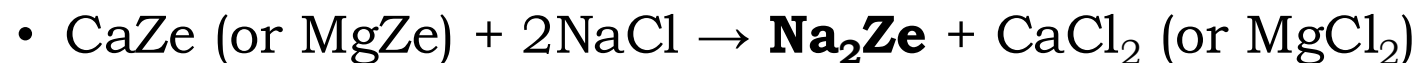
Zeolite Method



- After some time, all the sodium ions in zeolite are replaced by Ca and Mg ions giving CaZe/ MgZe. Such a zeolite bed is unable to soften water further and is said to be exhausted. It has to be regenerated to enable it to soften water again. It may be noted that the water obtained by zeolite process is used mostly for laundry purpose; it cannot be used in boilers.

- **Regeneration**

- When the zeolite bed is exhausted the supply of hard water is stopped and it is regenerated by treating with a concentrated brine (10% NaCl) solution.



(exhausted zeolite) (Brine) **Reclaimed** (Washings)

Zeolite Method

- The washings (containing CaCl_2 , MgCl_2 , etc.) are led to drain and the regenerated zeolite bed is used again for softening. (NaNO_3 , KCl , KNO_3 , etc. can also be used for regeneration instead of NaCl , but NaCl is mostly used because of its low cost and the products of regeneration process (CaCl_2 or MgCl_2 ,) are highly soluble and can be easily rinsed out of the zeolite bed).
- By knowing the amount of NaCl used for regeneration of the exhausted zeolite bed, the hardness of the water sample can be calculated by using the formula.

$$\text{Hardness (H)} = 50 \times m \times V_1 \times 10^3 / 58.5 \times V$$

V = Total Volume of water softened in litres;

V_1 = Total volume of NaCl used for regeneration and

M = amount of NaCl in g/L present in V_1

Zeolite Method



- **Advantages of Zeolite Process**

- Hardness is removed almost completely, and the residual hardness is about 10 ppm.
- The equipment is compact and occupies less space.
- It is a clean and rapid process. Sludge is not formed as the impurities are not precipitated.
- It requires less skill for maintenance as well as operation.

Zeolite Method

Limitations and Disadvantages of Zeolite Process

- Turbid water cannot be used as turbidity clogs the pores of zeolite bed making it inactive.
- Mn^{2+} and Fe^{2+} present must be removed first because these ions react with zeolite bed to give manganese and iron zeolites which cannot be easily regenerated.
- Mineral acids, if present in water, destroy the zeolite bed and hence they must be neutralised with soda in advance.
- This method does not remove anions. The bicarbonates present in hard water get converted into NaHCO_3 which goes into soft water effluent. If this water is used in boiler, NaHCO_3 dissociates as NaOH and CO_2 . NaOH leads to caustic embrittlement and CO_2 makes the water acidic and corrosive.
- The treated water contains more sodium salts.
- Moreover, high cost of the plant and material also acts as limiting factor.

Numericals on Zeolite Method



- A zeolite softener was used to remove the hardness of 95,000 liters of hard water completely. The softener required 475 liters of NaCl solution containing 18 g/liter of NaCl for regeneration. Calculate the hardness of hard water in ppm.

(Hardness (H) = 76.92 ppm)

- An exhausted zeolite softener was regenerated by 325 liters of NaCl solution containing 60 g/liter of NaCl. How many liters of hard water of hardness 250 mg/L can be softened by the zeolite softener.

(Total volume of hard water softened = 66666.67 liters)

1) Quantity of NaCl :

2) in terms of CaCO_3 eqvt. =

3) Quantity of water :

$$V_{\text{Water}} (l) \times \text{Hardness} \left(\frac{\text{mg}}{l} \right) = V_{\text{NaCl}} (l) \times \left(\text{NaCl} \frac{\text{mg}}{l} \right) \times \frac{50}{58.5}$$

$(\because 2 \text{NaCl} \equiv 1 \text{CaCO}_3)$

Numericals on Zeolite Method



1. A zeolite softener was completely exhausted and was regenerated by passing 100 liters of NaCl solution containing 120 g/liter of NaCl. How many liters of sample of water of hardness 500 ppm can be softened by this softener.

[Ans 20512.8 liters]

2. A zeolite softener was completely exhausted after softening 145,000 liters of hard water. To regenerate the zeolite softener 540 liters of NaCl solution containing 110 g/liter of NaCl is required. Calculate the hardness of one liter water sample in ppm.

[Ans 350.13 ppm]

3. 200 liters of NaCl solution containing 85 g/liter of NaCl was required to regenerate a completely exhausted zeolite softener. How many liters of hard water of hardness 600 ppm can be softened by the softener.

[Ans 24216.5 liters]

4. When a zeolite softener was completely exhausted it was regenerated by passing 200 liters of NaCl solution containing 120 g/liter of NaCl. How many liters of a sample of water of hardness 550 mg/liter can be softened by the zeolite softener before regenerating it again.

[Ans 37296.037 liters]

Unit 1: Purification of Water

Purification of Water: Performed by 2 processes

1. Membrane Process (RO & Electrodialysis)
2. Thermal Process (Distillation)

Membrane Process: Membranes are used in the water purification

Membranes act as barrier. Membranes blocks the different size molecules

Membranes are Organic, Inorganic and Biological (Kidney Tissues)

Types of Membranes:

Permeable

Impermeable

Semi-permeable

Selectively Permeable

Unit 1: Purification of Water

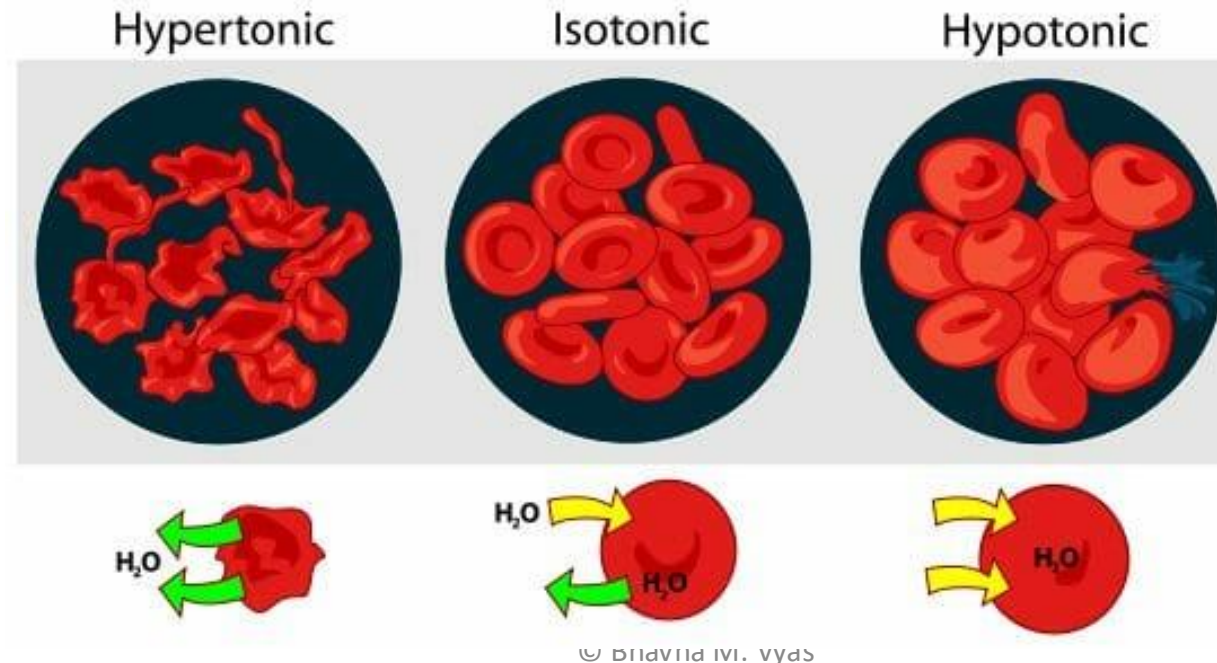


Key differences in Membranes:

- Permeable Membrane: Membrane which allows passage of all materials through it
- Impermeable Membrane: Membrane which does not allow the passage of materials through it.
- **Semi-permeable membrane:** Membrane which allows some materials (certain molecules or ions) to pass through it by diffusion or facilitated diffusion while blocking the passage of other molecules.
- **Selectively Permeable:** A membrane that is selectively permeable, i.e., being permeable to only certain molecules or ions and not to all molecules or ions.

Unit 1: Reverse Osmosis

Osmosis: Osmosis is the spontaneous net movement of solvent molecules through a selectively permeable membrane into a region of higher solute concentration due to difference in osmotic pressure, in the direction that tends to equalize the solute concentrations on the two sides. **Eg.: Roots of the plants absorbing water from the soil**



Unit 1: Reverse Osmosis

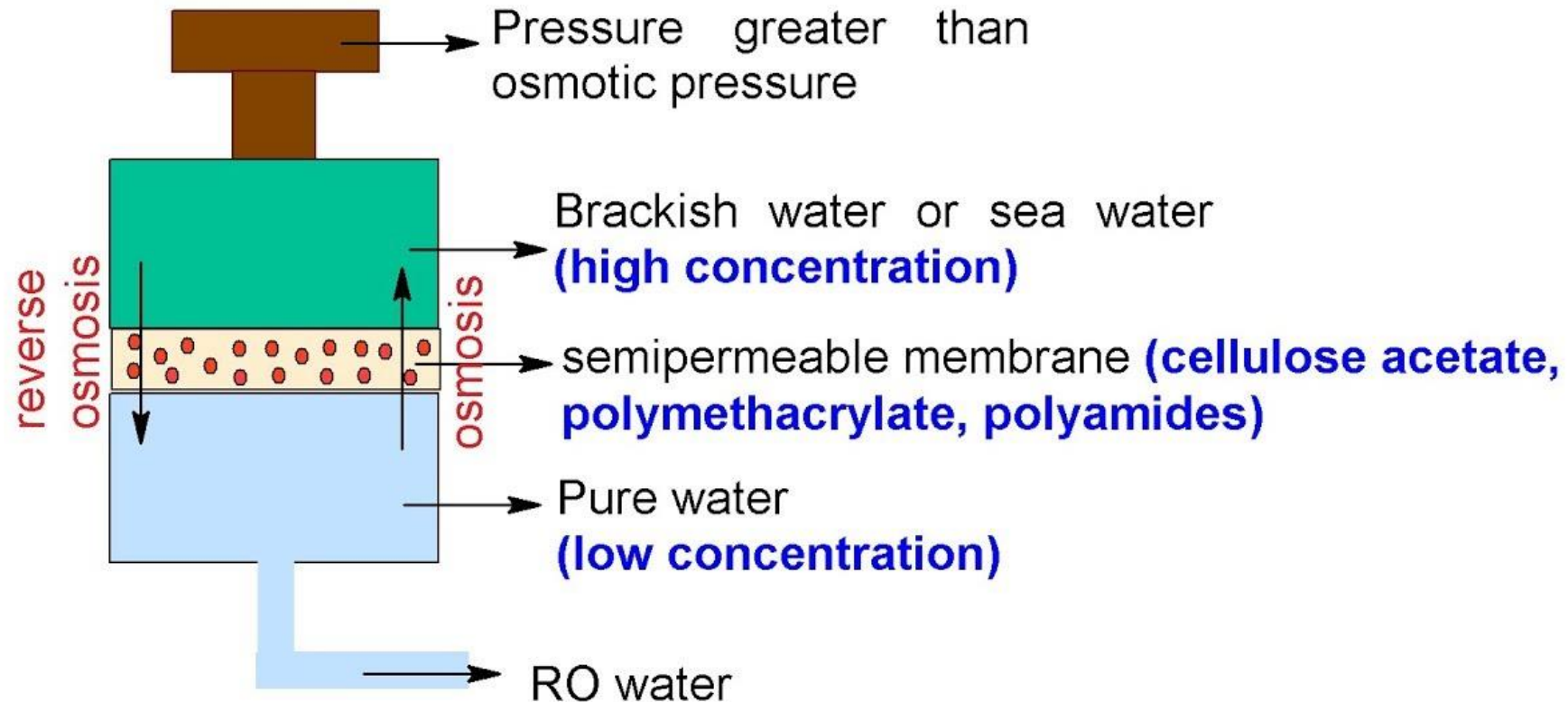
Reverse Osmosis System:

- It is a water purification process
- It uses a partially permeable membrane to separate ions, unwanted molecules and larger particles from contaminated or unfiltered water to obtain potable water.
- A semipermeable membrane has small pores that block contaminants but allow water molecules to flow through, which consists of very thin films of cellulose acetate, polymethacrylate, polyamides etc.
- Water flows from the more concentrated side (more contaminants) of the RO membrane to the less concentrated side (fewer contaminants) to provide clean drinking water.
- The fresh water produced is called the **permeate**. The concentrated water left over is called the **waste or brine**.
- In Reverse osmosis, pure water (solvent) is separated from its contaminants, rather than removing contaminants from the water. For example, when pressure is applied to a volume of saltwater during reverse osmosis, the salt is left behind and only clean water flows through.

- https://www.youtube.com/watch?v=4RDA_B_dRQ0

Unit 1: Reverse Osmosis

REVERSE OSMOSIS PROCESS



Unit 1: Reverse Osmosis

Distinct Advantages:

- It removes ionic as well as nonionic, colloidal and high MW organic matter.
- It removes colloidal silica which is not removed by demineralisation
- Maintenance cost is almost entirely on the replacement of semi permeable membrane
- Life of membrane is quite high almost 2 years
- Membranes can be replaced within few minutes
- Low capital cost low operating cost and high reliability

Unit 1: Electrodialysis

Electrodialysis:

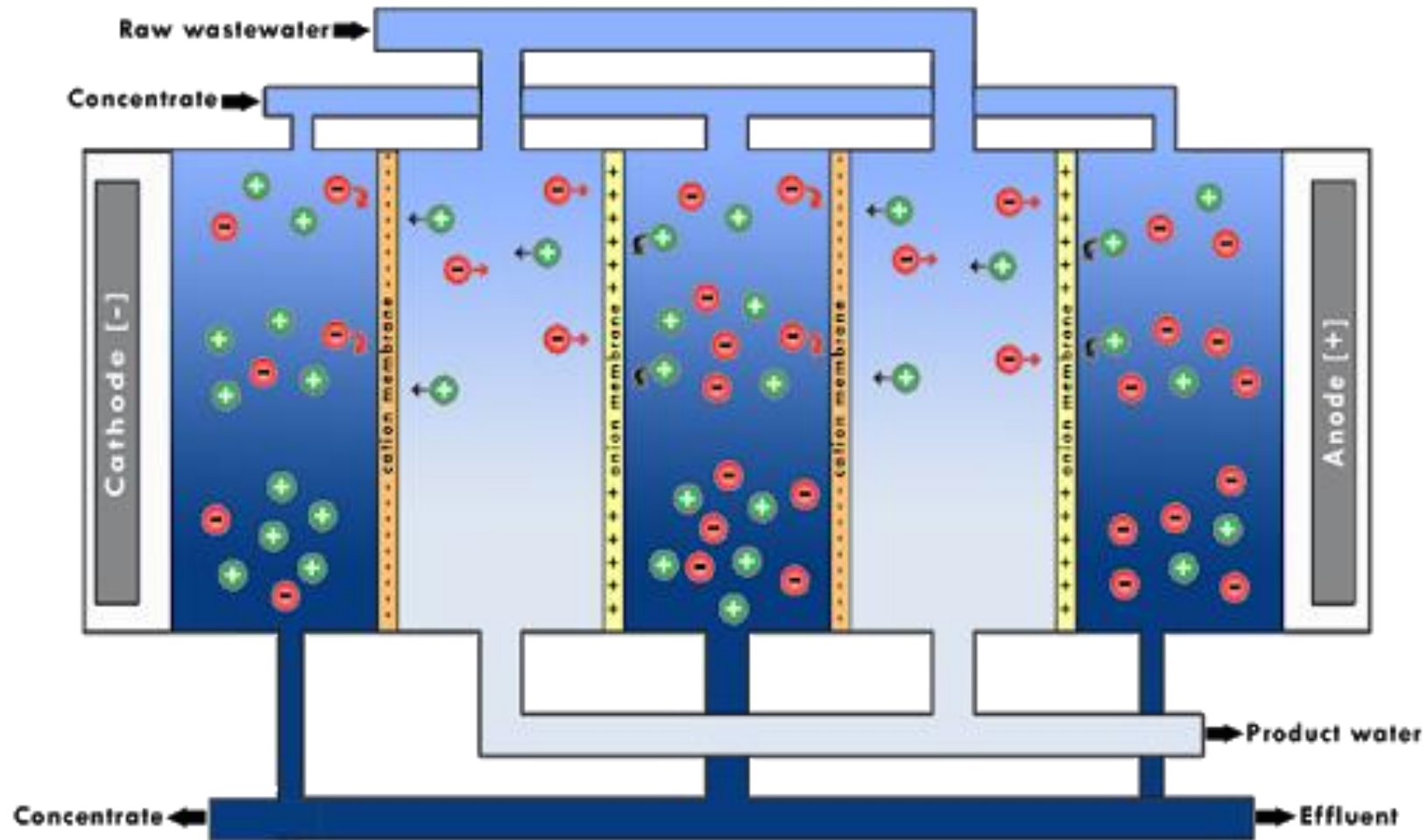
- For more **efficient separation** usually ion selective membranes are employed
- An **ion selective membrane** has permeability for only one kind of ions with specific charge
- **Cation selective membrane** is permeable to cation only because of presence of charged fixed functional groups inside the membrane which rejects anions
- Similarly, **anion selective membrane** has positively charged fixed functional groups which permeate anions only and rejects cations
- <https://www.youtube.com/watch?v=wYkkLUckmg4>

Unit 1: Electrodialysis

Electrodialysis:

- Electro Dialysis (ED) is a **membrane process**, during which ions are transported through semi permeable membrane, under the influence of an **electric potential**.
- By placing multiple membranes in a row, which alternately allow positively or negatively charged ions to flow through, the ions can be removed from wastewater.
- It is a method in which ions (of the salts presents) are pulled out of the salty water by passing direct current using electrodes and thin rigid plastic membranes (natural or synthetic)
- When direct electric current is passed through saline water the cations move towards negative pole (or cathode) while the anions start moving towards the positive pole (or anode) through its membrane
- As a result, the concentration of brine decreases in the central compartment while it increases in the side compartment

Unit 1: Electrodialysis



<https://www.youtube.com/watch?v=AFTWjU04yg4>

Unit 1: Electrodialysis

Electrodialysis Process:

- An Electro dialysis cell consist of large number of paired sets of rigid plastic membranes.
- Saline water is passed under pressure of about 5 to 6 kg/sq.m between membrane pairs and an electric field is applied **perpendicular to the direction** of water flow.
- Fixed positive charges inside the membrane repel positively charged ions yet permit negatively charged ions to pass through.
- Similarly, the fixed negative charged inside the other type of membrane repel negatively charged ions yet permit cations to pass through

Unit 1: Electrodialysis

Electrodialysis:

- Water in one compartment of cell is deprived of its salt while the salt concentration in adjacent compartment increases.
- Thus, we get alternate streams of pure water and concentrated brine.
- <https://www.youtube.com/watch?v=eW5efz2LTOo>

Advantages:

- Compact unit
- Economical cost of installation and operation
- Best suited if electricity is easily available

Unit 1: Electrodialysis

Limitations:

- Non-ionic matter cannot be removed
- Colloidal, silica cannot be removed

Applications of Electrodialysis:

- Used for conversion of sea water to potable water
- Desalination of boiler feed water for reuse
- Salt recovery from salt concentrated water

Design the Questions

Questions on RO & Electrodialysis:

1. Mention water purification processes
2. What is the principle of reverse osmosis?
3. How is sea water purified in reverse osmosis?
4. Explain desalination by reverse osmosis method
5. Explain electrodialysis for desalination of water with the help of a neat diagram

Thank You