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Department of Basic Sciences & Humanities

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Engineering Chemistry

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It is intended to supplement the prescribed textbooks and classroom discussions, offering students an accessible and structured reference for better understanding of the subject.

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MODULE 1: WATER

Learning Objectives

- To understand the types of impurities, present in water and their industrial impacts.
- To study the different types of hardness in water and appropriate softening methods.
- To learn modern water treatment technologies such as reverse osmosis and ion exchange.

Learning Outcomes

- Students will be able to **analyze water quality** and assess its suitability for various industrial and technological applications.
- Students will be able to **identify and differentiate types of hardness in water** and recommend appropriate softening methods.
- Students will gain the ability to **evaluate modern water treatment technologies** (e.g., reverse osmosis, ion exchange) and determine their relevance in different contexts.
- Students will be able to **apply knowledge of water treatment** to ensure efficiency, reliability, and sustainability in diverse engineering and scientific environments.

Structure

Introduction

Water is very crucial for the existence of all living beings. It occupies a unique position in industries. It's probably the most important material being used in every industry. Although water is nature's most wonderful and abundant compound, only less than 1% of the world's water resources are available for use. Therefore it is necessary to use water very judiciously without damaging the flora, fauna and the natural surroundings.

Water Quality Parameters—Self Study

The term "water quality" refers to the chemical, physical, and biological characteristics of water relative to the requirements of its intended use. Evaluating these parameters is crucial for ensuring water is safe for human consumption, suitable for industrial applications, and healthy for aquatic ecosystems. These parameters are broadly classified into three categories.

➤ **Physical Parameters:** These are characteristics that can be detected by the senses. They are often the first indicators of potential contamination. They include:

- Turbidity: A measure of the cloudiness or haziness of water caused by suspended particles.
- Color: True color is caused by dissolved substances, while apparent color is caused by suspended matter.
- Taste and Odor: Caused by dissolved organic materials, inorganic salts, or dissolved gases.
- Temperature: Affects chemical reaction rates and the amount of dissolved oxygen water can hold.

➤ **Chemical Parameters:** These parameters pertain to the dissolved substances within the water and are critical for determining its nature, including hardness. Key chemical parameters include:

- pH: A measure of how acidic or basic the water is.
- Alkalinity: The water's capacity to resist changes in pH that would make it more acidic.
- Total Dissolved Solids (TDS): The total amount of inorganic and organic substances dissolved in the water.
- Hardness: The concentration of dissolved multivalent cations, which is the primary focus of this report.

➤ **Biological Parameters:** This category involves the assessment of microorganisms present in the water, which is vital for public health. It includes testing for bacteria (like *E. coli*), viruses, protozoa, and other pathogens.

➤ PHYSICAL CHARACTERISTICS	CHEMICAL CHARACTERISTICS	BIOLOGICAL CHARACTERISTICS
Odour and taste due to algae, bacteria, industrial waste or irrigation drainage rich in chloride levels, high concentration of calcium or iron.	Acidity: Acidity is not a specific pollutant but determines the power to neutralize hydroxyl-ion and is usually expressed in ppm (parts per million) of CaCO_3 equivalent. Surface-water and Ground-water attain acidity from industrial-wastes like drainage, pickling-liquors, free CO_2 .	Algae, Pathogenic-bacteria, sewage-waste, pathogens, parasitic-worms, micro-organisms are usually abundant in surface-water as compared to deep-well water, etc.
Colour in water is caused by metallic substances like salts of iron, magnesium, tannins, peat, algae, weeds, protozoa, industrial-effluents,etc.	Alkalinity and Hardness: Mineral matters have origin from rocks and industrial effluents. These include Ca^{2+} , Mg^{2+} , Mn^{2+} , HCO_3^- , F^- , Cl^- , SO_4^{2-} , SiO_2 , Na^+ , K^+ , Fe^{2+} , CO_3^{2-} , etc.	
Turbidity expresses the optical properties of water containing insoluble substances which scatter light rather than transmit in straight-lines. It is due to colloidal-matter, extremely fine-suspensions like clay, slit, plankton, etc.	Dissolved gases like NH_3 in water arises from decomposition (aerobic or anaerobic) of nitrogenous organic water.	

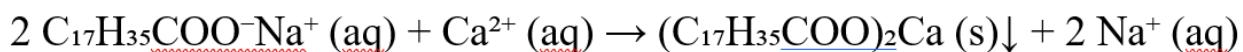
1.1-Hardness of Water

Hardness was originally defined as the soap-consuming capacity of a water-sample.

Soaps generally consist of sodium-salts (Na-salts) of long chain fatty acids such as Oleic-acid, Palmitic-acid and Stearic-acid.

The soap consuming capacity of water is mainly due to the presence of Calcium and Magnesium ions.

These ions react with the 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.



(*Soluble Soap + Calcium Ions → Insoluble Soap Scum + Sodium Ions*)

Other metal-ions like Fe^{2+} , Mn^{2+} and Al^{3+} also react with the soap, thus contribute to the hardness.

In practice (generally), the hardness of water sample is taken as a measure of Ca^{2+} and Mg^{2+} content.

1.1.1 - Degree of Hardness

The degree of hardness is defined as the sum of polyvalent cations present in a finite volume of water.

1.1.2 – Key Distinguishing Characteristics

The practical differences between hard and soft water are easily observable in daily life.

Feature	Hard Water	Soft Water
Interaction with Soap	Reacts with soap to form a sticky, insoluble precipitate known as "soap scum." This prevents the soap from lathering effectively, requiring more soap to be used.	Lathers readily and profusely with soap. No scum is formed, leading to efficient cleaning.
Feeling on Skin & Hair	Can leave a sticky film on the skin and hair as the soap scum is difficult to rinse away. Hair may feel dull and rough.	Can leave a "slippery" or smooth feeling on the skin after washing. This is because the soap remains soluble and is easily rinsed away completely.
Scale Formation	When heated, it forms hard, crusty mineral deposits called limescale (calcium carbonate). This scale builds up in pipes, water heaters, kettles, and on fixtures, reducing efficiency and causing blockages.	Does not produce scale deposits, thereby protecting appliances and plumbing systems from damage and efficiency loss.
Appearance of Dishes	Leaves spots or a cloudy film on glassware and dishes after they are washed and dried.	Leaves dishes and glassware clean and spot-free.
Taste	Often has a distinct chalky or "mineral" taste, which some people prefer.	Typically has a neutral or sometimes slightly salty taste, especially if it has been softened using a ion-exchange system.

Distinguish between Hard-Water and Soft-Water

Hard-Water	Soft-Water
1. Water which does not produce lather with soap-solution readily and forms a white curdy-deposit is called 'Hard-Water'.	1. Water which forms lather easily on shaking with soap-solution is called 'Soft-Water'
2. Hard-Water contains dissolved Calcium and Magnesium salts.	2. Soft-Water does not contain dissolved Calcium and Magnesium salts.
3. In Hard-Water, the cleansing quality of soap is depressed and a lot of it is wasted during washing and bathing.	3. In Soft-Water, the cleansing quality of soap is not depressed and so soap is not wasted during washing and bathing.
4. Due to the presence of dissolved hardness producing salts, the boiling point of water is elevated. Consequently, more fuel and time are required for cooking in hard water.	4. Less fuel and time are required for cooking in soft-water as there are no dissolved salts in it.

1.1.3- Distinguish between Temporary Hardness and Permanent Hardness

Temporary-Hardness	Permanent-Hardness
1. Temporary-hardness is caused by presence of dissolved bicarbonates, carbonates of calcium, magnesium, iron and other heavy metals. The salts responsible for temporary hardness are $\text{Ca}(\text{HCO}_3)_2$, $\text{Mg}(\text{HCO}_3)_2$.	1. Permanent hardness is due to the presence of dissolved chlorides, nitrates and sulphates of calcium, magnesium, iron and other heavy metals. The salts responsible for permanent hardness are CaCl_2 , CaSO_4 , MgCl_2 etc..
2. Temporary-hardness is called as Carbonate or Alkaline-Hardness.	2. Permanent-hardness is called as Non-Carbonate or Non-Alkaline Hardness.
3. Temporary-hardness can be removed by boiling, followed by filtration. It can be removed by boiling as:- $\text{Ca}(\text{HCO}_3)_2 \longrightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$ $\text{Mg}(\text{HCO}_3)_2 \longrightarrow \text{Mg}(\text{OH})_2 + 2\text{CO}_2$ Here $\text{Mg}(\text{OH})_2$ is insoluble in water while CaCO_3 is highly insoluble in water.	3. Permanent-hardness cannot be removed by boiling. It can only be removed using chemicals and not by boiling: eg; Lime-Soda Method OR ION EXCHANGE $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3 + 2 \text{NaCl}$

1.1.4-Disadvantages Of Hard Water Across Different Industries, Based On The Research:

1. Manufacturing & Industrial Cleaning

- **Reduced detergent efficiency:** Hard water minerals react with cleaning agents, forming insoluble scum that reduces effectiveness
- **Surface residue:** Leaves mineral deposits on machined parts, affecting quality.

2. Cooling Systems & Boilers

- **Scale formation:** $\text{Ca}^{2+}/\text{Mg}^{2+}$ precipitates as $\text{CaCO}_3/\text{Mg}(\text{OH})_2$, insulating heat transfer surfaces and increasing energy costs by up to 20%
- **Corrosion:** Chlorides in permanent hardness accelerate pitting in pipes

3. Textile Industry

- **Fabric damage:** Mineral deposits weaken fibers and cause uneven dye absorption.
- **Increased chemical use:** Requires 50–100% more dyes/softeners to compensate for hardness

4. Food & Beverage

- **Taste alteration:** High Mg^{2+} causes bitterness in beverages.
- **Equipment scaling:** Reduces efficiency of pasteurizers and sterilizers.

5. Pharmaceuticals

- **Reaction interference:** $\text{Ca}^{2+}/\text{Mg}^{2+}$ can destabilize formulations or form precipitates in solutions.

1.2.1 Equivalents of Calcium Carbonate

The concentration of hardness as well as non-hardness constituting ions are usually expressed in terms of equivalent amount of CaCO_3 .

The choice of CaCO_3 in particular is due to its molecular weight viz. 100. CaCO_3 is very insoluble and can be precipitated out in water-treatment processes. The calcium-carbonate equivalent of any hardness causing compound can be calculated as follows: eg;

1. $2 \text{RCOONa} + \text{CaCO}_3 \rightarrow (\text{RCOO})_2\text{Ca} \downarrow + \text{Na}_2\text{CO}_3$
2. $2 \text{RCOONa} + \text{MgSO}_4 \rightarrow (\text{RCOO})_2\text{Mg} \downarrow + \text{Na}_2\text{SO}_4$

From (1) and (2) we see that,

100g. of CaCO_3 reacts with the same amount of soap i.e. 'x' g. as that of 120g. of MgSO_4 . That is, 120 parts by weight of MgSO_4 (2 equivalents of MgSO_4) reacts with the same amount of soap as that of 100 parts by weight of CaCO_3 (2 equivalents of CaCO_3). Therefore, 'W' g parts by weight of MgSO_4 can be equated to $\frac{W \times 50}{60}$ parts by weight of CaCO_3 in terms of its capacity to react with the same amount of soap. What is the formula for CaCO_3 equivalent for a hardness causing substance ?

The formula for calculation of CaCO_3 equivalent for a hardness producing substance (hps) is as follows,

$$\text{CaCO}_3 \text{ eq. for hardness producing substance (hps)} = \frac{\text{weight of hps} \times \text{equivalent weight of CaCO}_3}{\text{equivalent weight of hps}}$$

1.2.2 Units of Hardness

(A) Parts per Million (p.p.m.):

It is the unit weight of solute per million unit weight of solution.

In dilute-solutions of density ~ 1 ppm = 1 mg/L

It is customary to express hardness in terms of equivalents of CaCO_3 .

(B) Milligrams per Litre (mg/L) :

$$1 \text{ ppm} = 1 \text{ mg/L}$$

Questions and Answers:

1 Explain degree of hardness.

Answer: The degree of hardness is defined as the sum of polyvalent cations present in a finite volume of water.

2 Why do we consider CaCO_3 and find hardness of different salts in terms of CaCO_3 equivalents ?

Answer: The choice of CaCO_3 in particular is due to its molecular-weight viz. 100. CaCO_3 is very insoluble and can be precipitated out in water-treatment processes.

1.2.3-Numerical Problems:

(At.Wt.: Ca = 40, Mg = 24, H = 1, C = 12, O = 16, S = 32)

1. Calculate the temporary and permanent hardness of a water sample having the following analysis:

$$\text{Mg}(\text{HCO}_3)_2 = 73 \text{ mg/L}$$

$$\text{Ca}(\text{HCO}_3)_2 = 162 \text{ mg/L}$$

$$\text{CaSO}_4 = 136 \text{ mg/L}$$

$$\text{MgCl}_2 = 95 \text{ mg/L}$$

$$\text{CaCl}_2 = 111 \text{ mg/L}$$

$$\text{NaCl} = 100 \text{ mg/L}$$

Solution:-

Constituent	Type	Quantity (mg/L)	M.F.	CaCO ₃ eq.
Mg(HCO ₃) ₂	Temporary	73	100/146	73*100/146 = 50
Ca(HCO ₃) ₂	Temporary	162	100/162	162*100/162 = 100
CaSO ₄	Permanent	136	100/136	136*100/136 = 100
MgCl ₂	Permanent	95	100/95	95*100/95 = 100
CaCl ₂	Permanent	111	100/111	111*100/111 = 100
NaCl	-	-	-	-

$$\begin{aligned}\text{Temporary hardness} &= \text{Total of CaCO}_3 \text{ eq. of Mg(HCO}_3)_2 + \text{Ca(HCO}_3)_2 \\ &= 50+100 \text{ mg/L} \\ &= \mathbf{150 \text{ mg/L}}\end{aligned}$$

$$\begin{aligned}\text{Permanent hardness} &= \text{Total of CaCO}_3 \text{ eq. of CaSO}_4 + \text{MgCl}_2 + \text{CaCl}_2 \\ &= 100+100+100 \text{ mg/L} \\ &= \mathbf{300 \text{ mg/L}}\end{aligned}$$

$$\begin{aligned}\text{Total Hardness} &= \text{Temporary hardness} + \text{Permanent hardness} = 150 + 300 \text{ mg/L} \\ &= \mathbf{450 \text{ mg/L}}\end{aligned}$$

2. A water sample contains the following impurities:

$$\text{Ca(HCO}_3)_2 = 32.4 \text{ mg/L}$$

$$\text{Mg(HCO}_3)_2 = 29.2 \text{ mg/L}$$

$$\text{CaSO}_4 = 13.5 \text{ mg/L}$$

Calculate temporary, permanent and total hardness of the sample

Answer: Temporary hardness = 40 mg/l, Permanent hardness = 9.9 mg/l, Total hardness= 49.9 mg/l

3. A water sample contain 204 mg of CaSO₄ per litre. Calculate the hardness in terms of CaCO₃ equivalents.

Answer: Hardness = 150 mg/l

NUMERICALS FOR PRACTICE

1. A water sample contains 16.8 mg of MgCO₃ and 6.0 g of SiO₂ per litre. Calculate the temporary and permanent hardness of the sample.

Ans: Temporary hardness = 20 ppm and Permanent hardness = 0 ppm

2. How many grams of CaCl₂ dissolved per litre gives 200 ppm of hardness?

Ans: weight of CaCl₂ = 0.222 g

3. Calculate the temporary and permanent hardness of a water sample having the following analysis:

$$\text{Mg}(\text{HCO}_3)_2 = 7.3 \text{ mg/L}$$

$$\text{Ca}(\text{HCO}_3)_2 = 16.2 \text{ mg/L}$$

$$\text{CaSO}_4 = 13.6 \text{ mg/L}$$

$$\text{MgCl}_2 = 9.5 \text{ mg/L}$$

$$\text{NaCl} = 7.7 \text{ mg/L}$$

Ans: Temporary hardness = 15 ppm, Permanent hardness = 20 ppm, Total hardness = 35 ppm

4. A hard water sample contains the following impurities (in mg/l):

$$\text{Mg}(\text{HCO}_3)_2 = 150 \text{ mg/L}$$

$$\text{MgSO}_4 = 85 \text{ mg/L}$$

$$\text{CaCl}_2 = 135 \text{ mg/L}$$

$$\text{NaCl} = 77 \text{ mg/L}$$

Calculate temporary, permanent and total hardness of the given sample of water.

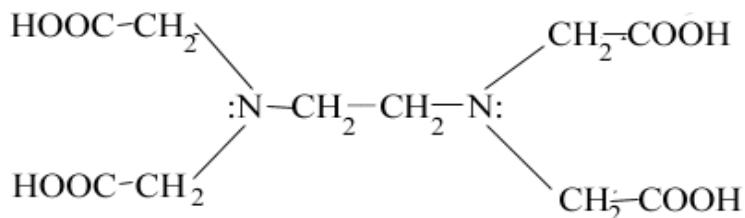
Ans: Temporary hardness = 102.74 ppm, Permanent hardness = 192.45 ppm, Total hardness = 295.19 ppm

5. Three water samples A, B and C were analysed for their salt content. Sample A was found to contain 168 mg/l MgCO_3 . Sample B was found to contain 82 mg/l of $\text{Ca}(\text{NO}_3)_2$ and 2 mg/l Silica. Sample C was found to contain 20 mg/l of Potassium nitrate and 20 mg of CaCO_3 per 500 ml . Determine the hardness in all the above samples.

Ans: Hardness of Sample A = 200 ppm, Hardness of Sample B = 50 ppm, Hardness of Sample C = 40 ppm

1.2.4- E.D.T.A. Method

E.D.T.A. - Ethylenediamine tetra acetic acid



structure of EDTA

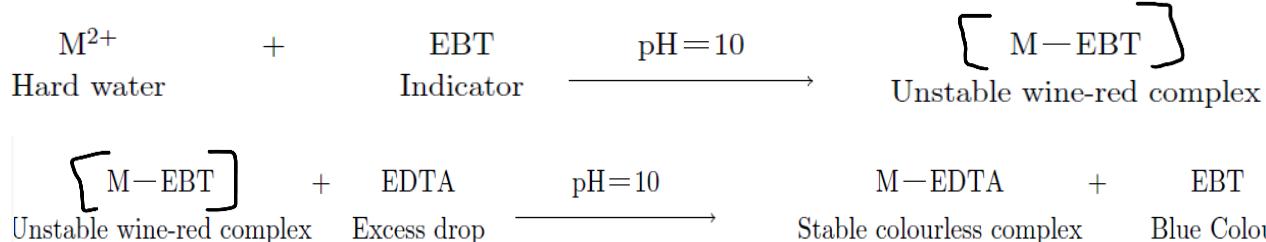
Principle: EDTA method for determining the hardness of water sample is also referred to as '**Complexometric Method**'. The principle of this method is based on the fact that hardness producing metal-ions like Ca^{2+} and Mg^{2+} (represented as M^{2+}) form unstable complexes with indicator Eriochrome Black-T (EBT).

When such an unstable complex of [M-EBT] is titrated with EDTA, the complex releases EBT and forms a stable metal ion-EDTA complex [M-EDTA].

EDTA forms complexes with metal ions like eg.; Ca^{2+} and Mg^{2+} of higher stability. It is able to displace the metal-ions from metal ion-indicator complex and release indicator (EBT) into solution.. At the end point of the titration when all metal ions are complexed with EDTA and free-indicator (EBT) is released into the solution and the end point is observed from wine red to blue.

Metal ion-indicator complex shows wine-red colour at pH=10 while the indicator is blue at pH=10 (basic)

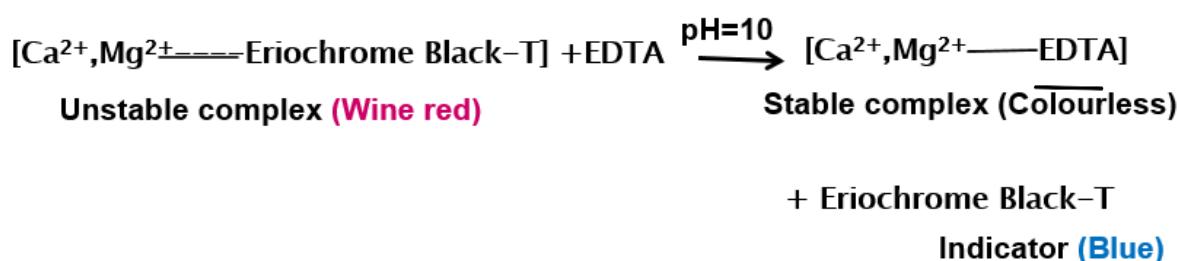
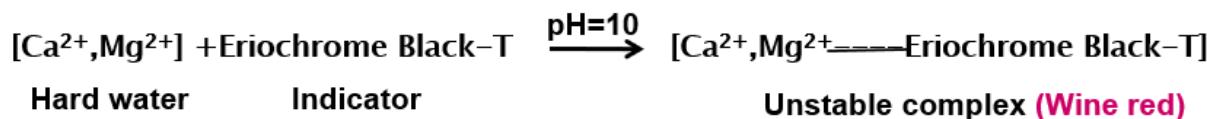
Reactions:-



The colour change for the titration is observed from wine-red to blue colour, however the change in colour is sharper at pH=10.

Therefore the titration is carried out in the presence of basic buffer ie: ammonia-ammonium chloride buffer ($\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$, pH = 10)

► Principle/Reactions



Steps:

- **Part A:** Standardize EDTA using $\text{Zn}^{2+}/\text{Ca}^{2+}$ solution.
- **Part B:** Titrate water sample (total hardness).
- **Part C:** Boil sample, filter precipitates, titrate (permanent hardness).
- **Temporary Hardness** = Total Hardness – Permanent Hardness.

Applications of EDTA Method

1. **Water Treatment:** Assess softening needs.
2. **Industrial Processes:** Prevent scale in boilers/cooling systems.
3. **Environmental Monitoring:** Evaluate river/groundwater quality.
4. **Household Use:** Test drinking water hardness.

Advantages: High accuracy, rapid, and applicable to low-concentration sample

Questions and Answers:

1. Explain the principle involved in EDTA method to determine hardness.

Hint to answer: include principle and reactions.

2. Comment on the nature of metal-EDTA complex formed in the EDTA method.

Answer: EDTA forms a ring (chelate-complex) with metal-ions of higher stability to form Metal-EDTA complex.

3. Why is the basic buffer (pH=10) used in the EDTA method for hardness determination?

Answer: The colour change for the titration is observed from wine-red to blue colour, (show reactions) however the change in colour is sharper at pH=10. (name the buffer used)

4. How will you determine the hardness of water sample by the EDTA method?

Hint to answer: include principle, reactions and method

1.3- Softening of Hardwater

The process of removing hardness producing salts from water is known as softening of water. The three main methods employed in the industry for softening of water are:

- 1) Lime-soda process
- 2) Zeolite process
- 3) Ion exchange process

Only Ion exchange principle will be discussed in detail as per the syllabus.

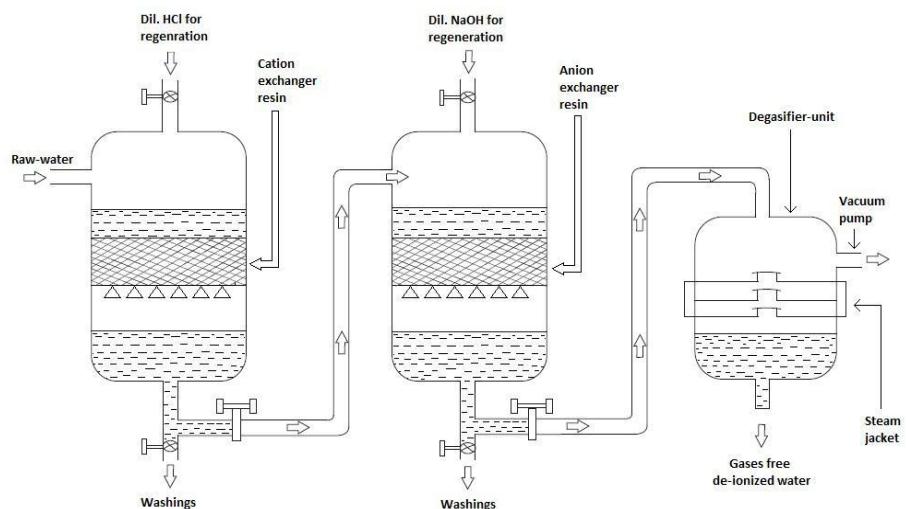
1.3.1-Ion-Exchange Process (De-ionisation or Demineralization)

Principle:-

Cation exchange resins containing acidic functional group are capable of exchanging their H^+ ions with other cations (Ca^{2+} , Mg^{2+} etc present in hard water) which comes in their contact where as anion exchange resins containing basic functional groups are capable of exchanging their OH^- ions with anions (SO_4^{2-} , Cl^- etc.). In this way, the water coming out from both the cation and anion exchanger is free from both cations and anions.

The cation and the anion exchange resins have a limited capacity and will eventually become exhausted. Cation-exchange resins are regenerated with hydrochloric or sulphuric acid and the anion exchange resins are regenerated with sodium hydroxide.

Diagram :- Ion-Exchange Process



Ion Exchange Resins: The Core Chemistry

Ion exchange resins are cross-linked polymer matrices (commonly styrene-divinylbenzene) with chemically active sites that engage in reversible ion exchange reactions. Ion exchange Resins

- ✓ Insoluble, cross-linked, long-chained,
- ✓ organic polymers
- ✓ Microporous structure
- ✓ Functional groups responsible for ion exchange properties

Cation Exchange Resin

- Ion exchange resins used for cation removal typically contain sulphonic acid ($-SO_3H$) or carboxylic acid ($-COOH$) functional groups.
- These resins are synthesized through the copolymerization of styrene and divinylbenzene, followed by post-functionalization via sulphonation or carboxylation to introduce the active ion-exchanging groups.
- **Cation exchange resins, RH₂** : These resins are capable of exchanging their functional group (acidic) like H⁺ with cations like Ca²⁺, Mg²⁺, Na⁺, etc. Eg. sulfonated poly(styrene-co-divinylbenzene)
- **Anion exchange resins, R(OH)₂** : These resins are capable of exchanging their functional group OH- with the anions like Cl⁻, SO₄²⁻, eg-amino formaldehyde resins, quaternary ammonium poly(styrene-co-divinylbenzene).

ION EXCHANGERS-EQUIPMENT

The equipment consists of two cylinders which contain the cation exchange resin and anion exchange resin - the cation exchanger and the anion exchanger.

The outlet from cation exchanger is connected to anion exchanger. Separate outlets are provided for draining purpose. Tanks are provided at the top of each cylinder that contain the regeneration chemicals.

Operational Principle and Chemical Cycles

The operation of a demineralization unit can be divided into Service and Regeneration phases, each involving specific chemical interactions.

Service Phase (Ion Exchange)

- The process of softening in the ion-exchange involves passing raw water first through the cation exchanger and then through the anion exchanger.
- The raw water is passed through the cation exchanger where the cations (calcium, magnesium and sodium) are exchanged for hydrogen ions. The treated water is now free of cations but is too acidic.
- This acidic water emerging from the cation exchanger is then passed through the anion exchanger where the anions (sulfate, chloride, carbonate) are exchanged for hydroxide ions.
- In this way, the water coming out from both the cation and anion exchanger is free from both cations and anions and is virtually deionised water.
- This means that this water does not have any hardness at all. However, this water may contain some dissolved gases.

- In order to remove the dissolved gases, the water is passed through a degasifier. The degasifier is a tower whose both sides are heated with a steam-jacket and is connected to a vacuum pump.
- High temperature and low pressure reduces the quantity of dissolved CO₂ and O₂ in water. Hence the softened water is obtained at the outlet of the degasifier which can be used for industrial purposes.

Cation exchange resin: Softening



Anion exchange resin: Softening



Regeneration Phase

Once the resins are saturated, they are chemically regenerated. When the capacity of the resin to exchange ions is lost, these are said to be exhausted and the supply of water is stopped.

- The exhausted cation exchange is regenerated by passing dil. HCl or H₂SO₄ through the cation exchanger.
- The exhausted anion exchange is regenerated by passing dil. solution of NaOH or KOH through the second tower.

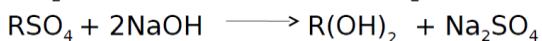
► **Ion exchange Process**

◦ **Principle-Regeneration process**

- Exhausted cation exchange resin is regenerated by passing dil.HCl or H_2SO_4



- Exhausted anion exchange resin is regenerated by NaOH or KOH



Advantages of Ion-exchange process :

- The residual hardness of water is 0-2 ppm.
- The process can be used to soften highly acidic or alkaline water.
- The water softened by this process can be used in high pressure boilers.

Disadvantages of ion-exchange process :

- The ion exchange equipment is costly.
- The turbidity in the raw water needs to be removed (by coagulation) before the softening process as these impurities can clog the ion exchange resins.

Questions and Answers:

1. Describe softening of water by ion exchange process.

Hint: include principle, diagram, reactions process, advantages-disadvantages

2. Explain why the water softened by the ion exchange process is suitable for high pressure boilers.

Hint to answer: residual hardness 0-2 ppm

1.3.2-Numerical Problems based on Ion Exchange Process:

1. After treating 10^4 L of water by ion exchanger, the cationic resin required 200 L of 0.1 N HCl and anionic resin required 200 L of 0.1 N NaOH solutions. Find the hardness of the above sample of water.

Solution:

For regeneration = 200 L of 0.1 N HCl \equiv 200 L of 0.1 N CaCO₃ eq

Hardness in 10⁴ L of water \equiv 200 L of 0.1 N HCl

\equiv 200 L of 0.1 N CaCO₃ eq

\equiv 200 x 0.1 x 50 g of CaCO₃ eq

= 1000 g CaCO₃ eq

= 1000 x 10³ mg CaCO₃ eq

Now, hardness in 1 L of water = $\frac{1000 \times 10^3}{10^4}$

= 100 mg/L

Answer: The hardness of water sample = 100mg/l

2. In the demineralisation process, the cation exchanger required 150 litres of 1 N HCl and the anion exchanger required 150 litres of 1 N NaOH. If the hardness is 250 ppm, then calculate how many litres of water was softened by this process?

Solution:

Hardness of the water = 250 ppm

ie: 1 litre of water = 250 mg of CaCO₃

For regeneration \equiv 150 L of 1 N HCl

\equiv 150 L of 1N CaCO₃ eq

\equiv 150 x 1 x 50 g of CaCO₃ eq

= 7500 g of CaCO₃ eq

= 7500 x 10³ mg CaCO₃ eq

if, 250 mg of CaCO₃ is present in 1 litre

then, 7500 x 10³ mg CaCO₃ is present in $\frac{7500 \times 10^3}{250} = 30,000$ L of water

Answer: The amount of water softened by the process = 30,000 L of water

1.4- Water Purification – Membrane Technology

1.4.1-Reverse Osmosis (R.O.)

What is Osmosis ?

Osmosis is the movement of molecules from a region of lower concentration to a region of higher concentration across a semi-permeable membrane. During natural osmosis, water flows from a less concentrated solution through a semi-permeable membrane to a more concentrated saline solution until concentrations on both the sides of the membrane are equal.

What is Reverse-Osmosis ? (Principle)

Reverse osmosis is the **reversal of the natural flow of osmosis**. It occurs when the water is moved across the semi-membrane against the concentration gradient, higher concentration to a region of lower concentration. A pressure-driven filtration process where solvent (water) moves from a high-solute concentration (impure water) to a low-solute concentration (pure water) through a semipermeable membrane.

Reverse Osmosis (R.O.) is a pressure driven membrane separation process that **separates dissolved and suspended substances from water (dissolved solids, organics, pyrogens, submicron colloidal matter, viruses and bacteria from water)**. The membrane acts as an selective barrier, removing unwanted substances such as salt, producing water safe for drinking.

Fundamental Relationship

In RO, **hydrostatic pressure (ΔP)** must exceed **osmotic pressure (π)** to force water through the semipermeable membrane:

- **Osmotic pressure (π):** Depends on solute concentration (Van't Hoff equation):
[$\pi = iCRT$]
Where:
 - (i) = van't Hoff factor (ions per molecule),
 - (C) = molar concentration,
 - (R) = gas constant (0.0821 L·atm/mol·K),
 - (T) = temperature (K).
- **Hydrostatic pressure (ΔP):** Applied externally (typically 15–80 bar for seawater RO)

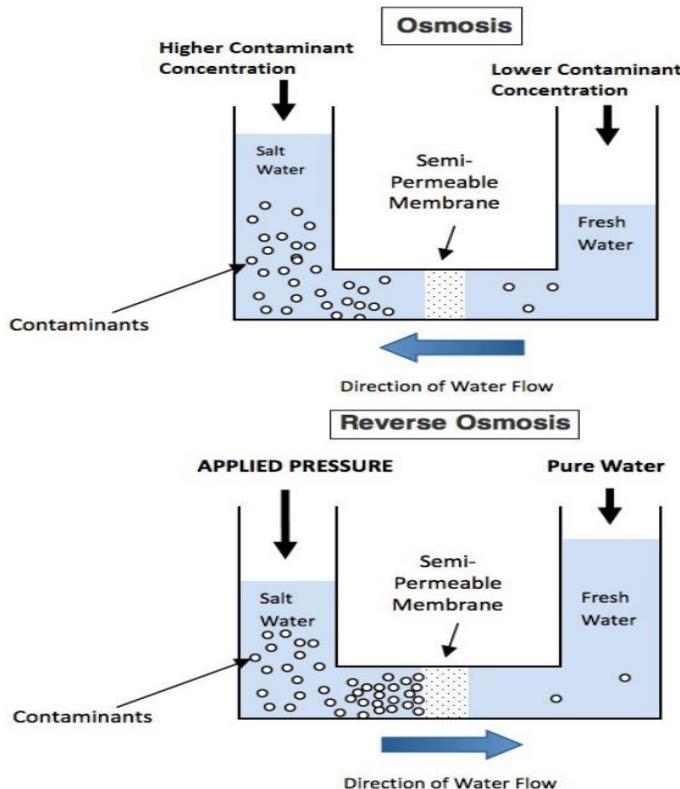
A **pressure can be applied to the concentrated which is greater than that of the osmotic pressure**. The direction of water passage through the membrane is reversed and this process is called 'Reverse Osmosis'.

1.4.2-RO Process Steps

1. **Pre-filtration:** Removes sediments/chlorine to protect the membrane.
2. **Pressurization:** High-pressure pump (50–80 bar for seawater) pushes water through the membrane.
3. **Separation:** Membrane blocks dissolved salts, microbes, and organics (>95% rejection rate).
4. **Post-treatment:** Remineralization or UV treatment for potable water

Diagram Flow:

Impure Water → Pre-filter → High-Pressure Pump → RO Membrane → Permeate (Pure Water) + Concentrate (Waste)

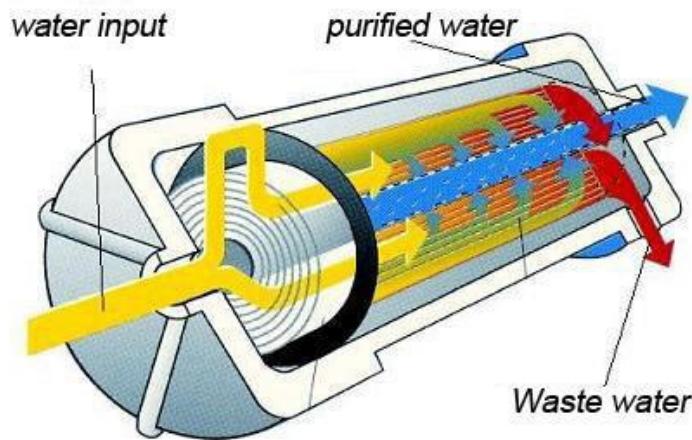


Method :-

In this process, **pressure (of the order 15 to 40 kg·cm⁻²)** is applied to impure water to force its pure water out through the semi-permeable membrane; leaving behind the dissolved solids. The RO membrane consists of very **thin films of cellulose acetate**, affixed to either side of a perforated tube. However, nowadays RO membranes made of a **polymethacrylate and polyamide polymers** have come into use.

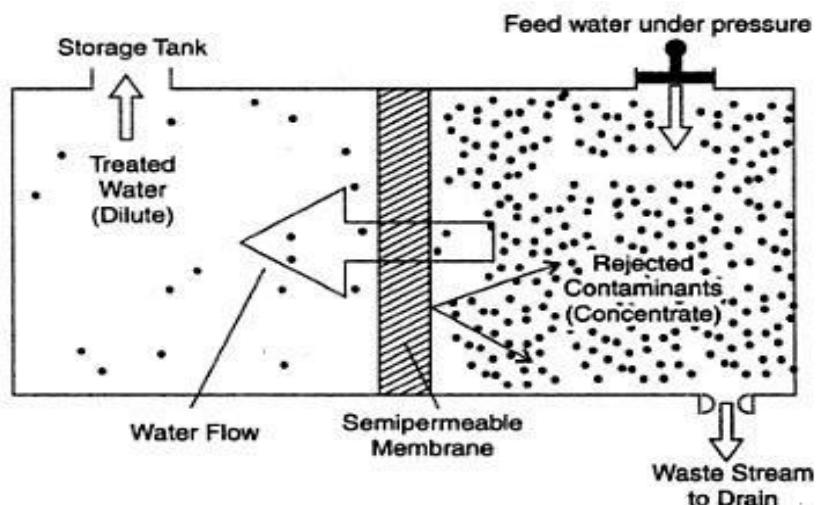
The RO membrane consists of several thin layers or sheets of film that are bonded together and rolled in a spiral configuration around a plastic tube. (This is also known as a Thin-Film Composite or TFC Membrane.) The material of the RO membrane is semi-permeable; it allows water molecules to pass through while acting as a barrier to dissolved solids i.e. mineral membrane chemical contaminants. The **pore size** of the RO membrane is around **0.0001 micron**.

When the feed-water stream passes across the surface of the RO membrane, the water molecules penetrate the membrane surface, working their way around the spiral and collecting in the center tube. The remaining contaminants are concentrated and washed from the surface of the membrane down the drain. Metals, organic compounds and other contaminants are either too large or chemically unable to pass through the reverse osmosis membrane.



<https://kysearo.com/2000-tpd-seawater-desalination-system/spiral-wound-ro-membrane/>

The reverse osmosis process cannot go on indefinitely without removing the contaminants. Ultimately, the membrane could become clogged by sludge and other impurities, requiring increasingly greater pressure to force water through the membrane. To solve this problem, the **membranes are configured to split the feed-water into two streams - one part to be purified and the other part to wash away the particles rejected by the membrane.**



1.4.3-Advantages and Applications of Reverse-Osmosis :-

1. Reverse Osmosis possesses a distinct advantage of removing ionic as well as non-ionic, colloidal and high molecular weight organic matter.
2. It removes colloidal silica, which is not removed by demineralization.
3. The maintenance cost is almost entirely on the replacement of the semi-permeable membrane.
4. The life-time of the RO membrane is quite high, about 2 years.
5. The RO membrane can be replaced within a few minutes, thereby providing nearly uninterrupted water supply.
6. Due to low capital-cost, simplicity, low operating-cost and high reliability, reverse osmosis is gaining ground at present for converting sea-water into drinking-water for obtaining water for very high pressure boilers.

7. **Desalination:** Removes 99% of salts ($\Delta P \sim 50\text{--}80$ bar for seawater).
8. **Wastewater Treatment:** Recycles industrial effluents.
9. **Pharmaceuticals:** Produces ultra-pure water ($\Delta P \sim 15\text{--}30$ bar)

1.4.4- Disadvantages of Reverse-Osmosis:-

1. Reverse Osmosis removes natural mineral such as iron, magnesium, calcium and sodium which are essential to the human body.
2. It produces lots of waste water.
3. **Energy Intensive:** High ΔP demands significant power.
4. **Brine Discharge:** 25–50% of feed becomes waste concentrate.
5. **Membrane Fouling:** Requires pre-filtration to avoid clogging

Multiple Choice Questions:

1. The temporary hardness of water is due to the presence of
 - a. Chlorides of Ca^{2+} and Mg^{2+}
 - b. Sulphates of Ca^{2+} and Mg^{2+}
 - c. Bicarbonates of Ca^{2+} and Mg^{2+}
 - d. Nitrates of Ca^{2+} and Mg^{2+}
2. Permanent Hardness of water is due to
 - a. Bicarbonates of Ca^{2+} and Mg^{2+}
 - b. Carbonates of Ca^{2+} and Mg^{2+}
 - c. Hydroxides of Ca^{2+} and Mg^{2+}
 - d. Sulphates of Ca^{2+} and Mg^{2+}
3. The degree of hardness is usually reported as an equivalent quantity of
 - a. Calcium bicarbonate
 - b. Calcium carbonate
 - c. Magnesium bicarbonate
 - d. Magnesium carbonate
4. Non-carbonate hardness of water is
 - a. Alkaline hardness
 - b. Total hardness
 - c. Temporary hardness
 - d. Permanent hardness
5. Alkaline hardness of water is
 - a. Non-carbonate hardness
 - b. Total hardness
 - c. Temporary hardness
 - d. Permanent hardness

6. Permanent hardness can be removed by
- Boiling
 - Filtering
 - Boiling followed by filtration
 - Chemical treatment
7. 1 parts per million is equal to
- 1 degree Clark
 - 1 degree French
 - 1 milligrams per litre
 - 1 grams per litre
8. The chemical name for EDTA is
- Ethylene diamine triacetic acid
 - Ethylene diamine tetraacetic acid
 - Ethylene diacetic triamine
 - Ethylene diacetic tetraamine
9. In the EDTA method of estimating hardness of water, the hard water sample
- Should have pH greater than 10
 - Should have pH Less than 10
 - Should be buffered at pH 10
 - None of the above
10. The buffer solution used in the EDTA method is usually
- Acetic acid-Sodium acetate
 - Sodium hydroxide-Potassium chloride
 - Ammonia-Ammonium chloride
 - Ammonia-Ammonium phosphate
11. The end-point of the EDTA method is
- Wine-red to blue
 - Blue to wine red
 - Blue to pink
 - Wine red to pink
12. The indicator used in EDTA method is
- Phenolphthalein
 - Methyl Red
 - Eriochrome Red B
 - Eriochrome Black T
13. Which of the following cannot be classified as an ion exchange process?
- Lime-soda process
 - Permutit process
 - De-ionisation process
 - De-mineralisation process
14. Resins containing carboxylic or sulphonic functional groups are called
- Cation exchange resins
 - Anion exchange resins

- c. Acid exchange resins
- d. Base exchange resins

15. Anion Exchange resins remove

- a. Cations like Ca^{2+} , Mg^{2+}
- b. Anions like SO_4^{2-} , Cl^-
- c. Ions like H^+ , OH^-
- d. None of these

16. The solution used for regeneration of a cation exchange resin is

- a. Dil. NaOH solution
- b. Dil. KOH solution
- c. Dil. HCl solution
- d. De-ionsed water

17. The residual hardness of water after a de-ionisation process is

- a. 0-3 ppm
- b. 5-10 ppm
- c. 15-30 ppm
- d. 50-60 ppm

18. The membrane pore size for RO process is

- a. 0.1 to 1 micron
- b. 0.01 to 0.1 microns
- c. 0.001 to 0.01 microns
- d. 0.0001 to 0.001 microns

19. In the RO process,

- a. no pressure is applied
- b. pressure applied is greater than the osmotic pressure.
- c. pressure applied is lesser than the osmotic pressure.
- d. pressure is equal to the osmotic pressure.

Self study-topics

1. Which of these is not a disinfection process?

- a. Coagulation
- b. Chlorination
- c. Ozonation
- d. UV radiation

2. Which of these is an incorrect statement?

- a. Bleaching powder produces salt impurities in water making it hard.
- b. Bleaching powder gives bad taste and odour if added in excess into water.
- c. Bleaching powder is stable and hence can be stored for long period of time.

- d. Bleaching powder can be used as a disinfectant in water treatment process.
- 3. Chlorination is effective at
 - a. high pH ranges
 - b. high temperatures
 - c. long time of contact
 - d. none of the above
- 4. The process of ozonation is preferred over chlorination as it is
 - a. a more expensive method.
 - b. stable and forms harmful products in water.
 - c. unstable and forms less harmful products in water.
 - d. produces unpleasant odour and taste to water.
- 5. Which of these cannot be used as a disinfectant in water treatment process?
 - a. Calcium hypochlorite
 - b. Sodium aluminate
 - c. Chlorine
 - d. Ozone