WATER - ANALYSIS, TREATMENTS, AND INDUSTRIAL APPLICATIONS

1. Sources of Water

- **Natural sources**: Rainwater, surface water (rivers, lakes, ponds), groundwater (wells, springs).
- **Man-made sources**: Reservoirs, dams, desalination plants.

2. Impurities in Water

- **Physical impurities**: Suspended particles, turbidity, color.
- **Chemical impurities**: Dissolved salts (Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}), heavy metals, dissolved gases (O_2, CO_2).
- **Biological impurities**: Bacteria, algae, microorganisms.

3. Hardness of Water

Hardness is caused by dissolved calcium (Ca^{2+}) and magnesium (Mg^{2+}) salts.

- **Types of Hardness**:
  - **Temporary Hardness**: Due to bicarbonates of Ca and Mg (removed by boiling).
  - **Permanent Hardness**: Due to sulfates and chlorides of Ca and Mg (removed by chemical treatment).
- **Units of Hardness**:
  1. **ppm (mg/L)**: mg of $CaCO_3$ per liter of water.
  2. **Degree Clark (°Cl)**: 1 °Cl = 14.25 mg/L of $CaCO_3$.
  3. **Degree French (°Fr)**: 1 °Fr = 10 mg/L of $CaCO_3$.
  4. **Milli-equivalent per liter (mEq/L)**: 1 mEq/L = 50 mg/L of $CaCO_3$.

4. Determination of Hardness by EDTA Method

A complexometric titration using **ethylenediaminetetraacetic acid (EDTA)** to determine hardness.

Procedure:

1. Take 50 mL of the water sample in a conical flask.
2. Add a buffer solution (pH ≈ 10) to maintain alkalinity.
3. Add **Eriochrome Black T** indicator (turns wine red in hard water).
4. Titrate with **0.01M EDTA** solution until the color changes from **wine red to blue** (end point).

Reaction:

Ca2++EDTA→[Ca-EDTA]\text{Ca}^{2+} + \text{EDTA} \rightarrow [\text{CaEDTA}]Ca2++EDTA→[Ca-EDTA] Mg2++EDTA→[Mg-EDTA]\text{Mg}^{2+} + \text{EDTA} \rightarrow [\text{MgEDTA}]Mg2++EDTA→[Mg-EDTA]

Calculation:

Total Hardness (mg/L of $CaCO_3$)=VEDTA×MEDTA×1000VSample\text{Total Hardness (mg/L of $CaCO_3$)} = \frac{V_{\text{EDTA}} \times M_{\text{EDTA}} \times 1000}{V_{\text{Sample}}}Total Hardness (mg/L of $CaCO_3$)=VSampleVEDTA×MEDTA ×1000 where:

- VEDTAV_{\text{EDTA}}VEDTA = Volume of EDTA used (mL)
- MEDTAM_{\text{EDTA}}MEDTA = Molarity of EDTA
- VSampleV_{\text{Sample}}VSample = Volume of water sample (mL)

Outcomes:

- Understanding different sources and impurities of water.
- Learning the concept of water hardness and its measurement units.
- Performing EDTA titration to determine water hardness.
- Applying water treatment methods in industrial applications.

Alkalinity & Its Determination

Definition:

Alkalinity is the ability of water to neutralize acids, mainly due to the presence of bicarbonates (HCO3−)(HCO_3^-)(HCO3−), carbonates (CO32−)(CO_3^{2-})(CO32−), and hydroxides (OH−)(OH^-)(OH−).

Types of Alkalinity:

1. **Carbonate Alkalinity** (CO32−)(CO_3^{2-})(CO32−)
2. **Bicarbonate Alkalinity** (HCO3−)(HCO_3^-)(HCO3−)
3. **Hydroxide Alkalinity** (OH−)(OH^-)(OH−)

Determination of Alkalinity (Titration Method):

Alkalinity is determined using acid-base titration with standard **HCl** using **phenolphthalein** and **methyl orange** as indicators.

- **Phenolphthalein Alkalinity (P-alkalinity):** Measures hydroxide (OH−)(OH^-)(OH−) and half of carbonate (CO32−)(CO_3^{2-})(CO32−).
- **Total Alkalinity (T-alkalinity):** Measures **OH^-**, **CO_3^{2-}**, and **HCO_3^-**.

Reactions:

1. **OH^- Neutralization:**

OH−+H+→H2OOH^- + H^+ \rightarrow H_2OOH−+H+→H2O

2. **Carbonate Neutralization:**
   CO32−+H+→HCO3−CO_3^{2-} + H^+ \rightarrow HCO_3^-CO32−+H+→HCO3−
   HCO3−+H+→H2CO3HCO_3^- + H^+ \rightarrow H_2CO_3HCO3−+H+→H2CO3

Calculation Formula:

Alkalinity (mg/L as $CaCO_3$)=Volume of acid×Normality of acid×50,000Volume of sample (mL)\text{Alkalinity (mg/L as $CaCO_3$)} = \frac{\text{Volume of acid} \times \text{Normality of acid} \times 50,000}{\text{Volume of sample (mL)}}Alkalinity (mg/L as $CaCO_3$)=Volume of sample (mL)Volume of acid×Normality of acid×50,000

Boiler Troubles

Boiler water should be free from impurities to avoid problems like sludge, scale, priming, foaming, boiler corrosion, and caustic embrittlement.

1. Sludge & Scale Formation

Cause: Deposition of dissolved salts like **$CaSO_4$, $Mg(OH)_2$, $CaCO_3$** when water is heated.

Sludge:

- **Forms in low-temperature zones**
- **Loose & soft deposits**
- **Easily removable**

Scale:

- **Forms in high-temperature zones**
- **Hard & difficult to remove**
- **Decreases heat transfer efficiency Prevention:**

- Use **softened water**
- Add **phosphate compounds** to convert scale-forming salts into non-adherent sludge • **Blowdown method** to remove sludge

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2. Priming & Foaming

Priming: The carryover of water droplets along with steam due to high velocity, improper design, or high water level.

Foaming: The formation of stable foam due to high dissolved solids or oil contamination.

Effects:

- Reduces boiler efficiency
- Causes **wet steam** leading to damage **Prevention:**

- Reduce boiler water **TDS (Total Dissolved Solids)**
- Use **anti-foaming agents**
- Proper boiler design

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3. Boiler Corrosion

Corrosion is the **deterioration of boiler material** due to chemical reactions.

Causes:

- **Dissolved oxygen:** Forms rust (Fe2O3.xH2O)(Fe_2O_3 \cdot xH_2O)(Fe2O3.xH2O) 4Fe+3O2+6H2O→4Fe(OH)34Fe + 3O_2 + 6H_2O \rightarrow 4Fe(OH)_34Fe+3O2+6H2 O→4Fe(OH)3
- **Acidic water:** Forms Fe^{2+} ions Fe+2H+→Fe2++H2Fe + 2H^+ \rightarrow Fe^{2+} + H_2Fe+2H+→Fe2++H2
- **Dissolved CO_2:** Forms carbonic acid, leading to metal decay **Prevention:**

- Remove **O_2** using **sodium sulfite (Na_2SO_3):** Na2SO3+O2→Na2SO4Na_2SO_3 + O_2 \rightarrow Na_2SO_4Na2SO3+O2→Na2SO4
- Maintain **proper pH (8.5 – 9.5)**
- Use **deaerators**

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4. Caustic Embrittlement

Definition:
Localized cracking of boiler material due to the concentration of **NaOH** at high pressure.

Cause:
Water containing **Na_2CO_3** undergoes hydrolysis, forming NaOH, which accumulates in boiler cracks and reacts with the boiler metal:
Fe+NaOH→NaFeO2+H2Fe + NaOH \rightarrow NaFeO_2 + H_2Fe+NaOH→NaFeO2+H2

Prevention:

- Use **sodium phosphate** instead of sodium carbonate
- Maintain proper **alkalinity levels**

Outcomes:

1. **Understand the importance of alkalinity measurement for water treatment.**

2. **Learn to determine alkalinity using titration.**
3. **Recognize common boiler problems and their causes.**
4. **Identify methods to prevent boiler troubles.**

Softening of Water & Internal Treatment Methods of Boilers

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1. Softening of Water

Hard water contains dissolved calcium and magnesium salts. Softening methods remove these ions to prevent scale formation in boilers and pipelines.

1.1 Lime-Soda Process

Principle: Precipitation of Ca^{2+} and Mg^{2+} as insoluble carbonates and hydroxides using **lime ($Ca(OH)_2$) and soda ash (Na_2CO_3)**.

Reactions:

1. **Removal of Temporary Hardness:** Ca(HCO3)2+Ca(OH)2→2CaCO3↓+2H2O$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O$Ca(HCO3)2+Ca(OH)2→2CaCO3↓+2H2O Mg(HCO3)2+2Ca(OH)2→Mg(OH)2↓+2CaCO3↓+2H2O$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow Mg(OH)_2 \downarrow + 2CaCO_3 \downarrow + 2H_2O$Mg(HCO3)2+2Ca(OH)2→Mg(OH)2↓+2CaCO3↓+2H2O
2. **Removal of Permanent Hardness:** CaCl2+Na2CO3→CaCO3↓+2NaCl$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + 2NaCl$CaCl2+Na2CO3→CaCO3↓+2NaCl MgSO4+Ca(OH)2→Mg(OH)2↓+CaSO4$MgSO_4 + Ca(OH)_2 \rightarrow Mg(OH)_2 \downarrow + CaSO_4$MgSO4+Ca(OH)2→Mg(OH)2↓+CaSO4

Advantages: Cheap, removes acidity.
Disadvantages: Sludge formation, requires skilled operation.

1.2 Zeolite Process

Principle: Hardness-causing Ca^{2+} and Mg^{2+} are exchanged with Na^+ ions using zeolite (hydrated aluminosilicates).

Reactions:

1. **Softening Reaction:** Ca2++Na2Z→CaZ+2Na+Ca^{2+} + Na_2Z \rightarrow CaZ + 2Na^+Ca2++Na2Z→CaZ+2Na+ Mg2++Na2Z→MgZ+2Na+Mg^{2+} + Na_2Z \rightarrow MgZ + 2Na^+Mg2++Na2Z→MgZ+2Na+
2. **Regeneration with NaCl solution:** CaZ+2NaCl→Na2Z+CaCl2$CaZ + 2NaCl \rightarrow Na_2Z + CaCl_2$CaZ+2NaCl→Na2Z+CaCl2 MgZ+2NaCl→Na2Z+MgCl2$MgZ + 2NaCl \rightarrow Na_2Z + MgCl_2$MgZ+2NaCl→Na2Z+MgCl2

Advantages: No sludge formation, easy operation.

Disadvantages: Does not remove silica and acids.

1.3 Ion Exchange Process

Principle: Uses **cation-exchange resins** ($R-SO_3H$) to remove Ca^{2+}/Mg^{2+} and **anionexchange resins** ($R-NH_2$) to remove anions.

Reactions:

1. **Cation Exchange:** 2R−SO3H+Ca2+→(R−SO3)2Ca+2H+2R-SO_3H + Ca^{2+} \rightarrow (RSO_3)_2Ca + 2H^+2R−SO3H+Ca2+→(R−SO3)2Ca+2H+
2. **Anion Exchange:** R−NH2+Cl−→R−NH2HClR-NH_2 + Cl^- \rightarrow R-NH_2HClR−NH2 +Cl−→R−NH2HCl **Regeneration:**

(R−SO3)2Ca+2HCl→2R−SO3H+CaCl2(R-SO_3)_2Ca + 2HCl → 2R-SO_3H + CaCl_2(R−SO3)2 Ca+2HCl→2R−SO3H+CaCl2 R−NH2HCl+NaOH→R−NH2+NaCl+H2OR-NH_2HCl + NaOH → R-NH_2 + NaCl + H_2OR−NH2HCl+NaOH→R−NH2+NaCl+H2O

Advantages: Highly effective, produces **deionized water**.
Disadvantages: Expensive, requires acids/bases for regeneration.

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2. Internal Treatment Methods for Boilers

To prevent scale, sludge, corrosion, and foaming in boilers.

2.1 Phosphate Treatment

- **Reaction:** Converts Ca^{2+} into **insoluble calcium phosphate**: 3Ca2++2Na3PO4→Ca3(PO4)2↓+6Na+3Ca^{2+} + 2Na_3PO_4 → Ca_3(PO_4)_2 ↓ + 6Na^+3Ca2++2Na3PO4→Ca3(PO4)2↓+6Na+
- **Types:** Sodium phosphate, Trisodium phosphate.

2.2 Colloidal Conditioning

- **Method:** Addition of organic substances like **kerosene, tannin, agar-agar** to prevent scale formation.

2.3 Carbonate Conditioning

- **Reaction:** Sodium carbonate converts Ca^{2+} into **soft $CaCO_3$ precipitate**: Ca2++Na2CO3→CaCO3↓+2Na+Ca^{2+} + Na_2CO_3 → CaCO_3 ↓ + 2Na^+Ca2++Na2CO3 →CaCO3↓+2Na+

2.4 Blow Down Operation

- **Process:** Periodic removal of concentrated boiler water to **prevent sludge accumulation**.

2.5 Complex Formation (Sequestering Agents)

- **Method:** Adding **EDTA (Ethylene Diamine Tetra Acetic Acid)** to form soluble complexes with Ca^{2+} & Mg^{2+}.

Outcomes

- **Lime-Soda, Zeolite, and Ion Exchange** remove hardness effectively.
- **Internal Boiler Treatments** prevent scale, corrosion, and increase efficiency.
- **Ion Exchange** provides **high-purity water** for industrial use.

1. Hardness of Water

Hardness is caused by dissolved salts of calcium (Ca^{2+}) and magnesium (Mg^{2+}). It is categorized as:

- **Temporary Hardness** – Due to bicarbonates ($Ca(HCO_3)_2$, $Mg(HCO_3)_2$). Removed by boiling or adding lime.
- **Permanent Hardness** – Due to sulfates, chlorides, nitrates ($CaSO_4$, $MgCl_2$). Removed by chemical methods.

Numerical Formula:

Hardness (in ppm)=Mass of $CaCO_3$ equivalent×1000000Volume of sample (mL)\text{Hardness (in ppm)} = \frac{\text{Mass of $CaCO_3$ equivalent} \times 1000000}{\text{Volume of sample (mL)}}Hardness (in ppm)=Volume of sample (mL)Mass of $CaCO_3$ equivalent×1000000

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2. Alkalinity of Water

Alkalinity is due to OH^-, CO_3^{2-}, and HCO_3^- ions. Expressed in terms of **$CaCO_3$ equivalent**.

Numerical Formula:

Alkalinity (in mg/L)=(B×N×50000)/V\text{Alkalinity (in mg/L)} = \left(B \times N \times 50000 \right) / VAlkalinity (in mg/L)=(B×N×50000)/V

where:

- **B** = Volume of titrant used (mL)
- **N** = Normality of acid
- **V** = Sample volume (mL)

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3. Water Softening Methods

(a) Lime-Soda Method

Chemical softening using lime ($Ca(OH)_2$) and soda ash (Na_2CO_3) to remove hardness.

$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O$\text{Ca(HCO$_3$)$_2$ + Ca(OH)$_2$} \rightarrow 2\text{CaCO$_3$} \downarrow + 2\text{H$_2$O}$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O$
$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 \downarrow + CaCl_2$\text{MgCl$_2$ + Ca(OH)$_2$} \rightarrow \text{Mg(OH)$_2$} \downarrow + \text{CaCl$_2$}$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 \downarrow + CaCl_2$

Numerical Problem:
Find the amount of **lime and soda** required to soften 1 million liters of water with a given hardness.

(b) Zeolite (Ion Exchange) Method

Formula for softening:

$Na_2Z + Ca^{2+} \rightarrow CaZ + 2Na^+$\text{Na$_2$Z + Ca^{2+}} \rightarrow \text{CaZ + 2Na$^+$}$Na_2Z + Ca^{2+} \rightarrow CaZ + 2Na^+$
$Na_2Z + Mg^{2+} \rightarrow MgZ + 2Na^+$\text{Na$_2$Z + Mg^{2+}} \rightarrow \text{MgZ + 2Na$^+$}$Na_2Z + Mg^{2+} \rightarrow MgZ + 2Na^+$

Numerical Problem:
Calculate the amount of **zeolite required** for softening a given volume of water.

(c) Reverse Osmosis (RO) Method

Uses **semi-permeable membrane** to remove ions. **No numerical derivation**, mostly efficiency-based calculations.

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4. Expected Outcomes

- Ability to solve **hardness, alkalinity, and softening-related problems**.
- Understanding of **chemical reactions and calculations** for softening water.
- Mastery in **lime-soda, zeolite, and RO methods** numerically.

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5. Notes (Arranged Properly)

Concept	Formula/Reaction	Key Points

Hardness Calculation	ppm=Mass of $CaCO_3$ equivalent×106Volume of water\text{ppm} = \frac{\text{Mass of $CaCO_3$ equivalent} \times 10^6}{\text{Volume of water}}ppm=Volume of waterMass of $CaCO_3$ equivalent×106	Expressed in ppm or mg/L
Alkalinity Calculation	Alkalinity=(B×N×50000)/V\text{Alkalinity} = \left(B \times N \times 50000 \right) / VAlkalinity=(B×N×50000)/V	Measures OH^-, CO_3^{2-}, HCO_3^-
Lime-Soda Reactions	**$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow CaCO_3 \downarrow + H_2O$**	Removes temporary hardness
Zeolite Reactions	**$Na_2Z + Ca^{2+} \rightarrow CaZ + 2Na^+$**	Removes permanent hardness
Reverse Osmosis	No direct formula	Removes all dissolved salts