

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 ($^{\circ}\text{Cl}$):** $1\ ^{\circ}\text{Cl} = 14.25\ \text{mg/L}$ of CaCO_3 .
 3. **Degree French ($^{\circ}\text{Fr}$):** $1\ ^{\circ}\text{Fr} = 10\ \text{mg/L}$ of CaCO_3 .
 4. **Milli-equivalent per liter (mEq/L):** $1\ \text{mEq/L} = 50\ \text{mg/L}$ of CaCO_3 .

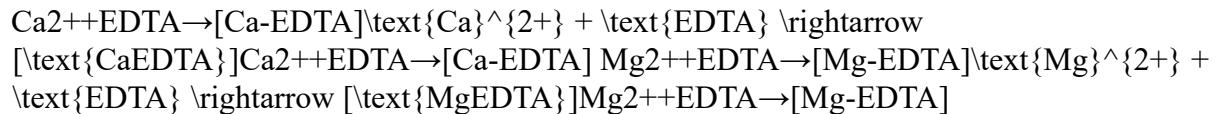
4. Determination of Hardness by EDTA Method

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 ($\text{pH} \approx 10$) 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:



Calculation:

Total Hardness (mg/L of CaCO_3) = $V_{\text{EDTA}} \times M_{\text{EDTA}} \times 1000 / V_{\text{Sample}}$

$$\text{Total Hardness (mg/L of CaCO}_3\text{)} = \frac{V_{\text{EDTA}} \times M_{\text{EDTA}} \times 1000}{V_{\text{Sample}}}$$

Total Hardness (mg/L of CaCO_3) = $V_{\text{Sample}} \times V_{\text{EDTA}} \times M_{\text{EDTA}} \times 1000$ where:

- V_{EDTA} = Volume of EDTA used (mL)
- M_{EDTA} = Molarity of EDTA
- V_{Sample} = 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 (HCO_3^-), carbonates (CO_3^{2-}), and hydroxides (OH^-).

Types of Alkalinity:

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

Determination of Alkalinity (Titration Method):

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

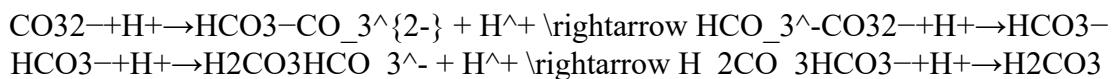
- **Phenolphthalein Alkalinity (P-alkalinity):** Measures hydroxide (OH^-) and half of carbonate (CO_3^{2-}).
- **Total Alkalinity (T-alkalinity):** Measures OH^- , CO_3^{2-} , and HCO_3^- .

Reactions:

1. OH^- Neutralization:



2. Carbonate Neutralization:



Calculation Formula:

Alkalinity (mg/L as CaCO₃) = Volume of acid × Normality of acid × 50,000 / Volume of sample (mL)

$$\text{Alkalinity (mg/L as CaCO}_3\text{)} = \frac{\text{Volume of acid} \times \text{Normality of acid} \times 50,000}{\text{Volume of sample}}$$

(mL) Alkalinity (mg/L as CaCO₃) = 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 CaSO₄, Mg(OH)₂, CaCO₃ 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

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 $(Fe_2O_3 \cdot xH_2O)(Fe_2O_3 \cdot xH_2O) \rightarrow 4Fe(OH)_3 + 3O_2 + 6H_2O \rightarrow 4Fe(OH)_3 + 3O_2 + 6H_2O \rightarrow 4Fe(OH)_3$
 - **Acidic water:** Forms Fe^{2+} ions $Fe + 2H^+ \rightarrow Fe^{2+} + H_2$
 - **Dissolved CO₂:** Forms carbonic acid, leading to metal decay **Prevention:**
 - Remove O₂ using **sodium sulfite (Na₂SO₃)**: $Na_2SO_3 + O_2 \rightarrow Na_2SO_4 + Na_2SO_3 + O_2 \rightarrow Na_2SO_4$
 - 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 **Na₂CO₃** undergoes hydrolysis, forming NaOH, which accumulates in boiler cracks and reacts with the boiler metal:



Prevention:

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

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:** $\text{Ca(HCO}_3)_2 + \text{Ca(OH)}_2 \rightarrow 2\text{CaCO}_3 \downarrow + 2\text{H}_2\text{O}$ $\text{Ca}(\text{HCO}_3)_2 + \text{Ca(OH)}_2 \rightarrow 2\text{CaCO}_3 \downarrow + 2\text{H}_2\text{O}$
 $\text{Mg(HCO}_3)_2 + 2\text{Ca(OH)}_2 \rightarrow \text{Mg(OH)}_2 \downarrow + 2\text{CaCO}_3 \downarrow + 2\text{H}_2\text{O}$ $\text{Mg}(\text{HCO}_3)_2 + 2\text{Ca(OH)}_2 \rightarrow \text{Mg(OH)}_2 \downarrow + 2\text{CaCO}_3 \downarrow + 2\text{H}_2\text{O}$
2. **Removal of Permanent Hardness:** $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{NaCl}$ $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{NaCl}$ $\text{MgSO}_4 + \text{Ca(OH)}_2 \rightarrow \text{Mg(OH)}_2 \downarrow + \text{CaSO}_4$ $\text{MgSO}_4 + \text{Ca(OH)}_2 \rightarrow \text{Mg(OH)}_2 \downarrow + \text{CaSO}_4$

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:** $\text{Ca}^{2+} + \text{Na}_2\text{Z} \rightarrow \text{CaZ} + 2\text{Na}^+ + \text{Ca}^{2+} \rightarrow \text{CaZ} + 2\text{Na}^+$ $\text{Ca}^{2+} + \text{Na}_2\text{Z} \rightarrow \text{CaZ} + 2\text{Na}^+ + \text{Mg}^{2+} + \text{Na}_2\text{Z} \rightarrow \text{MgZ} + 2\text{Na}^+ + \text{Mg}^{2+} + \text{Na}_2\text{Z} \rightarrow \text{MgZ} + 2\text{Na}^+$
 $\text{Ca}^{2+} + \text{Na}_2\text{Z} \rightarrow \text{CaZ} + 2\text{Na}^+$ $\text{Mg}^{2+} + \text{Na}_2\text{Z} \rightarrow \text{MgZ} + 2\text{Na}^+$
2. **Regeneration with NaCl solution:** $\text{CaZ} + 2\text{NaCl} \rightarrow \text{Na}_2\text{Z} + \text{CaCl}_2$ $\text{CaCl}_2 + \text{CaZ} \rightarrow \text{Na}_2\text{Z} + \text{CaCl}_2$ $\text{MgZ} + 2\text{NaCl} \rightarrow \text{Na}_2\text{Z} + \text{MgCl}_2$ $\text{MgCl}_2 + \text{MgZ} \rightarrow \text{Na}_2\text{Z} + \text{MgCl}_2$

Advantages: No sludge formation, easy operation.

Disadvantages: Does not remove silica and acids.

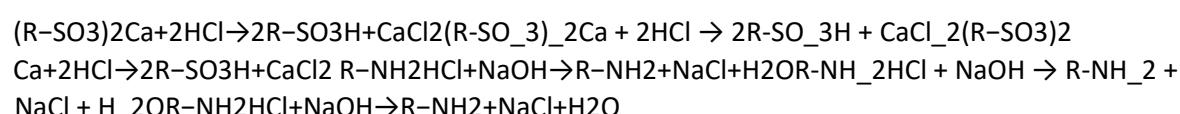
1.3 Ion Exchange Process

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:** $2R-SO_3H + Ca^{2+} \rightarrow (R-SO_3)_2Ca + 2H^+$
2. **Anion Exchange:** $R-NH_2 + Cl^- \rightarrow R-NH_2HCl$

Regeneration:



Advantages: Highly effective, produces **deionized water**.

Disadvantages: Expensive, requires acids/bases for regeneration.

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**:
 $3Ca^{2+} + 2Na_3PO_4 \rightarrow Ca_3(PO_4)_2 \downarrow + 6Na^+$
 $3Ca^{2+} + 2Na_3PO_4 \rightarrow Ca_3(PO_4)_2 \downarrow + 6Na^+$
- **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**:
 $Ca^{2+} + Na_2CO_3 \rightarrow CaCO_3 \downarrow + 2Na^+$
 $Ca^{2+} + Na_2CO_3 \rightarrow CaCO_3 \downarrow + 2Na^+$

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+} .
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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 ($\text{Ca}(\text{HCO}_3)_2$, $\text{Mg}(\text{HCO}_3)_2$). Removed by boiling or adding lime.
- **Permanent Hardness** – Due to sulfates, chlorides, nitrates (CaSO_4 , MgCl_2). Removed by chemical methods.

Numerical Formula:

$$\text{Hardness (in ppm)} = \frac{\text{Mass of CaCO}_3 \text{ equivalent} \times 1000000}{\text{Volume of sample (mL)}}$$

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:

$$\text{Alkalinity (in mg/L)} = \frac{(B \times N \times 50000) / V}{V}$$

$$\text{Alkalinity (in mg/L)} = \frac{B \times N \times 50000}{V}$$

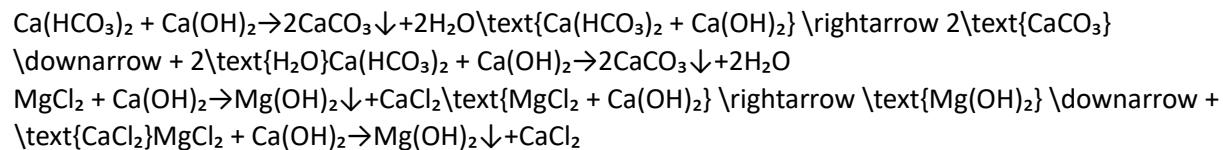
where:

- **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 ($\text{Ca}(\text{OH})_2$) and soda ash (Na_2CO_3) to remove hardness.

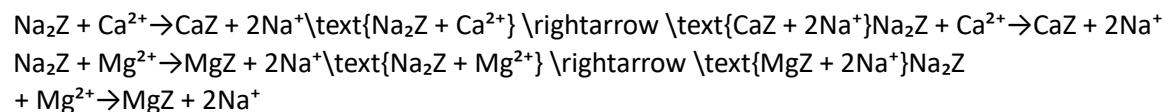


Numerical Problem:

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:



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.

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.

5. Notes (Arranged Properly)

Concept	Formula/Reaction	Key Points
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Hardness	$\text{ppm} = \frac{\text{Mass of CaCO}_3 \text{ equivalent} \times 10^6}{\text{Volume of water}} \text{ ppm}$	Expressed in ppm or mg/L Measures
Calculation	$\text{ppm} = \frac{\text{Volume of water} \times \text{Mass of CaCO}_3 \text{ equivalent} \times 10^6}{\text{Volume of water}}$	
Alkalinity	$\text{Alkalinity} = \frac{(B \times N \times 50000)}{V}$	OH^- , CO_3^{2-} , HCO_3^-
Calculation	$\text{Alkalinity} = \frac{(B \times N \times 50000)}{V}$	
Lime-Soda Reactions	$\text{Ca(HCO}_3)_2 + \text{Ca(OH)}_2 \rightarrow \text{CaCO}_3 \downarrow + \text{H}_2\text{O}$	Removes temporary hardness
Zeolite Reactions	$\text{Na}_2\text{Z} + \text{Ca}^{2+} \rightarrow \text{CaZ} + 2\text{Na}^+$	Removes permanent hardness
Reverse Osmosis	No direct formula	Removes all dissolved salts