BOILER PROBLEMS & SOFTENING METHODS

1. Boiler Problems

When hard water is used in boilers, it causes several problems due to the deposition of salts and impurities.

(i) Scale and Sludge Formation

- **Scales**: Hard, adherent deposits formed due to precipitation of **$CaSO_4$, $CaCO_3$, and $Mg(OH)_2$**.
    - Effects: Reduces heat transfer, decreases boiler efficiency, overheating, and tube failure.
- **Sludge**: Loose, non-adherent deposits formed by **$MgCl_2$, $MgSO_4$, and $CaCl_2$** in lower temperatures.
    - Effects: Causes corrosion and decreases boiler efficiency.

(ii) Boiler Corrosion

- Caused by dissolved **oxygen (O_2), carbon dioxide (CO_2), and acidic water**.
- Effects: Weakens boiler material, leading to failure.

(iii) Caustic Embrittlement

- Caused by NaOH accumulation, making the boiler brittle.
- Effects: Cracks and metal failure.

(iv) Priming and Foaming

- **Priming**: Water droplets carried with steam due to high surface tension (caused by dissolved salts).
- **Foaming**: Formation of stable bubbles due to oils and suspended solids.
- Effects: Reduces efficiency and damages turbine blades.

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2. Water Softening Methods

To remove hardness and prevent boiler problems, water softening is essential.

(i) Lime-Soda Process

- **Principle**: Addition of **$Ca(OH)_2$ (lime)** and **Na_2CO_3 (soda ash)** to precipitate Ca^{2+} and Mg^{2+} as insoluble salts.

Reactions:

$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O$\text{Ca(HCO₃)₂} + \text{Ca(OH)₂} \rightarrow

$2\text{CaCO}_3 \downarrow + 2\text{H}_2\text{O}$ $Ca(HCO_3)_2+Ca(OH)_2 \rightarrow 2CaCO_3\downarrow+2H_2O$
$Mg(HCO_3)_2+2Ca(OH)_2 \rightarrow 2CaCO_3\downarrow+Mg(OH)_2\downarrow+2H_2O$ $\text{Mg(HCO}_3\text{)}_2 + 2\text{Ca(OH)}_2 \rightarrow 2\text{CaCO}_3 \downarrow + \text{Mg(OH)}_2 \downarrow + 2\text{H}_2\text{O}$ $Mg(HCO_3)_2+2Ca(OH)_2 \rightarrow 2CaCO_3\downarrow+Mg(OH)_2\downarrow+2H_2O$
$CaCl_2+Na_2CO_3 \rightarrow CaCO_3\downarrow+2NaCl$ $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{NaCl}$ $CaCl_2+Na_2CO_3 \rightarrow CaCO_3\downarrow+2NaCl$

- **Types**:
  1. **Cold Lime-Soda Process**: Carried out at room temperature, requires longer settling time.
  2. **Hot Lime-Soda Process**: Performed at high temperature and pressure, gives faster results.
- **Advantages**: Cheap, removes temporary and permanent hardness.
- **Disadvantages**: Sludge formation, requires further filtration.

(ii) Zeolite Process (Permutit Process)

- **Principle**: Hardness-causing ions (Ca^{2+}, Mg^{2+}) are exchanged with Na^+ using **zeolite (sodium alumino-silicate)**.

Reaction:

$Na_2Ze+CaCl_2 \rightarrow CaZe+2NaCl$ $\text{Na}_2\text{Ze} + \text{CaCl}_2 \rightarrow \text{CaZe} + 2\text{NaCl}$ $Na_2Ze+CaCl_2 \rightarrow CaZe+2NaCl$ $Na_2Ze+MgSO_4 \rightarrow MgZe+Na_2SO_4$ $\text{Na}_2\text{Ze} + \text{MgSO}_4 \rightarrow \text{MgZe} + \text{Na}_2\text{SO}_4$ $Na_2Ze+MgSO_4 \rightarrow MgZe+Na_2SO_4$

- **Regeneration:**

  $CaZe+2NaCl \rightarrow Na_2Ze+CaCl_2$ $\text{CaZe} + 2\text{NaCl} \rightarrow \text{Na}_2\text{Ze} + \text{CaCl}_2$ $CaZe+2NaCl \rightarrow Na_2Ze+CaCl_2$

  Zeolite is regenerated using NaCl solution.

- **Advantages**: Continuous process, complete removal of hardness, no sludge formation.
- **Disadvantages**: Cannot remove Fe^{2+}, Mn^{2+}, and dissolved gases.

(iii) Ion Exchange Process

- **Principle**: Uses resins to exchange ions:
  - **Cation exchange resin ($R\text{-}H^+$)** removes Ca^{2+}, Mg^{2+}.
  - **Anion exchange resin ($R\text{-}OH^-$)** removes SO_4^{2-}, Cl^-.

Reactions:

R-H+$CaCl_2$→R-Ca+2HCl\text{R-H} + \text{$CaCl_2$} \rightarrow \text{R-Ca} + 2\text{HCl}R-H+$CaCl_2$→R-Ca+2HCl R-OH+HCl→R-Cl+H_2O\text{R-OH} + \text{HCl} \rightarrow \text{R-Cl} + \text{H_2O}R-OH+HCl→R-Cl+H_2O

- **Regeneration:**
  - Cation resin: Treated with **HCl or H_2SO_4**.
  - Anion resin: Treated with **NaOH**.
- **Advantages**: Removes all ions, produces **deionized (demineralized) water**.
- **Disadvantages**: Expensive, requires chemicals for regeneration.

Outcomes:

- Understanding boiler problems and their effects on efficiency.
- Learning different softening techniques and their principles.
- Ability to select appropriate water treatment methods for industrial applications.

Boiler Troubles

- **1□Sludge & Scale Formation**
- When hard water is heated in a boiler, dissolved salts precipitate out, forming sludge and scale.
- **Sludge Formation**
- Forms in **low-temperature zones**
  Consists of **$MgCl_2$, $MgCO_3$, $CaCl_2$, and $CaSO_4$**
  Soft, loose deposits
  Easily removable by blowdown
- **Prevention:**

✓ Use **softened water**

✓ Add **phosphates** to convert sludge into a non-adherent form

✓ **Blowdown method** – removes sludge periodically

- **Scale Formation**
- Forms in **high-temperature zones**
  Consists of **$CaSO_4$, $CaCO_3$, and $Mg(OH)_2$**
  Hard, adherent deposits
  Decreases heat transfer efficiency, leading to overheating and tube failure
- **Prevention:**

✓ **Lime-soda process** – Removes scale-forming salts

✓ **Phosphate treatment** – Converts $CaSO_4$ into soft sludge

✓ **EDTA treatment** – Forms soluble complexes with Ca^{2+} and Mg^{2+}

✓ **Descaling agents** – Dissolve scales chemically

- **2□Priming & Foaming • Priming (Water Carryover with Steam)**
- **Cause:**

✓ High steam velocity
✓ High water level in the boiler
✓ Sudden boiling

- **Effects:**

Carries water droplets into the steam engine
Reduces boiler efficiency

- **Prevention:**

✓ Maintain **proper water level**
✓ Use **anti-priming baffles**
✓ Reduce **steam velocity**

- **Foaming (Stable Foam Formation on Water Surface)**
- **Cause:**

✓ High dissolved solids (oil, soap, alkali)
✓ High concentration of NaCl

- **Effects:**

Lowers heat transfer
Leads to **wet steam**, damaging turbines

- **Prevention:**

✓ **Blowdown method** – Reduces dissolved solids
✓ **Anti-foaming agents** – E.g., sodium aluminates

- **3□Boiler Corrosion**
- Deterioration of boiler metal due to chemical reactions.
- **Causes of Boiler Corrosion**
- **1. Dissolved Oxygen Corrosion**
- ✓ Oxygen reacts with **iron** to form **rust**:
- 4Fe+3O2+6H2O→4Fe(OH)34Fe + 3O_2 + 6H_2O \rightarrow 4Fe(OH)_34Fe+3O2 +6H2O→4Fe(OH)3
- ✓ $Fe(OH)_3$ further dehydrates to form $Fe_2O_3 \cdot xH_2O$ (rust).
- **Prevention:**

✓ Remove O_2 using **sodium sulfite**:

- Na2SO3+O2→Na2SO4Na_2SO_3 + O_2 \rightarrow Na_2SO_4Na2SO3+O2→Na2 SO4
- ✓ Use **deaerators** to remove dissolved O_2

✓ Maintain **pH between 8.5-9.5**

- **2. Acidic Water Corrosion**
- ✓ Acidic water (low pH)(\text{low pH})(low pH) reacts with **Fe**, forming soluble **Fe^{2+}** ions:

- Fe+2H+→Fe2++H2Fe + 2H^+ \rightarrow Fe^{2+} + H_2Fe+2H+→Fe2++H2
- **Prevention:**

✓ Add **alkaline buffers** (e.g., NaOH) to maintain pH

- **3. Carbon Dioxide (CO_2) Corrosion** • ✓ CO_2 dissolves in water, forming carbonic acid **(H_2CO_3)**, which attacks metal:
- CO2+H2O→H2CO3CO_2 + H_2O \rightarrow H_2CO_3CO2+H2O→H2CO3 Fe+H2CO3→Fe(HCO3)2Fe + H_2CO_3 \rightarrow Fe(HCO_3)_2Fe+H2CO3 →Fe(HCO3)2 • **Prevention:**

✓ Remove CO_2 using **deaeration**

✓ Maintain **alkalinity with NaOH**

- **Outcomes:**

✓ Understand the major boiler troubles and their impact

✓ Learn preventive measures for scale, sludge, priming, foaming, and corrosion

✓ Apply water treatment methods for effective boiler operation

Caustic Embrittlement & Softening of Water

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1. Caustic Embrittlement

Definition:

Caustic embrittlement is a type of **intergranular cracking** that occurs in **high-pressure boilers** due to the accumulation of **NaOH (sodium hydroxide)** in certain areas. It weakens the boiler metal, making it brittle.

Cause:

- **High concentration of NaOH** in boiler water (due to improper water softening or excessive use of Na_2CO_3 in the Lime-Soda process).
- **Formation of minute cracks** due to differential concentration of NaOH.

Mechanism (Due to High NaOH concentration)

1. **Na_2CO_3 from softening methods decomposes in boiler water:** Na2CO3+H2O→2NaOH+CO2Na_2CO_3 + H_2O → 2NaOH + CO_2Na2CO3+H2O→2NaOH+CO2
2. **NaOH seeps into cracks via osmosis, concentrating at stressed areas.**
3. **Hydroxide ions (OH^-) attack iron in boiler metal:** Fe+2NaOH→Na2FeO2+H2↑Fe + 2NaOH → Na_2FeO_2 + H_2 ↑Fe+2NaOH→Na2FeO2+H2↑
4. **Sodium ferrite (Na_2FeO_2) forms, weakening metal structure and leading to cracking.**

Prevention Methods:

- **Use sodium phosphate instead of Na_2CO_3** for softening.
- **Maintain proper alkalinity levels.**
- **Use inhibitors like tannin or lignin** to block cracks.

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2. Softening of Water

Hard water contains dissolved **Ca^{2+} and Mg^{2+} ions**, which lead to scale formation. Softening removes these ions to prevent damage to boilers and pipes.

2.1 Lime-Soda Process

Principle: Converts Ca^{2+} and Mg^{2+} into **insoluble precipitates** 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.

2.2 Zeolite Process

Principle: Ion exchange of Ca^{2+} and Mg^{2+} with Na^+ 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:** 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, easy operation.
Disadvantages: Doesn't remove silica and acids.

2.3 Ion Exchange Process

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

Reactions:

1. **Cation Exchange:** 2R−SO3H+Ca2+→(R−SO3)2Ca+2H+2R-SO_3H + Ca^{2+} \rightarrow (R-SO_3)_2Ca + 2H^+2R−SO3H+Ca2+→(R−SO3)2Ca+2H+
2. **Anion Exchange:** R−NH2+Cl−→R−NH2HClR-NH_2 + Cl^- \rightarrow RNH_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)2Ca+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: Produces deionized water.
Disadvantages: Expensive, requires acids/bases for regeneration.

Outcomes:

- Understanding **Caustic Embrittlement** and its prevention.
- Knowledge of **Lime-Soda, Zeolite, and Ion Exchange** methods for water softening.
- Importance of **water softening in industrial applications** to prevent damage.

1. Lime-Soda Method

A chemical softening process that removes both **temporary** and **permanent** hardness using **lime ($Ca(OH)_2$)** and **soda ash (Na_2CO_3)**. **Chemical Reactions**

1. **For Temporary Hardness (Ca and Mg Bicarbonates)**

   $Ca(HCO_3)_2+Ca(OH)_2 \rightarrow 2CaCO_3\downarrow+2H_2O$\text{$Ca(HCO_3)_2$} + \text{$Ca(OH)_2$} \rightarrow 2\text{$CaCO_3$} \downarrow + 2\text{$H_2O$}$Ca(HCO_3)_2+Ca(OH)_2 \rightarrow 2CaCO_3\downarrow+2H_2O$
   $Mg(HCO_3)_2+2Ca(OH)_2 \rightarrow 2CaCO_3\downarrow+Mg(OH)_2\downarrow+2H_2O$\text{$Mg(HCO_3)_2$} + 2\text{$Ca(OH)_2$} \rightarrow 2\text{$CaCO_3$} \downarrow + \text{$Mg(OH)_2$}

\downarrow + 2\text{H_2O}$Mg(HCO_3)_2+2Ca(OH)_2 \rightarrow 2CaCO_3\downarrow+Mg(OH)_2\downarrow+2H_2O$

2. **For Permanent Hardness (Ca and Mg Chlorides/Sulfates)**
   $CaCl_2+Na_2CO_3 \rightarrow CaCO_3\downarrow+2NaCl$\text{$CaCl_2$} + \text{$Na_2CO_3$} \rightarrow \text{$CaCO_3$} \downarrow + 2\text{NaCl}$CaCl_2+Na_2CO_3 \rightarrow CaCO_3\downarrow+2NaCl$
   $MgSO_4+Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow+CaSO_4$\text{$MgSO_4$} + \text{$Ca(OH)_2$} \rightarrow \text{$Mg(OH)_2$} \downarrow + \text{$CaSO_4$}$MgSO_4+Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow+CaSO_4$

Numerical Problem Formula (Lime & Soda Calculation)

1. **Amount of Lime Required**

   Lime (kg)=100/74Equivalent Weight of $CaCO_3$×Total Hardness (in mg/L)×Water Volume (ML)\text{Lime (kg)} = \frac{100/74}{\text{Equivalent Weight of $CaCO_3$}} \times \text{Total Hardness (in mg/L)} \times \text{Water Volume (ML)}Lime (kg)=Equivalent Weight of $CaCO_3$100/74 ×Total Hardness (in mg/L)×Water Volume (ML)

2. **Amount of Soda Required**

   Soda (kg)=106/100Equivalent Weight of $CaCO_3$×Permanent Hardness×Water Volume\text{Soda (kg)} = \frac{106/100}{\text{Equivalent Weight of $CaCO_3$}} \times \text{Permanent Hardness} \times \text{Water Volume}Soda (kg)=Equivalent Weight of $CaCO_3$106/100 ×Permanent Hardness×Water Volume

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2. Zeolite (Permutit) Method

A **cation-exchange** process that replaces **Ca^{2+} and Mg^{2+} ions** with **Na^+ ions** using **sodium zeolite (Na_2Z)**.

Chemical Reactions

1. **Softening Reaction:** $Ca^{2+}+Na_2Z \rightarrow CaZ+2Na^+$\text{$Ca^{2+}$} + \text{$Na_2Z$} \rightarrow \text{CaZ} + 2\text{Na^+}$Ca^{2+}+Na_2Z \rightarrow CaZ+2Na^+$
   $Mg^{2+}+Na_2Z \rightarrow MgZ+2Na^+$\text{$Mg^{2+}$} + \text{$Na_2Z$} \rightarrow \text{MgZ} + 2\text{Na^+}$Mg^{2+}+Na_2Z \rightarrow MgZ+2Na^+$
2. **Regeneration with Brine (NaCl Solution):** $CaZ+2NaCl \rightarrow Na_2Z+CaCl_2$\text{CaZ} + 2\text{NaCl} \rightarrow \text{Na_2Z} + \text{$CaCl_2$}$CaZ+2NaCl \rightarrow Na_2Z+CaCl_2$
   $MgZ+2NaCl \rightarrow Na_2Z+MgCl_2$\text{MgZ} + 2\text{NaCl} \rightarrow \text{Na_2Z} + \text{$MgCl_2$}$MgZ+2NaCl \rightarrow Na_2Z+MgCl_2$

Numerical Problem Formula (Zeolite Calculation)

1. **Amount of Zeolite Required**

Zeolite (kg)=Hardness (in mg/L)×Water Volume (ML)Exchange Capacity of Zeolite (mg/L per kg)\text{Zeolite (kg)} = \frac{\text{Hardness (in mg/L)} \times \text{Water Volume (ML)}}{\text{Exchange Capacity of Zeolite (mg/L per kg)}}Zeolite (kg)=Exchange Capacity of Zeolite (mg/L per kg)Hardness (in mg/L)×Water Volume (ML)

2. **Amount of NaCl Required for Regeneration**

   NaCl (kg)=Total Hardness (kg)×NaCl required per kg of hardnessEfficiency Factor\text{NaCl (kg)} = \text{Total Hardness (kg)} \times \frac{\text{NaCl required per kg of hardness}}{\text{Efficiency Factor}}NaCl (kg)=Total Hardness (kg)×Efficiency FactorNaCl required per kg of hardness

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3. Ion Exchange (Resin) Method

A **modern softening technique** using synthetic resins to exchange ions.

Two-Step Process:

1. **Cation Exchange Resin:** Removes **Ca^{2+} and Mg^{2+}**

   $2RNa+Ca^{2+}\rightarrow R_2Ca+2Na^+$2\text{RNa} + \text{Ca²⁺} \rightarrow \text{R₂Ca} + 2\text{Na⁺}$2RNa+Ca^{2+}\rightarrow R_2Ca+2Na^+$ $2RNa+Mg^{2+}\rightarrow R_2Mg+2Na^+$2\text{RNa} + \text{Mg²⁺} \rightarrow \text{R₂Mg} + 2\text{Na⁺}$2RNa+Mg^{2+}\rightarrow R_2Mg+2Na^+$

2. **Anion Exchange Resin:** Removes **SO_4^{2-}, Cl^-, NO_3^-**

   $ROH+Cl^-\rightarrow RCl+OH^-$\text{ROH} + \text{Cl⁻} \rightarrow \text{RCl} + \text{OH⁻}$ROH+Cl^-\rightarrow RCl+OH^-$

3. **Regeneration of Resins:**
   - **Cation resin regenerated with NaCl solution.** ○ **Anion resin regenerated with NaOH solution.**

Numerical Problem Formula (Ion Exchange Calculation)

1. **Amount of Cation Resin Required**

   Resin (kg)=Hardness (mg/L)×Water Volume (ML)Resin Exchange Capacity (mg/L per kg)\text{Resin (kg)} = \frac{\text{Hardness (mg/L)} \times \text{Water Volume (ML)}}{\text{Resin Exchange Capacity (mg/L per kg)}}Resin (kg)=Resin Exchange Capacity (mg/L per kg)Hardness (mg/L)×Water Volume (ML)

2. **Amount of Regenerant (NaCl) Required**

   NaCl (kg)=Resin Used (kg)×NaCl per kg ResinEfficiency Factor\text{NaCl (kg)} = \text{Resin Used (kg)} \times \frac{\text{NaCl per kg Resin}}{\text{Efficiency Factor}}NaCl (kg)=Resin Used (kg)×Efficiency FactorNaCl per kg Resin

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4. Expected Outcomes

- **Understand and apply** chemical reactions in softening processes.
- **Solve numerical problems** related to water softening methods.
- **Calculate lime, soda, zeolite, resin, and NaCl requirements** for softening.
- **Differentiate between lime-soda, zeolite, and ion-exchange methods**.

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5. Summary Notes (Organized Table)

Method	Reaction	Key Features	Numerical Formula
Lime-Soda	$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow CaCO_3 \downarrow + H_2O$	Removes temporary & permanent hardness	Lime = (100/74) × Hardness × Water Volume
Zeolite	$Ca^{2+} + Na_2Z \rightarrow CaZ + 2Na^+$	Cation exchange with Na^+	Zeolite = Hardness × Water Volume / Zeolite Capacity
Ion Exchange	$2RNa + Ca^{2+} \rightarrow R_2Ca + 2Na^+$	Removes all ions (softens & deionizes)	Resin = Hardness × Water Volume / Resin Capacity