Water Softening and Hardness

1. Water Softening for Hardness Removal

2. Hardness in Water
   - High concentration of calcium (Ca²⁺) and magnesium (Mg²⁺) ions in water cause hardness
   - Generally, water containing more than 100 mg/l of hardness expressed as calcium carbonate (CaCO₃) is considered to be hard
   - Excessive hardness is undesirable because it causes the formation of soap curds, increased use of soap, deposition of scale in boilers, pipelines and home appliances, damage in industrial processes and can cause objectionable tastes.

3. Methods of Removing Hardness

<table>
<thead>
<tr>
<th>Treatment Method</th>
<th>Hardness Levels Retained</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lime Softening (Chemical Precipitation)</td>
<td>Solubility Level of about 35 mg/l (CaCO₃)</td>
</tr>
<tr>
<td>RO (Nanofiltration) (Membrane Filtration)</td>
<td>85 – 90% removal</td>
</tr>
<tr>
<td>Ion Exchange (Chemical Exchange)</td>
<td>Basically Zero Water must be blended</td>
</tr>
</tbody>
</table>
### Hardness Descriptions

<table>
<thead>
<tr>
<th>Description</th>
<th>Hardness (mg/l of CaCO₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extremely soft to soft</td>
<td>0 – 45</td>
</tr>
<tr>
<td>Soft to moderately hard</td>
<td>46-90</td>
</tr>
<tr>
<td>Moderately hard to hard</td>
<td>91-130</td>
</tr>
<tr>
<td>Hard to very hard</td>
<td>131-170</td>
</tr>
<tr>
<td>Very hard to excessively hard</td>
<td>171-250</td>
</tr>
<tr>
<td>Too hard for ordinary domestic use</td>
<td>Over 250</td>
</tr>
</tbody>
</table>

### Important Definitions in Lime Softening Treatment

- **Hardness** is caused mainly by the salts of calcium and magnesium, such as bicarbonate, carbonate, sulfate, chloride, and nitrate.
  - **Calcium Hardness** is caused by calcium ions (Ca²⁺)
  - **Magnesium Hardness** is caused by magnesium ions (Mg²⁺)
- **Total Hardness** is commonly measured by titration and is described in two ways:
  - The sum of the carbonate (temporary) and noncarbonate (permanent) hardness
  - The sum of the carbonate hardness and noncarbonate hardness
- **Calcium Carbonate (CaCO₃) Equivalent** is an expression of the concentration of a chemical in terms of its equivalent to calcium carbonate. It allows us to express different chemicals in “apples to apples” terms.
- **Carbonate Hardness** is caused by alkalinity present in the water up to the total hardness, which is the true measure of the water’s hardness. (Calc hardness = alkalinity)
- **Noncarbonate Hardness** is that portion of the total hardness in excess of the alkalinity. Requires use of both lime and soda ash to remove.
- **Alkalinity** is a measure of how much acid must be added to lower the pH to 4.5. It is caused by the water’s content of bicarbonate, carbonate, hydroxide, and occasionally sulfate, chloride, and phosphate. *(These are loosely grouped in with carbonate hardness)*

### Categories of Hardness

<table>
<thead>
<tr>
<th>Calcium Carbonate</th>
<th>Magnesium Carbonate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temporary</td>
<td>Temporary</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>Alkalinity</td>
</tr>
<tr>
<td>Carbonate</td>
<td>Carbonate</td>
</tr>
<tr>
<td>Noncarbonate</td>
<td>Noncarbonate</td>
</tr>
<tr>
<td>Sulfate, chloride, nitrate</td>
<td>Sulfate, chloride, nitrate</td>
</tr>
<tr>
<td>Permanent</td>
<td>Permanent</td>
</tr>
</tbody>
</table>
Benefits of Lime Softening

- Removal of Ca and Mg hardness
- Removal of iron, manganese, arsenic and uranium.
- Reduction of solids, turbidity and TOC
- Removal and inactivation of bacteria and viruses due to high pH.
- Raises pH and prevents corrosion
- Removal of excess fluoride.

Types of Lime Used in WTP

- Quick Lime (CaO) (molecular wt. 56)
  - 75% - 99% purity (typically 85%)
  - Dry powder and must be slaked for 15 - 30 minutes at cold temperature
  - Slaking (agitating with water) produces CaOH2 (Calcium Hydroxide)
  - Used at large WTP because lower cost
- Hydrated Lime Ca(OH)2 (molecular wt. 74)
  - Made when Quick Lime is slaked
  - $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{HEAT}$
  - Very stable
  - Small WTPs use directly due to convenience
  - Hydrated Lime shipped 80% - 99% purity (typically 95%)

Chemical Precipitation

- Hardness causing ions are converted from soluble to insoluble forms (Ca and Mg) at high pH
- Addition of lime:
  - Increases the hydroxide concentrations, increasing the pH
  - Converts alkalinity from the bicarbonate form to the carbonate form which causes the calcium to precipitate out as CaCO3
  - If more lime is added the phenolphthalein (P) alkalinity increases to a level where hydroxide becomes present (excess causticity) allowing magnesium to precipitate as magnesium hydroxide.
SUPERSATURATED

- Following the softening process the pH is high
- Water is supersaturated with excess caustic alkalinity in either the hydroxide or carbonate form
- Carbon dioxide can be used to decrease the causticity and scale-forming tendencies of the water prior to filtration

Relationships among pH, Alkalinity and Indicators

![Diagram showing relationships between pH, total alkalinity, phenolphthalein alkalinity, bicarbonate, and carbonate](image)

Types of Alkalinity that can be Present at pH Values

- Addition of lime to water increases the hydroxide concentration, thus raising the pH. It is important to control pH in the finished water in a lime softening plant to prevent scaling or corrosion.
- Below 4.5 only CO₂ present, no alkalinity
- Between 4.5 to 8.3, CO₂ and Bicarbonate present
- Above 8.3 alkalinity may consist of Bicarbonate, Carbonate, and Hydroxide (no CO₂ present)
- When pH is greater than 8.3, the amount of titrant used to reach pH 8.3 is the phenolphthalein alkalinity
- Between 10.2 to 11.3 Carbonate & Hydroxide
- At 9.4 Calcium Carbonate becomes insoluble and precipitates
- At 10.6 Magnesium Hydroxide becomes insoluble and precipitates
Chemical Titration with Methyl Orange (T) and Phenolphthalein (P)

- Methyl Orange is used to determine the combination of alkalinity provided by carbonate, bicarbonate and hydroxide or Total Alkalinity.
- A sample of the water is titrated by adding the Methyl Orange color indicator and adding measured amount of acid until the color is absent.
- The Total Alkalinity (T) is then computed.

- Phenolphthalein is used to determine the carbonate and hydroxide alkalinity present.
- A sample of the water is titrated by adding the Phenolphthalein color indicator and adding measured amount of acid until the color is absent.
- The Hydroxide and Carbonate Alkalinity (P) is then computed.

Calculation of Alkalinity Constituents in Drinking Water based on Methyl Orange and Phenolphthalein Titrations

<table>
<thead>
<tr>
<th>Equation</th>
<th>Titrated Result</th>
<th>Bicarbonate &gt; pH 4.5 to 8.3</th>
<th>Carbonate &gt; pH 8.3</th>
<th>Hydroxide &gt; pH 11.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>P = 0</td>
<td>T</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>P &lt; ½ T</td>
<td>T - 2P</td>
<td>2P</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>P = ½ T</td>
<td>0</td>
<td>2P</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>P &gt; ½ T</td>
<td>0</td>
<td>2T - 2P</td>
<td>2P - T</td>
</tr>
<tr>
<td>5</td>
<td>P = T</td>
<td>0</td>
<td>0</td>
<td>T</td>
</tr>
</tbody>
</table>

Key: P – phenolphthalein alkalinity; T – total alkalinity

Hardness Relationship to Alkalinity

- TH = CH + NCH (each expressed as mg/l as CaCO₃)
- The amount of carbonate and noncarbonate hardness depends on the alkalinity of the water
  - Alkalinity > Total Hardness (all hardness is in carbonate form)
    \[ TH = CH \]
  - Alkalinity < Total Hardness (both Carbonate Hardness and Noncarbonate Hardness are present)
    \[ CH = \text{Alkalinity} \]
    \[ NCH = TH - CH = TH - \text{Alkalinity} \]
Calculate the total hardness in grains per gallon for a water with a carbonate hardness of 250 mg/l and a non-carbonate hardness of 160 mg/l.

- From formula sheet
- NCH = TH - CH
- Therefore, TH = NCH + CH
- TH = 160 + 250 = 410 mg/l
- Change to grains per gallon
- \( \frac{410 \text{ mg/l}}{17.1 \text{ mg/l}} \times \frac{1 \text{ gr}}{\text{gal}} = 24 \text{ gpg} \)

Lime Softening Process Limitations

- Unable to remove all carbonate (~30 mg/l) and no Non-Carbonate hardness.
- High degree of operator control.
- Color removal for highly colored waters may be hindered due to high pH.
- Important to maintain proper pH to prevent scaling or corrosion.
- Sludge handling and disposal are costly (~2.5 mg/l per mg/l lime added).

Primary Coagulants Sometimes Used in Lime Softening

- Acidic compounds: aluminum sulfate (alum), ferrous sulfate, ferric sulfate, and ferric chloride.
  - Increase lime demand
  - Highly colored waters are best treated at low pH values
- Basic compounds: sodium aluminate
  - Lime required will be less
  - High pH values will tend to set color
- Cationic polymers
  - Not very pH sensitive and often used in softening
Secondary Coagulant Aids
Sometimes Used in Lime Softening

- Coagulant aids often added to help stimulate the production of floc.
- They include sodium aluminate, bentonite or clay, sodium silicate and various synthetic cationic and non-ionic polymers.
- Bentonite is often used in waters with high color and low turbidity to bind with small floc.

Types of Lime Treatment

- Excess Lime Treatment
  - Removes Ca & Mg
  - Produces an excessive amount of sludge.
- Partial Lime Softening
  - Used for low Mg FL waters
  - Only enough lime to remove calcium is added.
  - Sludge amounts reduced.
- Split Treatment
  - Split Treatment is sometimes used when non-carbonate hardness is low and Mg concentration high.
  - CO₂ requirements can be reduced or eliminated by blending the softened water with an unsoftened flow stream.
  - Generally 80% treated and 20% raw.
- Non-carbonate Hardness removal using Lime-Soda
  - When the water contains non-carbonate hardness (calcium sulfate) it requires the addition of soda ash (sodium carbonate, Na₂CO₃).
  - An alternative to the lime-soda ash process is the use of caustic soda (sodium hydroxide, NaOH).

When water cannot be softened to the desired level, what action do you take? Add soda ash or caustic soda.
Non-Carbonate Removal
First Identify the Amount of Non-Carbonate Hardness
- If Alkalinity > TH then CH = TH; NCH = 0
- If Alkalinity < TH then CH = Alkalinity
  Therefore NCH = TH - Alkalinity
- The amount of Soda Ash (Na₂CO₃) required is Equivalent to the Non-Carbonate Hardness adjusted to its Calcium Carbonate Equivalent
- Soda ash = NCH x (106/100)

Recarbonation in Lime Softening
- Lime softened water is supersaturated
- If not recarbonated, Ca and Mg carbonate will form on the filters and distribution piping
- Unused lime (calcium hydroxide and magnesium hydroxide) in solution at high pH (11), must be converted to a stable forms.
  - First, CO₂ is added to reduce Ca(OH)₂ to CaCO₃ which precipitates at about pH 10
  - Additional CO₂ is added to convert Mg(OH)₂ to soluble Mg(HCO₃)₂ which occurs at a pH of 8.4.
  - Reaction must be completed before filtration so that calcium carbonate will not precipitate in the filters or carry into distribution system.

Summary
- Hardness is from Calcium and Magnesium ions in the water (Ca²⁺⁺+Mg²⁺⁺)
- 100 mg/L expressed as CaCO₃ is considered to be hard
Summary

3 types of treatment for hardness
- Lime Softening
- Reverse Osmosis / Nanofiltration
- Ion Exchange

Carbonate hardness = alkalinity.
Noncarbonate hardness = excess over alkalinity

Summary

Alkalinity is the capacity of the water to neutralize acid.

(The more alkalinity, the more acid you have to add to lower the pH).