Lecture 9 - Lime-soda ash softening, Part 2

For waters with non-carbonate hardness, single-stage softening is insufficient. Leftover hardness is removed by addition of soda ash (Na₂CO₃).

\[ \text{Ca}^{2+} + \text{SO}_4^{2-} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{Na}^+ + \text{SO}_4^{2-} \]

\[ \text{Ca}^{2+} + 2\text{Cl}^- + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{Na}^+ + 2\text{Cl}^- \]

Practical limits of lime-soda ash softening are dictated by solubility of precipitates: CaCO₃ and Mg(OH)₂

Ca: 30 mg/L as CaCO₃
Mg: 10 mg/L as CaCO₃
Total hardness: 40 mg/L as CaCO₃

In practice, residual hardness = 50 to 80 mg/L

This water has high pH and needs to be recarbonated

Lime-soda ash treatment is usually treated by "two-stage softening" also called "excess-lime treatment" and "split recarbonation treatment".

See Lecture 8, page 10

Split treatment is similar, except only part of water is treated with lime. Other part by-passes lime treatment and gets soda-ash treatment along with lime-treated water. The CO₂ in untreated water neutralizes high pH in lime-treated water, and recarb. is not needed.

Water split is computed such that enough Mg is removed in lime-treated water to meet target Mg level in combined finished water.
Computing chemical doses for lime soda ash softening - Example 11.4

From Viessman and Hammer, pg. 445 - pg 3 and 4

\[ \text{CO}_2 = 8.8 \text{ mg/L as CO}_2 \]

\[ \text{Ca}^{2+} = 70 \text{ mg/L} \]

\[ \text{Mg}^{2+} = 9.7 \text{ mg/L} \]

\[ \text{Na}^+ = 6.9 \text{ mg/L} \]

\[ \text{AlK} = 115 \text{ mg/L as CaCO}_3 \]

\[ \text{SO}_4^{2-} = 96 \text{ mg/L} \]

\[ \text{Cl}^- = 10.6 \text{ mg/L} \]

Easiest method is to construct a table that converts all concentrations to equivalent concentrations, and then to equivalents of CaCO\(_3\). Also use chart from VH, Fig.11.8, pg.446

<table>
<thead>
<tr>
<th>Conc. (mg/L)</th>
<th>MW (gm/mole)</th>
<th>Equiv (eq/mole)</th>
<th>Eq wt (gm/mole-eq)</th>
<th>Meq/L</th>
<th>mg/L as CaCO(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)</td>
<td>8.8</td>
<td>44.0</td>
<td>2</td>
<td>22.0</td>
<td>0.4</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>70</td>
<td>40.0</td>
<td>2</td>
<td>20.0</td>
<td>3.5</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>9.7</td>
<td>24.4</td>
<td>2</td>
<td>12.2</td>
<td>0.80</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>6.9</td>
<td>23.0</td>
<td>1</td>
<td>23.0</td>
<td>0.30</td>
</tr>
<tr>
<td>AlK</td>
<td>115</td>
<td>100</td>
<td>2</td>
<td>50.0</td>
<td>2.3</td>
</tr>
<tr>
<td>SO(_4^{2-})</td>
<td>96</td>
<td>96.0</td>
<td>2</td>
<td>48.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>10.6</td>
<td>35.5</td>
<td>1</td>
<td>35.5</td>
<td>0.30</td>
</tr>
</tbody>
</table>

Total hardness = \[ \text{Ca}^{2+} + \text{Mg}^{2+} = 175 + 39.8 = 214.8 \text{ mg/L as CaCO}_3 \]

Carbonate hardness = \[ [\text{AlK}] = 115 \text{ mg/L as CaCO}_3 \]

Noncarbonate hardness = \[ \text{TH-CH} = 99.8 \text{ mg/L as CaCO}_3 \]

Mg noncarbonate hardness = \[ 39.8 \text{ mg/L as CaCO}_3 \]
### Milliequivalent Bar Graph for Example 11.4

**A** Bar graph & hypothetical chemical combinations in the raw water

<table>
<thead>
<tr>
<th></th>
<th>CO₂</th>
<th>Ca( HCO₃ )₂</th>
<th>CaSO₄</th>
<th>MgSO₄</th>
<th>NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>0</strong></td>
<td>0.4</td>
<td>2.3 meq</td>
<td>1.2 meq</td>
<td>0.8 meq</td>
<td>0.3 meq</td>
</tr>
</tbody>
</table>

(A) Bar graph of the water after lime & soda ash additions & settling but before recarbonation.

<table>
<thead>
<tr>
<th></th>
<th>Ca²⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Na⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>0</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>0.6</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>0.8</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>3.1</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(B) Bar graph & hypothetical chemical combinations in the raw water

<table>
<thead>
<tr>
<th></th>
<th>CO₂</th>
<th>Ca( HCO₃ )₂</th>
<th>CaSO₄</th>
<th>MgSO₄</th>
<th>NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>0</strong></td>
<td>0.4</td>
<td>2.3 meq</td>
<td>1.2 meq</td>
<td>0.8 meq</td>
<td>0.3 meq</td>
</tr>
</tbody>
</table>

(C) Bar Graph of the water after two-stage recarbonation & final filtration

<table>
<thead>
<tr>
<th></th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Na⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>0</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>0.6</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>0.8</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>3.1</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure by MIT OCW.

**Before treatment:**

<table>
<thead>
<tr>
<th></th>
<th>CO$_2$</th>
<th>Ca$_{2+}$</th>
<th>Mg$_{2+}$</th>
<th>Na$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>0</td>
<td>3.5</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td>0.4 CO$_2$</td>
<td>2.3 meq Ca(HCO$_3$)$_2$</td>
<td>Carbonate hardness</td>
<td>1.2 meq CaSO$_4$</td>
<td>Non-carb. hardness</td>
</tr>
</tbody>
</table>

**After treatment with lime Ca(OH)$_2$ and intermediate reaction to remove carbonate hardness:**

(chemical equations 1, 2, & 3)

| 1.25 | 0 | 1.2 | 2.0 | 2.3 |
| Ca$_{2+}$ | Ca$_{2+}$ | Mg$_{2+}$ | Na$^+$ |
| OH$^-$ | SO$_4^{2-}$ | Cl$^-$ |
| 1.25 meq excess lime | 2.0 meq NCH | 0.3 NaCl |

**After treatment with lime and intermediate reaction to remove noncarbonate Mg hardness:**

(chemical equations 4 & 5)

| 1.25 | 0 | 1.8 | 2.0 | 2.3 |
| Ca$_{2+}$ | Ca$_{2+}$ | Mg | Na$^+$ |
| OH$^-$ | SO$_4^{2-}$ | Cl$^-$ |
| 1.25 meq excess lime | 2.0 meq NCH | 0.3 NaCl |

**After treatment with soda ash Na$_2$CO$_3$:**

(chemical equations 8 & 9)

| 1.25 | 0 | 0.6 | 0.8 | 2.8 | 3.1 |
| Ca$_{2+}$ | Ca$_{2+}$ | Mg | Na$^+$ |
| OH$^-$ | CO$_3^{2-}$ | SO$_4^{2-}$ | Cl$^-$ |
| 1.25 meq excess lime | residual | 2.0 meq | 0.3 NaCl |
| 0.8 meq hardness | added soda ash |

**After recarbonation:**

(chemical equations 6 & 7)

| 0 | 0.6 | 0.8 | 2.8 | 3.1 |
| Ca$_{2+}$ | Mg | Na$^+$ |
| HCO$_3^-$ | SO$_4^{2-}$ | Cl$^-$ |
| residual | 2.0 meq | 0.3 NaCl |
| 0.8 meq hardness | added soda ash |
Lime required

For CO$_2$ - 20.0 mg/L as CaCO$_3$
For carbonate hardness - 115.0
For Mg noncarbonate hardness - 39.8

\[
\frac{174.8 \text{ mg/L as CaCO}_3}{(2.5 \text{ meq})}
\]

Convert from CaCO$_3$ to CaO

\[
\frac{\text{CaO}}{\text{CaCO}_3} = \frac{40+16}{40+12+3\times16} = \frac{56}{100} = \frac{28}{50}
\]

\[174.8 \text{ mg/L as CaCO}_3 = 97.9 \text{ mg/L as CaO}\]

Include excess lime of 35 mg/L

Reqd lime = 133 mg/L

Soda Ash for noncarbonate hardness

NCH = 99.8 mg/L as CaCO$_3$ (2.0 meq)

(recall that Mg NCH was treated with lime but simply swaps Ca for Mg, so still needs treatment with soda ash)

Reqd Soda Ash = 99.8 mg/L as CaCO$_3$

Convert to Na$_2$CO$_3$:

\[
\frac{\text{Na}_2\text{CO}_3}{\text{Ca CO}_3} = \frac{2\times23+12+3\times16}{40+12+3\times16} = 1.06
\]

\[\text{Reqd soda ash} = 1.06 \times 99.8 = 106 \text{ mg/L}\]

Note that pg 14 shows HCO$_3^-$ but will actually be an equilibrium between CO$_2$, HCO$_3^-$, CO$_3^{2-}$ depending on pH per pg 6.
Carbonate system equilibrium

\[ D_0, D_1, D_2 \]

\[ D_1 - [\text{HCO}_3^-] \]

\[ D_2 - [\text{CO}_3^{2-}] \]

\[ D_0 - [\text{H}_2\text{CO}_3] \]
## Required Chemical Dosage Calculations for Lime & Lime-Soda Ash Softening

### Single-Stage Lime:
- **Lime addition for softening:**
  \[
  CaO = (\text{carbonic acid concentration}) + (\text{calcium carbonate hardness})
  \]
- **Soda ash addition for softening:**
  \[
  Na_2CO_3 = \text{none}
  \]
- **Carbon dioxide for pH adjustment after softening:**
  \[
  CO_2 = \left(\frac{\text{estimated carbonate alkalinity of softened water}}{\text{source water alkalinity}}\right) - \frac{\text{source water calcium hardness}}{\text{calcium carbonate hardness of softened water}}
  \]

### Excess Lime:
- **Lime addition for softening:**
  \[
  CaO = (\text{carbonic acid concentration}) + (\text{total alkalinity}) + (\text{magnesium hardness}) + (\text{excess lime dose})
  \]
- **Soda ash addition for softening:**
  \[
  Na_2CO_3 = \text{none}
  \]
- **Carbon dioxide for pH adjustment after softening:**
  \[
  CO_2 = \left(\frac{\text{source water total hardness}}{\text{source water alkalinity}}\right) - \frac{\text{excess lime dose}}{\text{estimated residual calcium hardness of softened water}} + \left(\frac{\text{estimated residual magnesium hardness of softened water}}{\text{excess lime dose}}\right)
  \]

### Single-Stage Lime Soda Ash:
- **Lime addition for softening:**
  \[
  CaO = (\text{carbonic acid concentration}) + (\text{calcium carbonate hardness})
  \]
- **Soda ash addition for softening:**
  \[
  Na_2CO_3 = (\text{calcium noncarbonate hardness}) + (\text{magnesium noncarbonate hardness})
  \]
- **Carbon dioxide for pH adjustment after softening:**
  \[
  CO_2 = \left(\frac{\text{source water total hardness}}{\text{source water alkalinity}}\right) + \left(\frac{\text{soda ash dose}}{\text{calcium carbonate hardness}}\right) + \left(\frac{\text{estimated residual magnesium hardness of softened water}}{\text{excess lime dose}}\right)
  \]

### Excess Lime - Soda Ash:
- **Lime addition for softening:**
  \[
  CaO = (\text{carbonic acid concentration}) + (\text{calcium carbonate concentration}) + (\text{magnesium carbonate hardness}) + (\text{magnesium noncarbonate hardness})
  \]
- **Soda ash addition for softening:**
  \[
  Na_2CO_3 = (\text{calcium noncarbonate hardness})
  \]
- **Carbon dioxide for pH adjustment after softening:**
  \[
  \begin{align*}
  CO_2, \text{first stage} &= \left(\frac{\text{estimated hydroxide alkalinity of softened water}}{\text{source water alkalinity}}\right) - \frac{\text{excess lime dose}}{\text{estimated residual magnesium hardness of softened water}}
  \\
  CO_2, \text{second stage} &= \left(\frac{\text{estimated hydroxide alkalinity of softened water}}{\text{source water alkalinity}}\right) + \left(\frac{\text{soda ash dose}}{\text{calcium carbonate hardness}}\right) - \left(\frac{\text{source water total hardness}}{\text{soda ash dose}}\right)
  \end{align*}
  \]

*All quantities are expressed as mg/L as CaCO₃

Figure by MIT OCW.