Lecture 8 - Lime-soda ash softening, Part 1

Often necessary to remove certain chemicals from water and wastewater:

Water: iron and manganese, arsenic, hardness, nitrates, radionuclides, organic chemicals.

Industrial wastewater: virtually any chemical, but especially metals, organic chemicals.

Hardness

A water is "hard" if:
1. soap does not easily form a foam or lather.
2. the water leaves scale in hot-water pipes, boilers, etc.

Hardness arises from divalent metal ions in the water:

\[
\begin{align*}
\text{Ca}^{++} & \quad \text{come from natural rocks in source area,} \\
\text{Mg}^{++} & \quad \text{especially: limestones:} \\
\text{Sr}^{++} & \quad \text{calcite, } \text{CaCO}_3 \\
\text{Fe}^{++} & \quad \text{dolomite, } \text{CaMg(CO}_3)_2
\end{align*}
\]

Prevalence of hard water nationwide reflects geology - see Figure 19-8 from MWH, 2005.
Soft water, 0-55 mg/L
Moderately hard water, 55-120 mg/L
Hard water, 120-250 mg/L
Very hard water, 250+ mg/L

Distribution of hard water in United States.
The areas shown define approximate hardness values for municipal water supplies.

Figure by MIT OCW.
Different definitions of hardness

Total hardness = \[ \sum [M^{\text{eq. wt.}}] \times \frac{50}{\text{eq. wt. of } M^{++}} \]

Hardness is expressed in equivalents of CaCO₃

Ca = MW = 40 \times 1 = 40
C = MW = 12 \times 1 = 12
O = MW = 16 \times 3 = \frac{48}{100} = \text{MW}

Since Ca^{++} and CO₃^{2-} have valence of 2,
equivalent weight of CaCO₃ = \frac{100}{2} = 50

Example water (Ex. 11.4, pg. 445 of V+H):

CO₂ = 8.8 mg/L as CO₂
Ca^{2+} = 70 mg/L as CaCO₃
Mg^{2+} = 9.7 mg/L
Na^{+} = 6.9 mg/L
AlK(HCO₃) = 115 mg/L as CaCO₃
SO₄^{2-} = 96 mg/L
Cl⁻ = 10.6 mg/L

<table>
<thead>
<tr>
<th>M^{++}</th>
<th>conc. (mg/L)</th>
<th>MW</th>
<th>eq. wt.</th>
<th>hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca^{2+}</td>
<td>70</td>
<td>40</td>
<td>20</td>
<td>175</td>
</tr>
<tr>
<td>Mg^{2+}</td>
<td>9.7</td>
<td>24.4</td>
<td>12.2</td>
<td>\frac{39.8}{214.8}</td>
</tr>
</tbody>
</table>
Most hardness is due to Ca and Mg.

\[
\text{Ca hardness} = \text{that due to Ca} \\
\text{Mg hardness} = \text{that due to Mg}
\]

Total hardness = Ca hardness + Mg hardness

Carbonate hardness = part of total hardness equivalent to carbonate plus bicarbonate alkalinity

**Refresher on alkalinity** [AIK]:

\[
\text{AIK} = \text{capacity for solutes to neutralize a strong acid}
\]

\[
= \varepsilon \left[\text{strong bases}\right] - \varepsilon \left[\text{strong acids}\right]
\]

in equivalents per liter

Strong acids are those that completely dissociate in water: \(\text{HCl, H}_2\text{SO}_4, \text{HNO}_3, \text{HBr, HI, HClO}_4\)

Strong bases completely dissociate: \(\text{NaOH, KOH, Ca(OH)}_2, \text{Mg(OH)}_2, \text{LiOH, RbOH, Sr(OH)}_2, \text{Ba(OH)}_2\)

\[
\text{[AIK]} = [\text{Na}^+] + [\text{K}^+] + 2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] - [\text{Cl}^-] - 2[\text{SO}_4^{2-}] - [\text{NO}_3^-]
\]

\[
= \varepsilon [\text{SB}] - \varepsilon [\text{SA}]
\]

Can also find charge balance assuming carbonates dominate system.

\[
\varepsilon [\text{SB}] + [\text{H}^+] = \varepsilon [\text{SA}] + [\text{OH}^-] + 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-]
\]

\[
\varepsilon [\text{SB}] - \varepsilon [\text{SA}] = [\text{AIK}]
\]

\[
= [\text{OH}^-] - [\text{H}^+] + 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-]
\]
Natural water charge balance for an alkaline system (Alk = a-b) and an acid system (Alk = a-b = d-c).

Figure by MIT OCW.

Carbonate hardness (for [AIK] in terms of CaCO₃)

If [AIK] < total hardness,

then carbonate hardness = [AIK]

If [AIK] > total hardness,

then carbonate hardness = total hardness

Carbonate hardness causes scaling at high temps:

$$Ca^{++} + 2HCO_3^- \xrightarrow{△} CaCO_3 \downarrow + CO_2 + H_2O$$

Non-carbonate hardness = total hardness - carbonate hardness

For water treatment, carbonate hardness is removed by adding lime \( \text{Ca(OH)}_2 \):

First lime reacts with any \( CO_2 \):

1. \( CO_2 + \text{Ca(OH)}_2 \rightarrow CaCO_3 \downarrow + H_2O \)

Then lime reacts to remove carbonate hardness

2. \( Ca^{2+} + 2HCO_3^- + \text{Ca(OH)}_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O \)

3. \( Mg^{2+} + 2HCO_3^- + 2\text{Ca(OH)}_2 \rightarrow 2CaCO_3 \downarrow + Mg(\text{OH})_2 \downarrow + 2H_2O \)

And finally to remove non-carbonate Mg hardness

4. \( Mg^{2+} + \text{SO}_4^{2-} + \text{Ca(OH)}_2 \rightarrow Mg(\text{OH})_2 \downarrow + Ca^{2+} + \text{SO}_4^{2-} \)

5. \( Mg^{2+} + 2Cl^- + \text{Ca(OH)}_2 \rightarrow Mg(\text{OH})_2 \downarrow + Ca^{2+} + 2Cl^- \)
Reactions 4. and 5. Simply swap Mg noncarbonate hardness for Ca noncarbonate hardness.

Reactions 1 - 5. Remove magnesium hardness and calcium carbonate hardness. Calcium noncarbonate hardness in original solution plus that created removing Mg hardness remain.

For waters low in Mg and with carbonate Ca hardness, this would be sufficient treatment - called "single-stage lime treatment", "single-stage softening", or "undersoftening".

Typical process in water-treatment plant:

\[ \text{CaCO}_3 \text{ added in flash mixer} \] -> \[ \text{Ca(OH)}_2 \text{ slurry} \]

Water -> 

Water/lime mix goes into flocculator, then clarifier to precipitate and remove \text{CaCO}_3 \ (T_R = 1-2 \text{ hrs})

Water is then "recarbonated".

Recarbonation is needed because addition of \text{Ca(OH)}_2 raises pH of water to 10.2 to 10.5.

Recarbonation consists of bubbling \text{CO}_2 through treated water, lowering pH to 8.7 to 9.0:

\[ 6. \quad \text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 \downarrow + \text{H}_2\text{O} \]

\[ 7. \quad \text{CO}_3^{2-} + \text{CO}_2 + \text{H}_2\text{O} \rightarrow 2 \text{HCO}_3^- \]
Recarbonation is also done to "stabilize" the water.

If water is supersaturated with CaCO₃, it will precipitate as "scale".

If water is undersaturated, water can be "aggressive" and cause pipe corrosion.

Ideal is to keep water slightly oversaturated to maintain a thin protective coat of CaCO₃ on inside of pipe.

Scale precipitation involves two chemical reactions:

$$\text{Ca}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CaCO}_3(s) \quad 1/K_s$$

$$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} \quad K_2$$

$$K_s = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{[\text{CaCO}_3(s)]}$$

$$K_2 = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]}$$

Overall reaction:

$$\text{Ca}^{2+} + \text{HCO}_3^- \rightleftharpoons \text{CaCO}_3(s) + \text{H}^+$$

$$K = \frac{[\text{Ca}^{2+}][\text{HCO}_3^-]}{[\text{H}^+]^2} = \frac{K_s}{K_2}$$

Rearrange to get:

$$[\text{H}^+] = \frac{[\text{Ca}^{2+}][\text{HCO}_3^-]}{K}$$
\[
[H^+] = \frac{[Ca^{2+}][HCO_3^-]}{K}
\]

\[
\log [H^+] = \log [Ca^{2+}] + \log [HCO_3^-] - \log K
\]

\[
-\log [H^+] = -\log [Ca^{2+}] - \log [HCO_3^-] + \log (K_s/K_2)
\]

\[
\text{pH}_{eq} = \text{pCa} + \text{pHCO}_3^- + \log \left(\frac{K_s}{K_2}\right)
\]

\[
\text{pH}_{eq} = \text{pCa} + \text{pAI} + \log \left(\frac{K_s}{K_2}\right)
\]

\[
\text{I} = \text{pH}_{actual} - \text{pH}_{eq} \equiv SI
\]

Langlier Stability Index

\[
I > 0 \rightarrow \text{CaCO}_3 \text{ precipitates } \quad (\text{pH}_{actual} > \text{pH}_{eq})
\]

\[
I = 0 \rightarrow \text{stable}
\]

\[
I < 0 \rightarrow \text{CaCO}_3 \text{ dissolves}
\]

\[
I = 0.2 \quad \text{is desirable} \quad \text{carbonation steps}
\]

\[
\text{seeks to set } I = 0.2
\]

\[
K_2, K_s \text{ are functions of temp.}
\]

\[
\text{pK}_s = 8.4 \quad \text{pK}_2 = 10.4 \quad \text{at } T = 15 \text{C}
\]

Conventional lime treatment process looks like:

![Diagram of lime treatment process](image)

See pg 10 Fig 19-12(a)
Process flow diagram of common softening treatment techniques: (a) Single-stage lime treatment; (b) two-stage excess lime-soda treatment; (c) split-flow lime treatment

Figure by MIT OCW.