REMOVAL OF HARDNESS BY PRECIPITATION

Hardness $= \sum$ divalent cations

$= Ca^{2+} + Mg^{2+} + Fe^{2+} + Mn^{2+} + Sr^{2+}....$

If hardness is too high → precipitation of soap, scaling on pipes, boilers, cooling towers, heat exchangers.

If too low → water is corrosive.

Principle cations causing hardness in water and major anions associated with them are as follows:

Cations	**Anions**
Ca^{+2}	HCO_3^{-} or CO_3^{-2}
Mg^{+2}	SO_4^{-2}
Sr^{+2}	Cl^{-}
Fe^{+2}	NO_3^{-}
Mn^{+2}	SiO_3^{-2}

Hard water causes bathtub rings.

Ca^{2+} + (Soap) → $Ca(Soap)_2$ (s)

This increases the amount of soap needed for washing.

Calcium carbonate scale on a piece of pipe.

Ref: http://water.me.vccs.edu/courses/ENV115/lesson9.htm

Table: International classification of hard waters (after Kunin 1972)

Hardness Range (mg/L $CaCO_3$)	Hardness Description
0-50	Soft
50-100	Moderately soft
100-150	Slightly hard
150-200	Moderately hard
200-300	Hard
>300	Very hard

Forms of hardness

Total hardness (TH)

- Represents the sum of multivalent metallic cations.
- Generally, these are Ca^{2+} and Mg^{2+}.
- In addition to Ca^{2+} and Mg^{++}, iron (Fe^{2+}), strontium (Sr^{2+}), and manganese (Mn^{2+}) may also contribute to hardness. However, the contribution of these ions is usually negligible.

Carbonate hardness (CH)

- Due to the presence of bicarbonate, $Ca(HCO_3)_2$, $Mg(HCO_3)_2$, and carbonate $CaCO_3$, $MgCO_3$ salts.
- Carbonate hardness is chemically equivalent to alkalinity.

Noncarbonate hardness (NCH)

- Contributed by salts such as calcium chloride ($CaCl_2$), magnesium sulfate ($MgSO_4$), and magnesium chloride ($MgCl_2$).

$$\mathbf{TH = CH + NCH}$$

Forms of hardness

Ca – hardness – due to Ca
Mg – hardness – due to Mg

} TH (total hardness)

Carbonate hardness – associated with CO_3 and HCO_3 alkalinity
Noncarbonate hardness – associated with other anions

} TH

Total Hardness = Carbonate hardness + Non-carbonate hardness

$$\left.\begin{matrix} Ca(HCO_3)_2 \\ Mg(HCO_3)_2 \end{matrix}\right\}$$ Carbonate hardness, associated with CO_3^{-2} $and\ HCO_3^{-}$

$$\left\{\begin{matrix} Ca^{+2} \\ Mg^{+2} \\ Sr^{+2} \\ Fe^{+2} \\ Mn^{+2} \end{matrix}\right. + \left.\begin{matrix} SO_4^{-2} \\ Cl^{-} \\ NO_3^{-} \\ SiO_3^{-2} \end{matrix}\right\}$$ Non-carbonate hardness associated with other ions

CARBONATE HARDNESS= Sensitive to heat and precipitates readily at high temperatures. Therefore , can be removed by boiling the water.

HARDNESS

Carbonate (**temporary)** hardness because precipitates readily at high temperatures .

Non-carbonate (**permanent**) hardness because does not precipitate readily at high temperatures .

Lime-Soda Ash Softening Process

- Chemical precipitation is among the most common methods used to soften water.
- Chemicals used are lime (calcium hydroxide, $Ca(OH)_2$) and soda ash (sodium carbonate, Na_2CO_3).
- Lime is used to remove chemicals that cause carbonate hardness.
- Soda ash is used to remove chemicals that cause non-carbonate hardness.

Ref: http://water.me.vccs.edu/exam_prep/limesodaash.htm

Lime-Soda Ash Softening Process

- When lime and soda ash are added, hardness-causing minerals form ***nearly insoluble precipitates***.
- In lime-soda ash softening process Ca^{2+} is removed from water in the form of calcium carbonate, $CaCO_3(s)$ and
- Mg^{2+} is removed in the form of magnesium hydroxide, $Mg(OH)_2\ (s)$.
- These precipitates are then removed by conventional processes of coagulation/flocculation, sedimentation, and filtration.
- Because precipitates are **very slightly soluble**, some hardness remains in the water -- usually about 50 to 85 mg/l (as $CaCO_3$).
- This hardness level is desirable to prevent corrosion problems associated with water being too soft and having little or no hardness.

Lime-Soda Ash Softening Process

- Precipitation of these salts is affected by:
  1. Carbonate species
  2. pH of the system

- The least expensive form of lime is *quick lime*, *CaO*.
- Quick lime must be hydrated or slaked to $Ca(OH)_2$ before application.

Lime-Soda Ash Softening Process

Lime : $Ca(OH)_2$ or CaO $\longrightarrow$ $Ca^{2+} + OH^-$

Soda : Na_2CO_3 $\longrightarrow$ $Na^+ + CO_3^=$

Reactions

$Ca^{2+} + CO_3^= \longleftrightarrow$ **$CaCO_3$ (s)**

$Ksp = [Ca^{2+}]\,[CO_3^=] = 5.2 \times 10^{-9}$ at 20^0 C

$Mg^{2+} + 2OH^- \longleftrightarrow$ **$Mg(OH)_2$ (s)**

$Ksp = [Mg^{2+}]\,[OH]^2 = 1.8 \times 10^{-11}$ at 20^0 C

Lime-Soda Softening Process

Strategy

Raise the pH using lime

1) $HCO_3^- + OH^- \longleftrightarrow CO_3^= + H_2O$

so, $CaCO_3$ will precipitate.

2) $Mg(OH)_2$ will also precipitate.

Hints:

- For precipitation of $CaCO_3$, sufficient $CO_3^=$is needed.
- If it is not enough, add Na_2CO_3 as a source of $CO_3^=$. (Na_2CO_3 is 3 x more expensive than lime)
- Do not rely on precipitation of $Ca(OH)_2$, Ksp $=5.5x10^{-6}$
- Do not rely on precipitation of $MgCO_3$, Ksp $=5.6 x10^{-5}$

Possible Reactions with Lime

1) Reaction of H_2CO_3 with lime

$$H_2CO_3 \quad + \quad Ca(OH)_2 \qquad \longleftrightarrow \qquad CaCO_3(s) \; + \; 2\,H_2O$$

1 mol **1 mol**

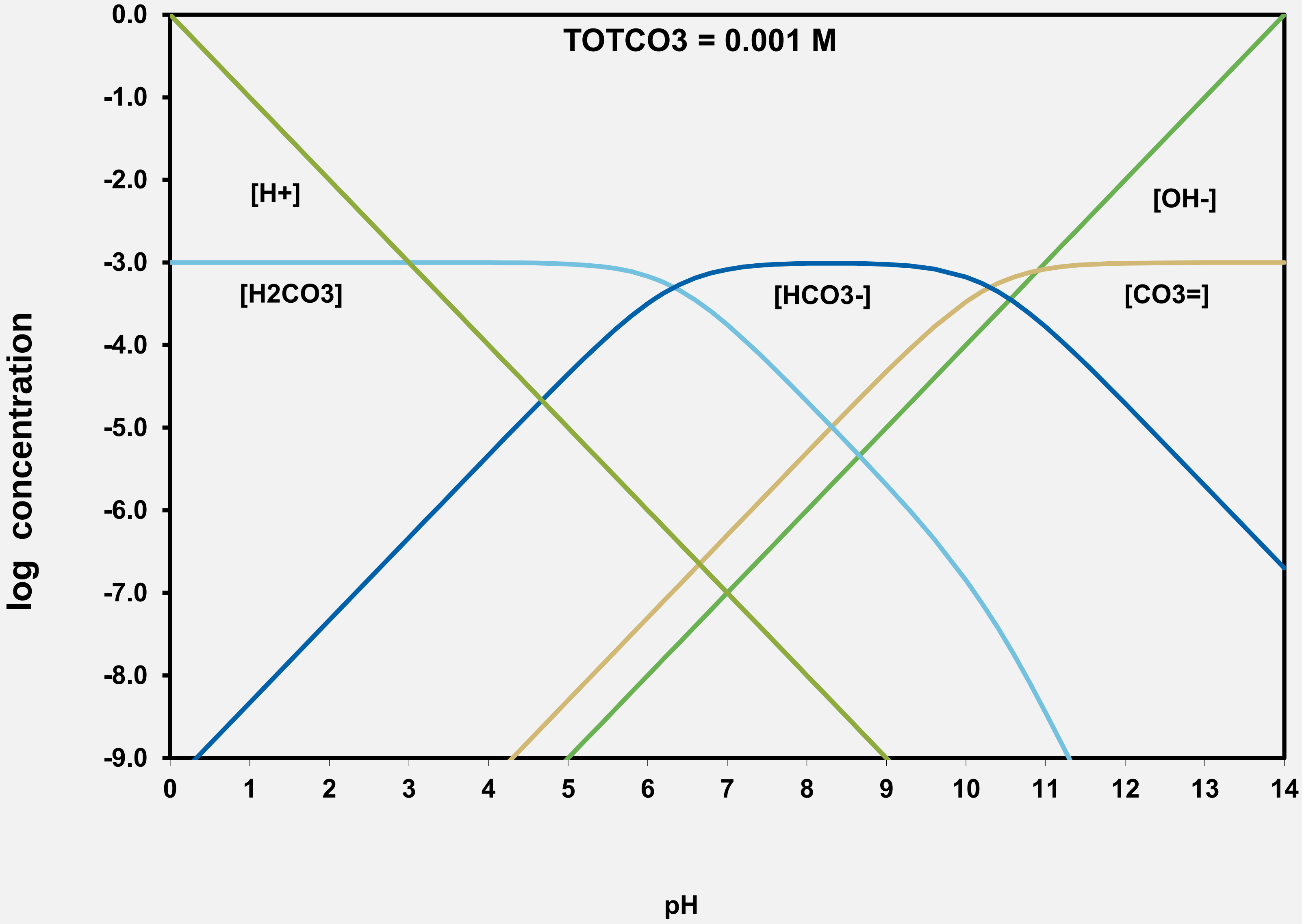
$$Ca(OH)_2 \quad \longleftrightarrow \quad Ca^{2+} \; + \; 2OH^-$$

$$H_2CO_3 + OH^- \quad \longleftrightarrow \quad HCO_3^- + H_2O$$

$$HCO_3^- + OH^- \quad \longleftrightarrow \quad CO_3^= + H_2O$$

$$Ca^{2+} + CO_3^= \quad \longleftrightarrow \quad CaCO_3(s)$$

Only 1 mol of $CO_3^=$ is formed with 1 mol of $Ca(OH)_2$ added. Therefore, no original Ca^{2+} is precipitated.


TOTCO3 = 0.001 M
[H+]
[OH-]
[H2CO3]
[HCO3-]
[CO3=]
log concentration
pH
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14

Possible Reactions with Lime

1) Reaction of H_2CO_3 with lime

- H_2CO_3 does not contribute to the hardness, but it reacts with the lime, and therefore uses up some lime before the lime can start removing the hardness.
- Therefore, although no net change in water hardness occurs as a result of the previous equations, these reactions must be considered because they exert a lime demand.

2) Removal of Ca-carbonate hardness

$pH \geq 6.3$

$$Ca(OH)_2 \longleftrightarrow Ca^{2+} + 2OH^-$$

$$2OH^- + 2HCO_3^- \longleftrightarrow 2CO_3^{=} + 2H_2O$$ (if there is enough alkalinity)

$$Ca^{2+} + (Ca^{2+})_{orig.} + 2CO_3^{=} \longleftrightarrow 2CaCO_3(s)$$

$$(Ca^{2+})_{orig.} + Ca(OH)_2 + 2HCO_3^- \longleftrightarrow 2CaCO_3(s) + 2H_2O$$

1 mol	**1 mol**	**2 mol**
2 eq	**2 eq**	**2 eq**

This chemical equation shows that 1 eq of lime will remove 1 eq of calcium carbonate hardness.

3) Removal of Mg-carbonate hardness (there is enough alkalinity)

$$2\ Ca(OH)_2 \longleftrightarrow 2\ Ca^{2+} + 4\ OH^-$$

$$2\ OH^- + 2HCO_3^- \longleftrightarrow 2CO_3^= + 2H_2O$$ (if there is enough alkalinity)

$$Mg^{2+} + 2\ OH^- \longleftrightarrow Mg(OH)_2\ (s)$$

$$2\ Ca^{2+} + 2CO_3^= \longleftrightarrow 2CaCO_3(s)$$

$$Mg^{2+} + 2\ Ca(OH)_2 + 2HCO_3^- \longleftrightarrow 2\ CaCO_3(s) + Mg(OH)_2 + 2H_2O$$

1 mol **2 mol** **2 mol**

2 eq **4 eq** **2 eq**

This chemical equation shows that 2 eq of lime are required to remove 1 eq of magnesium carbonate hardness.

Why is alkalinity required to remove Mg hardness?

4) Removal of Ca noncarbonate hardness (There is not enough alkalinity.)

When there is not enough $CO_3^{=}$, add Na_2CO_3 for the removal of non-carbonate hardness.

$$\begin{array}{lcl} Na_2CO_3 & \longleftrightarrow & 2\,Na^+ + CO_3^{=} \\ Ca^{2+} + CO_3^{=} & \longleftrightarrow & CaCO_3(s) \\ \hline Ca^{2+} + Na_2CO_3 & \longleftrightarrow & CaCO_3\,(s)\ + 2\,Na^+ \end{array}$$

1 mol **1 mol**

2 eq **2 eq**

This chemical equation shows that 1 eq of soda ash will remove 1 eq of Ca noncarbonate hardness.

5) Removal of Mg noncarbonate hardness (There is not enough alkalinity.)

Added lime will remove Mg^{2+} ions first.

$$Ca(OH)_2 \longleftrightarrow Ca^{2+} + 2\ OH^-$$

$$Mg^{2+} + 2\ OH^- \longleftrightarrow Mg(OH)_2(s)$$

$$Ca^{2+} + Na_2CO_3 \longleftrightarrow CaCO_3 + 2\ Na^+$$

$$Mg^{2+} + Ca(OH)_2 + Na_2CO_3 \longleftrightarrow Mg(OH)_2 + CaCO_3 + 2Na^+$$

1 mol	**1 mol**	**1 mol**
2 eq	**2 eq**	**2 eq**

This chemical equation shows that 1 eq of lime and 1 eq of soda ash are required to remove 1 eq of magnesium noncarbonate hardness.

Process Variations

1) Straight lime addition

i. The source water has high Ca but low magnesium hardness.

ii. Mg-H < 40 mg/L as $CaCO_{3.}$

iii. There is no non-carbonate hardness. In other words, alkalinity is enough for the removal of Ca.

2) Excess lime process

i. The source water has high Ca and Mg hardness.

ii. There is no non-carbonate hardness. In other words, alkalinity is enough for the removal of Ca and Mg hardness.

iii. High Mg hardness requires excess lime to increase pH to 12-13 so that reaction kinetics is fast (super saturated solution).

excess ~ 1.25 meq/L

iv. One- or two-stage recarbonation may be necessary.

Process Variations

3. Lime-soda ash treatment

i. The source water has high Ca but low magnesium hardness.

ii. Mg-H < 40 mg/L as $CaCO_3$.

iii. There is some calcium non-carbonate hardness. In other words, there is not enough alkalinity for the removal of Ca.

4) Excess lime-soda ash treatment

i. The source water has high Ca and Mg hardness.

ii. Under such conditions, usually, there is not enough alkalinity, so Na_2CO_3 is added.

iii. High Mg hardness requires excess lime to increase pH to 12-13 so that reaction kinetics is fast (super saturate solution).

excess ~ 1.25 mg/L

iv. One- or two-stage recarbonation may be necessary.

Recarbonation

- After lime and/or soda ash treatment is applied, the treated water will generally have a pH greater than 10.
- In addition, after softening, water becomes supersaturated with calcium carbonate.
- If this water is allowed to enter the distribution system in this state, the high pH would cause corrosion of pipes and the excess calcium carbonate would precipitate out, causing scale.
- So the water must be **recarbonated**, which is the process of stabilizing the water by lowering the pH and precipitating out excess lime and calcium carbonate.

Ref: http://water.me.vccs.edu/courses/ENV115/lesson9.htm

Recarbonation

- Therefore, the goal of recarbonation is to produce **stable water**.
- Stable water has a calcium carbonate level, which will
  - neither tend to precipitate out of the water (causing scale)
  - nor dissolve into the water (causing corrosion.)
- This goal is usually achieved by pumping CO_2 into the water.
- Enough CO_2 is added to reduce the pH of the water to less than 8.7.

Ref: http://water.me.vccs.edu/courses/ENV115/lesson9.htm

Recarbonation

- When CO_2 is added, the excess lime will react with CO_2 as shown in the reaction shown below, producing $CaCO_3(s)$:

Lime + Carbon dioxide → Calcium carbonate + Water

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3(s) + H_2O$$

- Recarbonation will also lower the pH.

Ref: http://water.me.vccs.edu/courses/ENV115/lesson9.htm

Single-Stage Recarbonation

- For treatment of low magnesium water, single-stage recarbonation is used.
- The water is mixed with lime or soda ash in the rapid-mix basin, resulting in a pH of 10.2 to 10.5.
- If non-carbonate hardness removal is required, soda ash will also be added at this step.
- After rapid mixing, the resulting slurry is mixed gently for a period of 30 to 50 minutes to allow the solids to flocculate.
- After flocculation, the water is allowed to flow into a sedimentation basin where the solids will be removed by sedimentation.
- Following sedimentation the clear water flows to the recarbonation basin where carbon dioxide is added to reduce the pH to between 8.3 and 8.6.
- Any particles remaining in suspension after recarbonation are removed by filtration.

Ref: http://water.me.vccs.edu/courses/ENV115/lesson9.htm

Two-Stage Recarbonation

- When high magnesium water is softened, excess lime needs to be added to raise the pH above 11, and magnesium hydroxide precipitates out.
- After treatment, enough CO_2 must be added to neutralize the excess hydroxide ions, as well as to convert carbonate ions to bicarbonate ions.

$$2OH^{-} + CO_2 \rightarrow CO_3^{=} + H_2O$$

- This reaction reduces the pH to between 10.0 and 10.5.
- As a result of the above reaction, $CaCO_3$ is formed.

$$Ca^{2+} + 2OH^{-} + CO_2 \rightarrow CaCO_3(s) + H_2O$$

- Furthermore, $Mg(OH)_2$ that did not precipitate, is converted to $MgCO_3$.

$$Mg^{2+} + 2OH^{-} + CO_2 \rightarrow MgCO_3 + H_2O$$

Ref: http://water.me.vccs.edu/courses/ENV115/lesson9.htm

Two-Stage Recarbonation

- Additional CO_2 needs to be added to lower the pH to between 8.4 and 8.6.
- The previously formed $CaCO_3$ re-dissolves and $CO_3^{=}$ ions are converted to bicarbonate ions as shown below:

$$CaCO_3(s) + H_2O + CO_2 \rightarrow Ca^{2+} + 2HCO_3^{-}$$

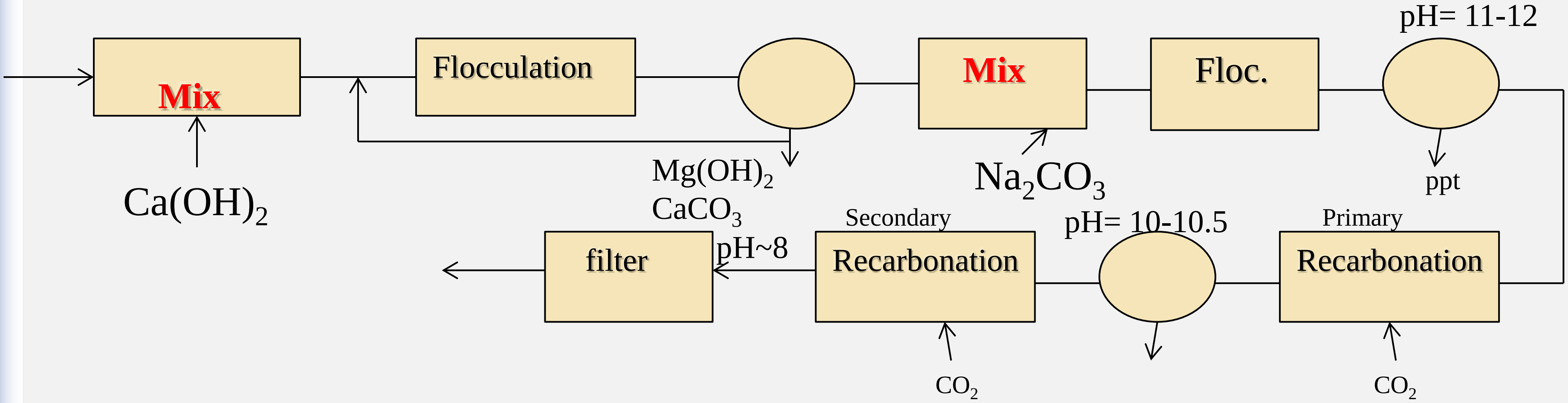
$$Mg^{2+} + CO_3^{=} + CO_2 + H_2O \rightarrow Mg^{2+} + 2HCO_3^{-}$$

1) Add CO_2 → $H_2CO_3^*$, titrate excess OH^-

$H_2CO_3^* + OH^-$ → $HCO_3^- + H_2O$
$HCO^-_3 + OH^-$ → $CO_3^= + H_2O$
$Ca^{2+} + CO_3^=$ → $CaCO_3$

pH ~10-10.5 and $[Ca^{++}]$ at minimum, and all C_T is in $CO_3^=$ form.

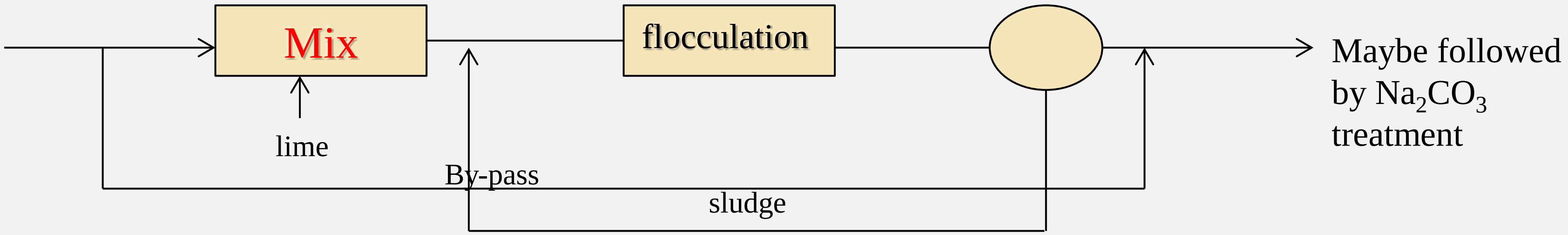
2) $H_2CO_3 + CO_3^=$ → $2HCO_3^-$
Desired pH determines CO_2 requirement.



Add $Ca(OH)_2$ Na_2CO_3 separately, otherwise
$Ca(OH)_2 + Na_2CO_3$ → $CaCO_3 + 2NaOH$

Split Treatment

Not the entire flow but only some part of the flow is treated.



Maybe followed by Na_2CO_3 treatment

Advantages : - less chemical required
- recarbonation maybe eliminated due to lower pH of by-pass

Limitation: - less removal of hardness
- applied only to clean waters which are usable w/o coagulation. (by-pass portion)

Example 1

A groundwater was analyzed and found to have the following composition (all concentrations are as $CaCO_3$):

pH = 7.0	Alk = 260 mg/L
Ca^{2+} = 210 mg/L	Temp = 10°C
Mg^{2+} = 15 mg/L	

Calculate the lime dose required to soften the water.

At 10°C, $K_{a1} = 3.47 \times 10^{-7}$ $K_{a2} = 3.1 \times 10^{-11}$

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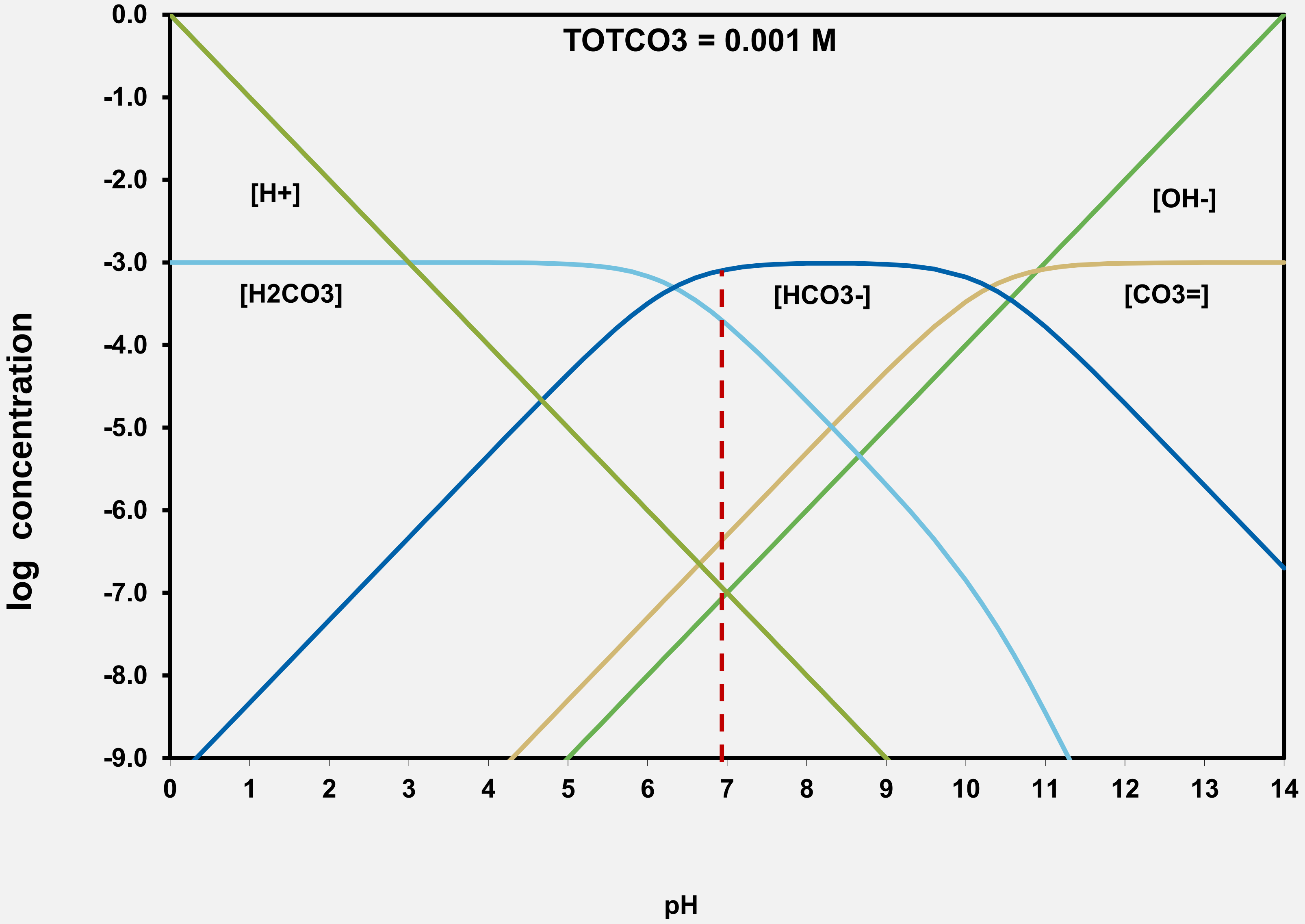
Calculate the lime dose required to soften the water.

At 10°C, $K_{a1} = 3.47 \times 10^{-7}$ $K_{a2} = 3.1 \times 10^{-11}$

$pK_{a1} = 6.45$


TOTCO3 = 0.001 M
[H+]
[OH-]
[H2CO3]
[HCO3-]
[CO3=]
log concentration
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
0
1
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pH

$$\alpha_0 = \frac{[H_2A]}{TOTA} = \frac{1}{1 + \frac{K_{a,1}}{[H^+]} + \frac{K_{a,1} \times K_{a,2}}{[H^+]^2}}$$

$$\alpha_1 = \frac{[HA^-]}{TOTA} = \frac{1}{1 + \frac{[H^+]}{K_{a,1}} + \frac{K_{a,2}}{[H^+]}}$$

$$\alpha_2 = \frac{[A^-]}{TOTA} = \frac{1}{1 + \frac{[H^+]^2}{K_{a,1} \times K_{a,2}} + \frac{[H^+]}{K_{a,2}}}$$

Solution

1. Determine the HCO_3^- concentration in moles/L.

At pH=7, alkalinity is mainly in the HCO_3^- form.

$$[HCO_3^-] = \frac{260\ mg/L}{50\ mg/meq}\ x\ \frac{1x10^{-3} mol}{1\ meq} = 5.2x10^{-3} mol/L\ HCO_3^-$$

2. Estimate the H_2CO_3 concentration in moles/L.

At 10°C, $K_{a1} = 3.47x10^{-7}$ $K_{a2} = 3.1x10^{-11}$

i. Compute α_1

$$\alpha_1 = \frac{[HCO_3^-]}{TOTCO_3} = \frac{1}{1 + \frac{[H^+]}{K_{a,1}} + \frac{K_{a,2}}{[H^+]}}$$

$$\alpha_1 = \frac{[HCO_3^-]}{TOTCO_3} = \frac{1}{1 + \frac{[10^{-7}]}{3.47x10^{-7}} + \frac{3.1x10^{-11}}{[10^{-7}]}} = 0.77$$

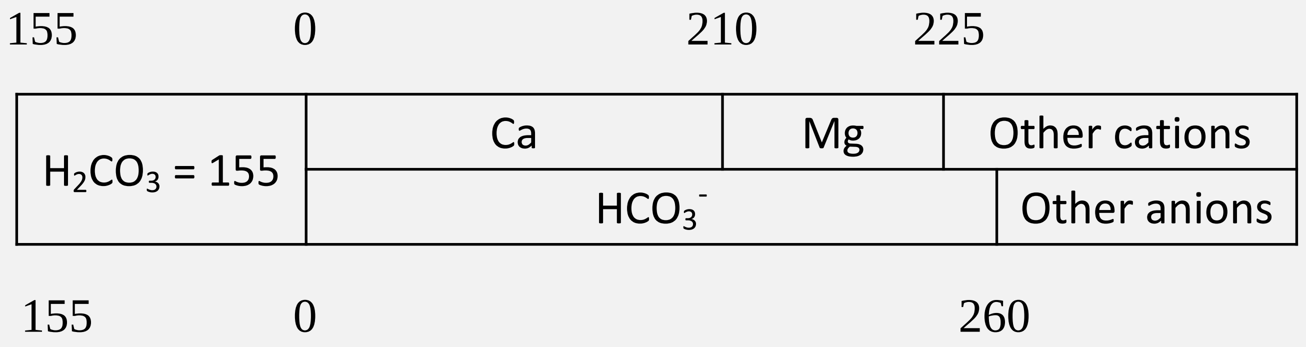
$$TOTCO_3 = \frac{[HCO_3^-]}{\alpha_1} = \frac{5.2x10^{-3}}{0.77} = 6.75x10^{-3} mol / L$$

$$[H_2CO_3] = TOTCO_3 - [HCO_3^-]$$

$$[H_2CO_3] = 6.75x10^{-3} - 5.2x10^{-3} = 1.55x10^{-3} mol / L$$

$$[H_2CO_3] = 155\ mg / L\ as\ CaCO_3$$

Bar Diagram of the untreated water



155 0 210 225

H_2CO_3 = 155

Ca

Mg

Other cations

HCO_3^-

Other anions

155 0 260

Total Hardness = 210 + 15 = 225 mg/L

Calcium carbonate hardness = 210 mg/L

Magnesium carbonate hardness = 15 mg/L

Straight lime addition

i. The source water has high Ca but low magnesium hardness.
ii. Mg-H < 40 mg/L as $CaCO_{3.}$
iii. There is no non-carbonate hardness.

Lime dose = Lime consumed by H_2CO_3 + lime consumed to remove calcium carbonate hardness

$$\underset{\textbf{1 mol}}{H_2CO_3} + \underset{\textbf{1 mol}}{Ca(OH)_2} \rightarrow \mathbf{CaCO_3(s)} + 2\,H_2O$$

$$\begin{array}{lcl}
Ca(OH)_2 & \rightarrow & Ca^{2+} + 2OH^- \\
2OH^- + 2HCO_3^- & \rightarrow & 2CO_3^= + 2H_2O \\
Ca^{2+} + (Ca^{2+})_{orig.} + 2CO_3^= & \rightarrow & 2CaCO_3(s) \\
\hline
\underset{\textbf{1 mol}}{(Ca^{2+})_{orig.}} + \underset{\textbf{1 mol}}{Ca(OH)_2} + \underset{\textbf{2 eq}}{2HCO_3^-} & \rightarrow & \mathbf{2CaCO_3(s)} + 2H_2O
\end{array}$$

Lime dose = 155 + 210 = 365 mg/L as $CaCO_3$

$$\text{Lime dose} = \frac{365\ \text{mg}/\text{L}}{50\ \text{mg}/\text{meq}}\ \text{x}\ \frac{37\text{mg}}{1\ \text{meq}} = 270\ \text{mg}/\text{L as Ca(OH)}_2$$

This calculation assumes that lime is 100% pure.

Sludge generation = Sludge generation by H_2CO_3 + Sludge generation by removal of calcium carbonate hardness

Sludge generation = 155 + 2 x (210) = 575 mg/L as $CaCO_3$

Example 2

H_2CO_3 = 16 mg/L

HCO_3^- = 183 mg/L

$CO_3^=$ = 0 mg/L

Ca^{2+} = 100 mg/L

Mg^{2+} = 40 mg/L

Calculate the lime dose required to soften the water.

$K_{a1} = 5.01 \times 10^{-7}$

Example

H_2CO_3 = 16 mg/L
HCO_3^- = 183 mg/L
$CO_3^=$ = 0 mg/L
Ca^{2+} = 100 mg/L
Mg^{2+} = 40 mg/L

Calculate the lime dose required to soften the water.

$K_{a1} = 5.01 \text{ x}10^{-7}$

pH = ?