Lime Soda Water Softening Calculations

by

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1.   Introduction

Hardness in water is due to the presence of divalent cations, primarily calcium and magnesium (Ca^{++} and Mg^{++}), in water and causes problems with the water such as scaling in pipes and excessive usage of soap. The two primary processes for removing hardness from water are ion exchange softening and chemical precipitation with lime and soda ash. Ion exchange softening is widely used for home water softeners and is often used for softening of groundwater in public water supply treatment plants. Chemical precipitation of hardness with lime and soda ash, commonly called lime soda softening, is used in most cases where surface water supplies are softened in public water supply treatment and in some softening of groundwater for public water supplies.

Lime soda softening is the subject of this course, which includes coverage of calculating the different types of hardness in a water sample from lab analysis results, conversions among different units for hardness, information about three lime soda water softening process alternatives (two stage excess lime water softening, split treatment, and selective calcium removal); calculation of the dosages needed for lime soda ash and carbon dioxide; calculation of daily chemical requirements; and calculation of solids production rates. A sample spreadsheet is included with the course. It will calculate the different types of hardness in a water sample from entered lab analysis results and will calculate the chemical dosages and solids production rates for the selective calcium removal process. The sample spreadsheet is useable for either U.S units or S.I. units.

2.   Learning Objectives

At the conclusion of this course, the student will

- Be able to determine an estimated value for concentrations of carbonate ion, bicarbonate ion, hydroxide ion, and carbon dioxide, in a water sample of specified pH and total alkalinity.

- Be able to calculate the calcium carbonate hardness, magnesium carbonate hardness, calcium non carbonate hardness, and magnesium non carbonate

hardness for a water sample with specified total hardness, calcium hardness, and alkalinity.

- Be able to convert concentrations from mg/L as $CaCO_3$ to meq/L and from meq/L to mg/L as $CaCO_3$.

- Know the differences among the three lime soda softening process alternatives described

- Be able to recommend the choice of the three lime soda softening process alternatives to use for a water sample with a known value of magnesium hardness and knowledge of whether the water is from a groundwater source or from a surface water source.

- Be able to calculate the lime, soda ash, and carbon dioxide dosages needed for the two stage excess lime softening process, if concentrations are known or can be calculated for CO_2, calcium carbonate hardness, calcium noncarbonate hardness, magnesium carbonate hardness, and magnesium noncarbonate hardness, using design values for excess lime concentration and lower limit of residual magnesium hardness.

- Be able to calculate the lime, soda ash, and carbon dioxide dosages needed for the split treatment softening process, if concentrations are known or can be calculated for CO_2, calcium carbonate hardness, calcium noncarbonate hardness, magnesium carbonate hardness, and magnesium noncarbonate hardness, using design values for final total hardness and final magnesium hardness.

- Be able to calculate the lime, soda ash, and carbon dioxide dosages needed for the selective calcium removal softening process, if concentrations are known or can be calculated for CO_2, calcium carbonate hardness, and calcium noncarbonate hardness.

- Be able to calculate the daily chemical requirements for lime, soda ash and carbon dioxide from the calculated dosages and the design plant flow rate.

- Be able to calculate the daily solids production rates for calcium solids, magnesium solids, and total solids for each of the three lime soda softening process alternatives.

3.   Topics Covered in this Course

I.   Background on Hardness in Water and Types of Hardness

II.   Calculation of Types of Hardness in a Water Sample

III.   Unit Conversions for Water Softening Concentrations

IV.   Process Alternatives for Lime Soda Water Softening

V.   Dosage Calculations for Two-Stage Excess Lime Softening process

VI.   Dosage Calculations for Split Treatment softening process

VII.   Dosage Calculations for Selective Calcium Removal softening process

VIII.   Calculation of Daily Chemical Requirements

IX.   Calculation of Daily Solids Production Rates

4.   Background on Hardness in Water and Types of Hardness

As noted in the introduction, hardness in water is caused by positive ions with two positive charges (divalent cations) and the two main divalent cations typically present in water are calcium (Ca^{++}) and magnesium (Mg^{++}). In some cases, water hardness is classified in terms of the cation, as **calcium hardness** or **magnesium hardness**. The **total hardness** or simply the **hardness** of the water is the sum of the **calcium hardness** and the **magnesium hardness**.

For lime soda softening dosage calculations, knowledge about the anions (negative ions) in the water is needed in addition to knowledge about the amount of **calcium hardness** and **magnesium hardness**. With reference to the type of anions present, hardness in water can be classified as **carbonate hardness** or **noncarbonate hardness**. Hardness that is due to Ca^{++} and/or Mg^{++} together with carbonate ($CO_3^=$) or

bicarbonate (HCO_3^-) is called **carbonate hardness**. Hardness due to Ca^{++} and/or Mg^{++} together with any anion other than carbonate or bicarbonate is called **noncarbonate hardness**. Typical noncarbonate anions present in water are sulfate ($SO_4^=$) and chloride (Cl^-). At a typical pH for drinking water, the anion associated with carbonate hardness is almost completely the bicarbonate ion. The carbonate ion is only present at higher pH's as shown in the diagram below.

This is shown in Figure 1 below, which shows the concentrations of carbon dioxide, carbonate ion, bicarbonate ion, and hydroxide ion in water for pH from 6.5 to 11 for water with a total alkalinity of 100 mg/L as $CaCO_3$.
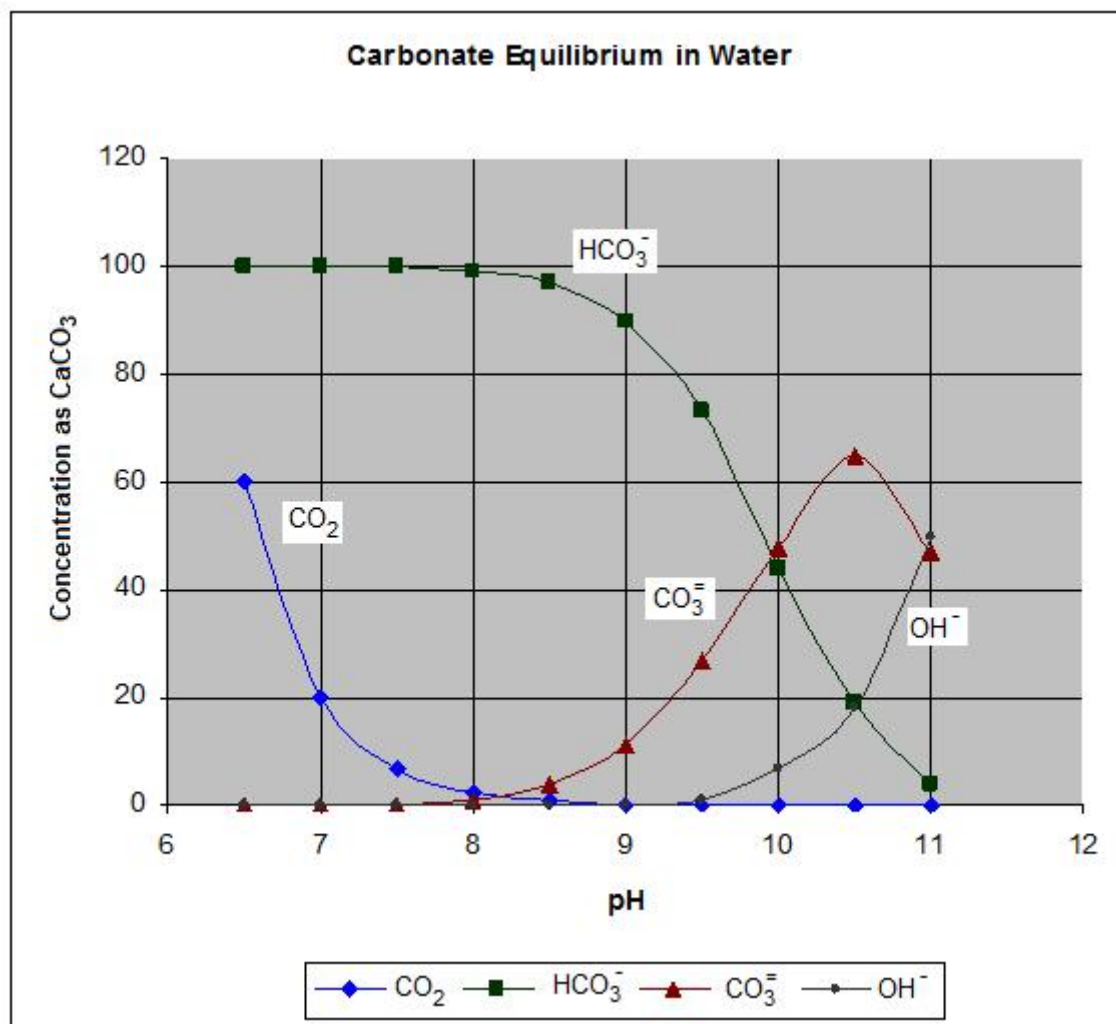

Figure 1. Carbonate Equilibrium in Water

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Example #1: What would be the concentration of carbonate ion expressed as mg/L $CaCO_3$ and the concentration of bicarbonate ion expressed as mg/L $CaCO_3$ in a water sample of pH 8 that has a total alkalinity of 100 mg/L? Repeat for pH = 9.

Solution: Reading directly from the diagram above: For pH = 8: $CO_3^=$ concentration is about 1 mg/L as $CaCO_3$ and HCO_3^- concentration is about 99 mg/L as $CaCO_3$. For pH = 9: $CO_3^=$ concentration is about 10 mg/L as $CaCO_3$ and HCO_3^- concentration is about 90 mg/L as $CaCO_3$.

Carbonate and bicarbonate concentrations for a water sample with total alkalinity other than 100 mg/L as $CaCO_3$ can be estimated similarly as a proportion of the concentration for 100 mg/L $CaCO_3$. Example #2 below illustrates this.

Example #2: What would be the concentration of carbonate ion expressed as mg/L $CaCO_3$ and the concentration of bicarbonate ion expressed as mg/L $CaCO_3$ in a water sample of pH 8 that has a total alkalinity of 150 mg/L? Repeat for pH = 9.

Solution: The answers from **Example #1** simply need to be multiplied by 150/100. Thus for pH = 8: $CO_3^=$ concentration is about (1)(150/100) = 1.5 mg/L as $CaCO_3$ and HCO_3^- concentration is about (99)(150/100) = 148.5 mg/L as $CaCO_3$. For pH = 9: $CO_3^=$ concentration is about (10)(150/100) = 15 mg/L as $CaCO_3$ and HCO_3^- concentration is about (90)(150/100) = 135 mg/L as $CaCO_3$.

5. Calculation of Types of Hardness in a Water Sample

With analytical values for total hardness, calcium hardness, alkalinity and pH in a water sample, concentrations can be calculated for all of the needed types of hardness as follows:

If we use the following symbols: total hardness = **TH**; calcium hardness = **CaH**; alkalinity = **ALK**; and pH = **pH**, then the equations for the needed calculations are:

Magnesium Hardness: **MgH = TH - CaH**

CO_2 concentration = **$[(10^{-pH})*(ALK)/K1]*(2 \text{ equiv/mole})$**

(**K1** is the CO_2 equilibrium constant = 4.02×10^{-7})

(Alkalinity must be in meq/L and the CO_2 conc. will be in meq/L)

If **CaH > ALK**, Then:

Calcium Carbonate Hardness: **CaCH = ALK**

Magnesium Carbonate Hardness: **MgCH = 0**

Calcium Non Carbonate Hardness: **CaNCH = CaH - ALK**

Magnesium Non Carbonate Hardness: **MgNCH = TH – CaH**

If **CaH < ALK**, Then:

Calcium Carbonate Hardness: **CaCH = CaH**

Calcium Non Carbonate Hardness: **CaNCH = 0**

If TH > ALK: Magnesium Carbonate Hardness: **MgCH = ALK - CaH**

Magnesium Non Carbonate Hardness: **MgNCH = TH - ALK**

If TH < ALK: Magnesium Carbonate Hardness: **MgCH = TH - CaH**

Magnesium Non Carbonate Hardness: **MgNCH = 0**

Example #3: Calculate the calcium carbonate hardness, the magnesium carbonate hardness, the calcium noncarbonate hardness and the magnesium noncarbonate hardness for a water sample with the following analysis.

- Total hardness = 150 mg/L as $CaCO_3$

- Calcium hardness = 120 mg/L as $CaCO_3$
- Alkalinity = 110 mg/L as $CaCO_3$

Solution: Since the calcium hardness is greater than the alkalinity, the first set of equations given above should be used.

CaCH = **ALK** = <u>110 mg/L as $CaCO_3$</u>

MgCH = <u>0</u>

CaNCH = CaH - ALK = 120 - 110 = <u>10 mg/L as $CaCO_3$</u>

MgNCH = TH - CaH = 150 - 120 = <u>30 mg/L as $CaCO_3$</u>

Example #4: Calculate the calcium carbonate hardness, the magnesium carbonate hardness, the calcium noncarbonate hardness and the magnesium noncarbonate hardness for a water sample with the following analysis.

- Total hardness = 150 mg/L as $CaCO_3$
- Calcium hardness = 100 mg/L as $CaCO_3$
- Alkalinity = 120 mg/L as $CaCO_3$

Solution: Since the calcium hardness is less than the alkalinity, the second set of equations given above (with **TH > ALK**) should be used.

CaCH = **CaH** = <u>100 mg/L as $CaCO_3$</u>

MgCH = Alk - CaCH = 120 - 100 = <u>20 mg/L $CaCO_3$</u>

CaNCH = <u>0</u>

MgNCH = TH - ALK = 150 - (100 + 20 + 0)

= <u>30 mg/L as $CaCO_3$</u>

The "**Basic Info**" worksheet in the spreadsheet provided with the course can be used to calculate the values of the different types of hardness based on user input values for total hardness, calcium hardness and alkalinity, as illustrated in Example #3 and Example #4. Figure 2, on the next page, shows a screenshot of that worksheet set up to solve Example #4.

Note that there is a drop-down list near the top of the worksheet that is used to select either U.S. units or S.I. units for the calculations. (For Examples #3 and #4 the calculations and results are the same for either set of units.) In the "**INPUTS**" section of the worksheet, there are blue cells for user entered values. The only values needed for Example #4 are ALK = 120 mg/L $CaCO_3$, TH = 150 mg/L $CaCO_3$, and CaH = 100 mg/L $CaCO_3$.

The yellow cells in the "**CALCULATIONS**" section in the bottom portion of the worksheet are calculated by the worksheet. The bottom four yellow cells on the left in the screenshot are the values of **CaCH** (calcium carbonate hardness), **MgCH** (magnesium carbonate hardness), **CaNCH** (calcium non-carbonate hardness), and **MgNCH** (magnesium non-carbonate hardness). The values shown in those cells are, of course, the same as those shown above in the solution to Example #4.

The "**Basic Info**" worksheet includes other inputs and quite a few additional calculations that will be discussed as you proceed through the course. Also, a summary of the equations used in the calculations is included on the right side of the worksheet in the course spreadsheet.

6.   Unit Conversions for Water Softening Concentrations

The unit often used for hardness and alkalinity concentrations in water is mg/L as $CaCO_3$. This is the unit that has been used in the examples and discussion so far. Its meaning is "the concentration of $CaCO_3$ that would have the same normality (concentration in equivalents/liter).   In some of the calculations to be discussed in this course it will be convenient to use concentration in meq/L (milliequivalents/liter) and in others it will be convenient to have the concentration of a chemical as mg/L of that chemical. Thus it will be necessary for us to be able to convert among these different units.

Lime Soda Softening Calculations - U.S. or S.I. Units					
1. Basic Source Water Information					
Instructions: Enter values in blue boxes. Spreadsheet calculates values in yellow boxes					

Click on the blue cell below and on the arrow to the right of it. Then use the drop down list to select the units you want to use:

	U.S. Units	

Inputs

(Source Water Parameters)			(Other Inputs)		
Alkalinity, **ALK** =	120	mg/L $CaCO_3$	Plant Flow Rate, **Q** =	4.5	MGD
Total Hardness, **TH** =	150	mg/L $CaCO_3$	Design Final TH, **TH_f** =	80	mg/L $CaCO_3$
			(typical values - changeable by user)		
Calcium Hardness, **CaH** =	100	mg/L $CaCO_3$	CO_2 Equil. Const., **K1** =	4.02E-07	
pH =	7.5		Lower limit of MgH resid. =	0.20	meq/L
			Lower limit of CaH resid. =	0.80	meq/L

Calculations (values are calculated by the worksheet)

Alkalinity, **ALK** =	2.40	meq/L	Calcium Hardness, **CaH** =	2.00	meq/L
Total Hardness, **TH** =	3.00	meq/L			
Magnesium Hdns, **MgH** =	50	mg/L $CaCO_3$	Magnesium Hdns, **MgH** =	1.00	meq/L
Calcium CH, **CaCH** =	100	mg/L $CaCO_3$	Calcium CH, **CaCH** =	2.00	meq/L
Magnesium CH, **MgCH** =	20.0	mg/L $CaCO_3$	Magnesium CH, **MgCH** =	0.40	meq/L
Calcium NCH, **CaNCH** =	0.0	mg/L $CaCO_3$	Calcium NCH, **CaNCH** =	0.00	meq/L
Magnes. NCH, **MgNCH** =	30.0	mg/L $CaCO_3$	Magnes. NCH, **MgNCH** =	0.60	meq/L
CO_2 conc., **CO_2** =	8.31	mg/L $CaCO_3$	CO_2 conc., **CO_2** =	0.38	meq/L

Figure 2. Course Spreadsheet Solution to Example #4

In order to convert from mg/L as $CaCO_3$ to meq/L, one must simply divide by the equivalent weight of calcium carbonate, which is 50 g/equivalent (or mg/meq). Thus:

concentration in meq/L = (concentration in mg/L as $CaCO_3$)/50

In order to convert from meq/L to mg/L of a specific chemical, one must multiply by the equivalent weight of the particular chemical. Thus:

mg/L of chemical A = (meq/L of chemical A)(equivalent weight of chemical A)

Equivalent weights of the chemicals for which we'll be making dosage calculations in this course are shown in the following table.

Table 1. Equivalent Weights of Water Softening Chemicals

Chemical Name	Chemical Formula	Equivalent Weight
Quicklime	CaO	28
Hydrated Lime	$Ca(OH)_2$	37
Soda Ash	Na_2CO_3	53
Carbon Dioxide	CO_2	22

Example #5: Convert the calcium carbonate hardness, magnesium carbonate hardness, calcium noncarbonate hardness, and magnesium noncarbonate hardness values from Example #4 to units of meq/L.

Solution: Each of the hardness concentrations given in Example #4 must be divided by 50 mg/meq to convert to meq/L, as follows:

CaCH = (100 mg/L as $CaCO_3$)/(50 mg/meq) = <u>2 meq/L</u>

MgCH = (20 mg/L $CaCO_3$)/(50 mg/meq) = <u>0.4 meq/L</u>

CaNCH = (0 mg/L $CaCO_3$)/(50 mg/meq) = <u>0 meq/L</u>

MgNCH = (30 mg/L as $CaCO_3$)/(50 mg/meq) = <u>0.6 meq/L</u>

Example #6: Calculate the carbon dioxide concentration (in mg/L CO_2) in a water sample with pH = 7.5 and total alkalinity = 120 mg/L as $CaCO_3$.

Solution: The pH and the alkalinity in meq/L can be substituted into the equation for CO_2 concentration given in the previous section to calculate the CO_2 concentration in meq/L. This can then be converted to mg/L of CO_2.

Alkalinity = (120 mg/L as $CaCO_3$)/(50 mg/meq) = 2.4 meq/L

CO_2 concentration = $[(10^{-pH})*(ALK)/K1](2)$ = $[(10^{-7.5})*(2.4)/(4.02 \times 10^{-7})](2)$

$$= 0.378 \text{ meq/L}$$

CO_2 concentration = (0378 meq/L)(22 mg/meq) = <u>8.31 mg/L</u>

Note that the concentrations in meq/L calculated in Example #5 and the CO2 concentration calculated in Example #6 can be calculated with the "Basic Info" worksheet, as shown in the screenshot in Figure 2.

7. Process Alternatives for Lime Soda Water Softening

Three commonly used process alternatives for lime soda softening are a) two-stage, excess lime treatment, b) single-stage, selective calcium removal, and c) split treatment. Following are a flow diagram and brief description for each of them.

Two-Stage Excess Lime Softening: Of these three process alternatives, the two-stage, excess lime softening process is capable of providing the most complete

hardness removal. This process is capable of removing calcium and magnesium carbonate and noncarbonate hardness down to the solubility limits of about 30 to 40 mg/L of calcium hardness and about 10 mg/L of magnesium hardness.

This is accomplished by adding lime in the first stage to a level in excess of the stoichiometric dosage needed to precipitate the calcium carbonate hardness as $CaCO_3\downarrow$ and to precipitate the magnesium carbonate hardness as $Mg(OH)_2\downarrow$. The excess lime is neutralized by recarbonation at the end of the first stage and then soda ash is added in the second stage to precipitate noncarbonate hardness as $CaCO_3\downarrow$. The chemicals used and the general flow pattern are shown in Figure 3 below.
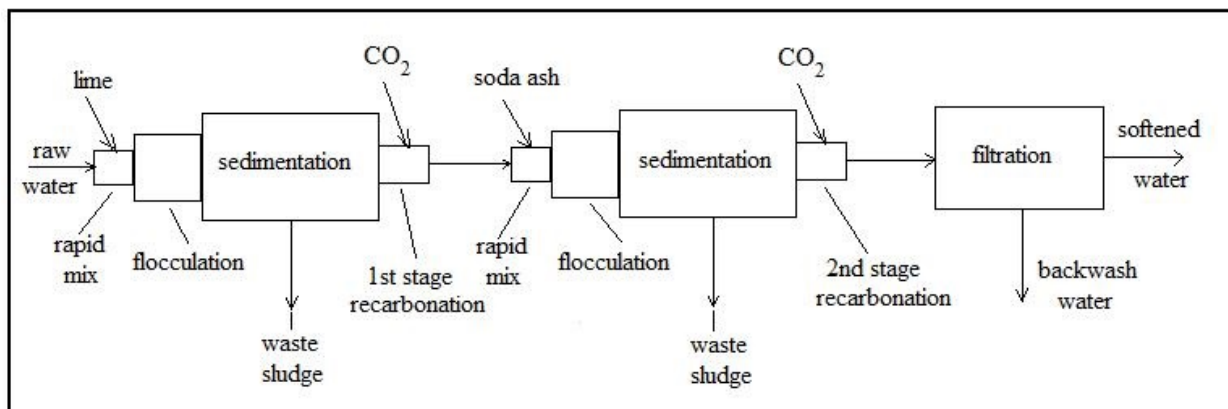

Figure 3. Two-Stage Excess Lime Softening Process

Each stage in this process consists of chemical addition/rapid mix, flocculation, and sedimentation processes, followed by recarbonation by addition of carbon dioxide. A filtration process is used after the second stage.

Single-Stage, Selective Calcium Removal: This water softening option works well for water sources with magnesium hardness of 40 mg/L or less. A softened water should have less than 40 mg/L of magnesium hardness, and as indicated by the name of this process, it only removes calcium hardness, so this is the reason for the requirement that the source water have less than 40 mg/L of magnesium hardness. This is a simpler process than the two-stage excess lime process. It basically consists of the first stage of the two-stage process, followed by filtration, as shown in the flow diagram in Figure 4 on the next page.
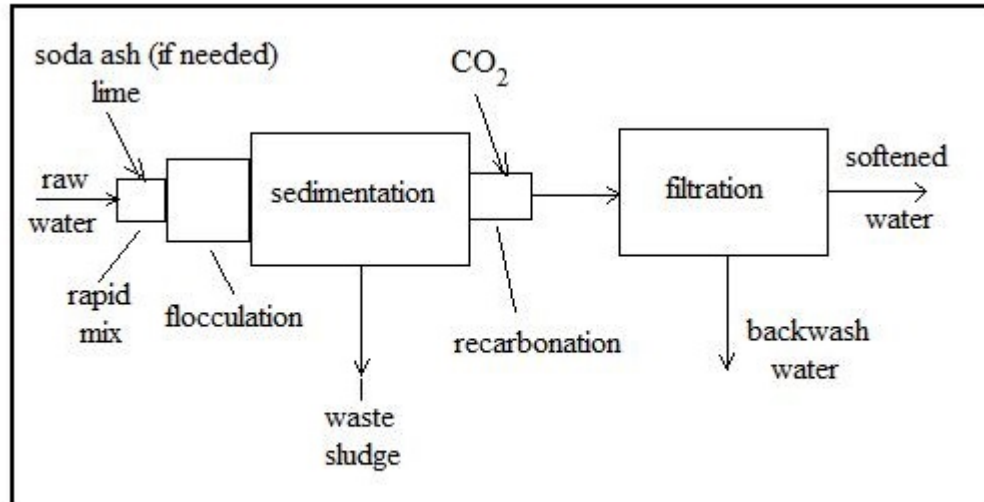
Figure 4. Single-Stage Selective Calcium Removal Softening Process

Split Treatment Lime Soda Water Softening: The split treatment lime soda water softening process is a two-stage alternative that typically uses less chemicals than the two-stage excess lime softening process. This is accomplished by treating only a portion of the influent with excess lime and using the bypassed (untreated) portion of the influent to neutralize the excess lime at the end of the first stage. Soda ash is used in a second stage to remove noncarbonate hardness. Typically recarbonation is not required for the split treatment process. This is shown in Figure 5, the flow diagram for the split treatment process, on the next page.
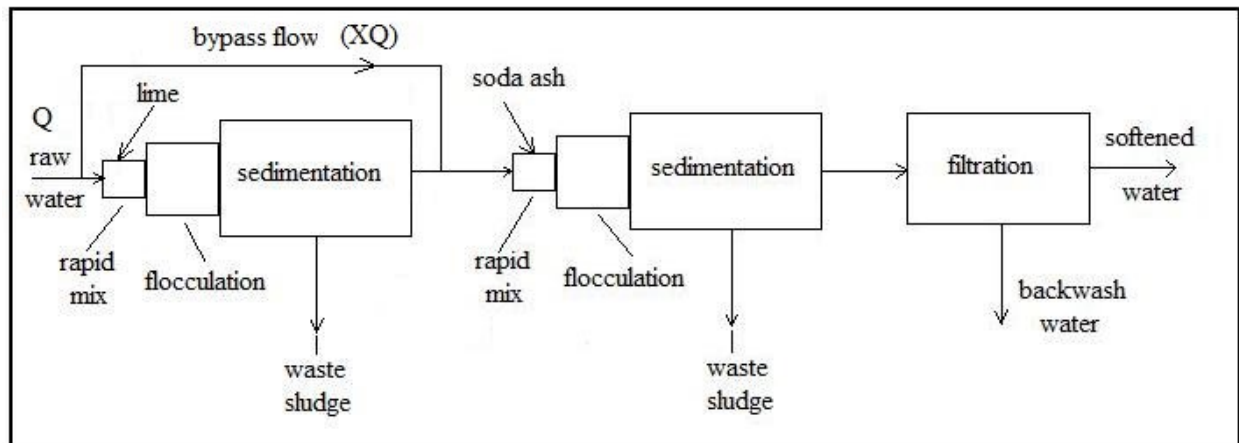
Figure 5. Split Treatment Softening Process

Selection of the Lime Soda Softening Process to Use: The decision of which lime soda softening process to use is based on i) the level of magnesium hardness in the water to be softened and ii) whether the water to be softened is from a groundwater source or a surface water source.

The maximum concentration of magnesium hardness that should remain in softened water is about 40 mg/L as $CaCO_3$. Since the selective calcium removal process doesn't remove any of the magnesium hardness, it is suitable only if the magnesium hardness in the raw water is less than 40 mg/L. If the raw water magnesium hardness is greater than 40 mg/L, then either split treatment or the two stage excess lime softening process should be used.

The split treatment lime soda softening process is most suitable for groundwater sources, while surface water sources typically require the more complete, two stage excess lime softening process

Example #7: Which lime soda treatment process should be used for the water described in Example #4, which has the following analysis?

- Total hardness = 150 mg/L as $CaCO_3$
- Calcium hardness = 100 mg/L as $CaCO_3$
- Alkalinity = 120 mg/L as $CaCO_3$

Assume that this water is from a surface water source.

Solution: As shown in the solution to Example #4, the magnesium hardness of this water sample is 50 mg/L CaCO$_3$. This is more than the maximum of 40 mg/ L CaCO$_3$ for the selective calcium removal process, so that process would not be suitable to use. Since this is a surface water source, the two stage excess lime softening process should be used.

Example #8: Which lime soda treatment process should be used for the water described in Example #4, which has the following analysis?

- Total hardness = 150 mg/L as CaCO$_3$
- Calcium hardness = 100 mg/L as CaCO$_3$
- Alkalinity = 120 mg/L as CaCO$_3$

 Assume that this water is from a groundwater source.

Solution: As shown in the solution to Example #4, the magnesium hardness of this water sample is 50 mg/L CaCO$_3$. This is more than the maximum of 40 mg/ L CaCO$_3$ for the selective calcium removal process, so that process would not be suitable to use. Since this is a groundwater source, the split treatment softening process should be used.

8. Dosage Calculations for Two Stage Excess Lime Softening

The lime dosage for the first stage of the two-stage excess lime softening process must be adequate to i) neutralize the carbon dioxide in the water, ii) react with the calcium carbonate hardness present to precipitate CaCO$_3\downarrow$, iii) react with the magnesium carbonate hardness present to precipitate Mg(OH)$_2\downarrow$ and CaCO$_3\downarrow$, and iv) react with the magnesium noncarbonate hardness present to convert it to calcium non carbonate hardness. In addition there must be enough excess lime to bring the pH high enough to precipitate the Mg(OH)$_2\downarrow$. The equations for these chemical reactions with lime are as follows:
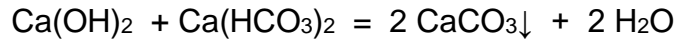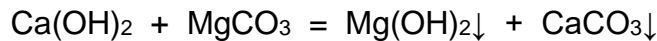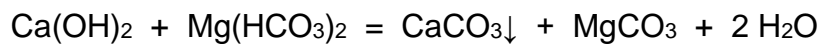
  i.   Reaction with carbon dioxide:

$$Ca(OH)_2 + CO_2 = CaCO_3\downarrow + H_2O$$
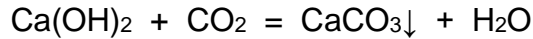
ii. Reaction with calcium carbonate hardness:

$$Ca(OH)_2 + Ca(HCO_3)_2 = 2\,CaCO_3\downarrow + 2\,H_2O$$

iii. Reaction with magnesium carbonate hardness:

$$Ca(OH)_2 + Mg(HCO_3)_2 = CaCO_3\downarrow + MgCO_3 + 2\,H_2O$$

$$Ca(OH)_2 + MgCO_3 = Mg(OH)_2\downarrow + CaCO_3\downarrow$$

iv. Reaction with magnesium noncarbonate hardness to convert it to calcium noncarbonated hardness:

$$Ca(OH)_2 + MgSO_4 = Mg(OH)_2\downarrow + CaSO_4$$
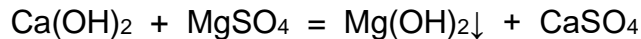
Note that the $SO_4^=$ represents any anion other than bicarbonate that is present in the water, so $MgSO_4$ represents magnesium noncarbonate hardness.

As shown in the above chemical equations, the lime dosage needed for the first stage of a two-stage excess lime water softening process is one equivalent of lime per equivalent of carbon dioxide plus one equivalent of lime per equivalent of calcium carbonate hardness plus two equivalents of lime per equivalent of magnesium carbonate hardness plus one equivalent of lime per equivalent of magnesium noncarbonate hardness plus excess lime.

Using the terminology introduced in Section 5, this can be summarized as shown below, with each term in meq/L:

Lime Dosage = CO_2 + CaCH + 2 MgCH + MgNCH + Excess Lime

All of the terms in the above equation should be in the same units, either meq/L or mg/L $CaCO_3$. The level of excess lime used is typically about 35 mg/L as $CaCO_3$ (about 0.7 meq/L).

The Soda Ash dosage in the second stage is needed to precipitate noncarbonate hardness to the extent required to bring the softened water to the desired hardness level. The chemical reaction is as follows:

$$Na_2CO_3 \ + \ CaSO_4 \ = \ CaCO_3\downarrow \ + \ Na_2SO_4$$
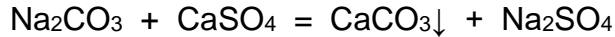
Thus one equivalent of soda ash is needed for each equivalent of noncarbonate hardness to be removed, or:

Soda Ash Dosage = CaNCH + MgNCH - design MgH residual

As with the lime dosage equation, all of the terms in this equation should be either in meq/L or in mg/L as $CaCO_3$.

The Carbon Dioxide Dosage needed is the sum of that needed for the first stage recarbonation and for the second stage recarbonation, with each calculated as follows:

First stage CO_2 dosage = Excess lime concentration + design MgH residual

The design magnesium hardness residual is typically either 40 mg/L $CaCO_3$ (0.2 meq/L) or the magnesium hardness in the raw water, whichever is less.

Second stage CO_2 dosage = (fraction of residual $CO_3^=$ to be converted to HCO_3^-)*(lower limit for calcium hardness residual)

The fraction of residual carbonate ion to be converted to bicarbonate ion is a design parameter and is often about 50%. The lower limit for calcium hardness residual is about 0.8 meq/L (40 mg/L as $CaCO_3$)

Example #9: Calculate the lime dosage, soda ash dosage, first stage carbon dioxide dosage and second stage carbon dioxide dosage (all in meq/L) for two stage excess lime softening of the water described in Example #4, which has the following analysis?

- Total hardness = 150 mg/L as $CaCO_3$
- Calcium hardness = 100 mg/L as $CaCO_3$
- Alkalinity = 120 mg/L as $CaCO_3$
- pH = 7.5

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As calculated in Example #6, the carbon dioxide concentration of the raw water is 8.31 mg/L. Use 0.7 meq/L excess lime dosage. Use 0.5 as the fraction of carbonate ion to be converted to bicarbonate ion in the first stage recarbonation. Use 0.8 meq/L as the design magnesium hardness residual and use 0.8 meq/L as the lower limit for calcium hardness residual.

Solution: As calculated in Example #4, the types of hardness in this water are:

CaCH = 100 mg/L as $CaCO_3$ = <u>2 meq/L</u>

MgCH = 20 mg/L $CaCO_3$ = <u>0.4 meq/L</u>

CaNCH = 0 mg/L $CaCO_3$ = <u>0 meq/L</u>

MgNCH = 30 mg/L as $CaCO_3$ = <u>0.6 meq/L</u>

The carbon dioxide concentration in meq/L is: (8.31 mg/L)/(22 mg/meq) = 0.378 meq/L

From the discussion above:

Lime Dosage = CO_2 + CaCH + 2 MgCH + MgNCH + Excess Lime

Substituting values:

<u>**Lime Dosage = 0.378 + 2 + (2)(0.4) + 0.6 + 0.8 meq/L = 4.578 meq/L**</u>

Also from the discussion above:

Soda Ash Dosage = CaNCH + MgNCH - design MgH residual

Substituting values:

<u>**Soda Ash Dosage = 0 + 0.6 - 0.8 meq/L = -0.2 meq/L**</u>   (The negative calculated value
                                                                                                                              shows that no soda ash
Also from the discussion above: addition is needed.)

First stage CO_2 dosage = Excess lime concentration + design MgH residual

Substituting values:

First stage CO_2 dosage = 0.7 + 0.8 meq/L = 1.5 meq/L

Also from the discussion above:

Second stage CO_2 dosage = (fraction of residual $CO_3^=$ to be converted to HCO_3^-)*(lower limit for calcium hardness residual)

Substituting values:

Second stage CO_2 dosage = (0.5)(0.8 meq/L) = 0.4 meq/L

9.   Dosage Calculations for Split Treatment Lime Soda Softening

Introduction: As described previously, the split treatment lime soda softening process reduces the chemical requirement by treating only a portion of the incoming raw water with lime in the first stage. The bypassed portion of the raw water is used to neutralize the first stage effluent and a second stage is used to remove noncarbonate hardness with soda ash. The dosage calculations needed are i) calculation of the fraction of the raw water flow to be bypassed, ii) the lime dosage for the first stage process, and iii) the soda ash dosage for the second stage process.

Chemical Dosage Calculations

The equations used for the three dosage related calculations listed above are as follows:

Fraction of flow to bypass = X = $(MgH_f – MgH_{limit})/(MgH – MgH_{limit})$

Where:

- **MgH_f** = design final magnesium hardness in the treated water

- **MgH** = magnesium hardness in the raw water

- **MgH**$_{limit}$ = lower limit of magnesium hardness residual (typically about 10 mg/L $CaCO_3$)

Lime dosage = CO₂_conc + CaCH + (1 – X)(2*MgCH + MgNCH)

Where:

- **CO₂_conc** = carbon dioxide concentration in the raw water

- **CaCH** = calcium carbonate hardness in the raw water

- **MgCH** = magnesium carbonate hardness in the raw water

- **MgNCH** = magnesium noncarbonate hardness in the raw water

Soda Ash Dosage = CaNCH + MgNCH - (TH$_f$ - CaH$_{limit}$)

Where:

- **CaNCH** = calcium noncarbonate hardness in the raw water

- **MgNCH** = magnesium noncarbonate hardness in the raw water

- **TH$_f$** = design final total hardness in the treated water

- **CaH$_{limit}$** = lower limit of calcium hardness residual (typically about 40 mg/L $CaCO_3$ or 0.8 meq/L)

Example #10: Calculate the bypass fraction, lime dosage (meq/L), and soda ash dosage, (meq/L) for split treatment lime soda softening of the water described in Example #4, which has the following analysis?

- Total hardness = 150 mg/L as $CaCO_3$

- Calcium hardness = 100 mg/L as $CaCO_3$
- Alkalinity = 120 mg/L as $CaCO_3$

The carbon dioxide concentration of the raw water is 4.85 mg/L. Use 1.6 meq/L as the design final total hardness, use 0.8 meq/L as the design final magnesium hardness, use 0.2 meq/L as the lower limit of magnesium hardness, and use 0.8 meq/L as the lower limit for calcium hardness residual.

Solution: As calculated in Examples #4, the types of hardness in this water are:

CaCH = 100 mg/L as $CaCO_3$ = <u>2 meq/L</u>

MgCH = 20 mg/L $CaCO_3$ = <u>0.4 meq/L</u>

CaNCH = 0 mg/L $CaCO_3$ = <u>0 meq/L</u>

MgNCH = 30 mg/L as $CaCO_3$ = <u>0.6 meq/L</u>

The carbon dioxide concentration in meq/L is: (4.85 mg/L)/(22 mg/meq) = 0.221 meq/L

From the discussion above:

Fraction of flow to bypass = X = (MgH$_f$ – MgH$_{limit}$)/(MgH – MgH$_{limit}$)

Substituting values:

<u>**Fraction of flow to bypass = X = (0.8 - 0.2)/(0.4 + 0.6 - 0.2) meq/L = 0.75**</u>

Also from the discussion above:

Lime dosage = CO$_2$_conc + CaCH + (1 – X)(2*MgCH + MgNCH)

Substituting values:

<u>**Lime Dosage = 0.221 + 2 + (1 – 0.75)(2*0.4 + 0.6) meq/L = 2.57 meq/L**</u>

Also from the discussion above:

Soda Ash Dosage = CaNCH + MgNCH - (TH$_f$ - CaH$_{limit}$)

Substituting values:

Soda Ash Dosage = 0 + 0.6 - (1.6 - 0.8) meq/L = - 0.2 meq/L (no soda ash is needed)

10. Dosage Calculations for Single Stage Selective Calcium Removal Softening

Introduction: As described previously, the single stage selective calcium removal softening process uses lime (and soda ash if needed) in a single stage followed by recarbonation. This process is only suitable if the magnesium hardness in the water is low enough to be acceptable in the treated water. Typically a limit of 40 mg/L of magnesium hardness or less is used. The dosage calculations needed are ii) the lime dosage, ii) the soda ash dosage, and iii) the carbon dioxide dosage needed for recarbonation.

Chemical Dosage Calculations

The equations used for the three dosage related calculations listed above are as follows:

Lime dosage = CO$_2$_conc + CaCH + CaNCH

Where:

- **CO$_2$_conc** = carbon dioxide concentration in the raw water

- **CaCH** = calcium carbonate hardness in the raw water

- **CaNCH** = calcium noncarbonate hardness in the raw water

Soda Ash Dosage = CaNCH

Where:

- **CaNCH** = calcium noncarbonate hardness in the raw water

CO_2 dosage = (fraction of residual $CO_3^=$ to be converted to HCO_3^-)*(lower limit for calcium hardness residual)

Example #11: Calculate the lime dosage, soda ash dosage, and carbon dioxide dosage (all in meq/L) for selective calcium removal lime soda softening of the water described in Example #3, which has the following analysis.

- Total hardness = 150 mg/L as $CaCO_3$
- Calcium hardness = 120 mg/L as $CaCO_3$
- Alkalinity = 110 mg/L as $CaCO_3$

The carbon dioxide concentration of the raw water is 7.61 mg/L. Use 0.8 meq/L as the lower limit for calcium hardness residual and use 0.5 as the fraction of carbonate to be converted to bicarbonate in the recarbonation process.

Solution: As calculated in Examples #3, the types of hardness in this water are:

CaCH = 110 mg/L as $CaCO_3$ = <u>2.2 meq/L</u>

MgCH = 0 mg/L $CaCO_3$ = <u>0 meq/L</u>

CaNCH = 10 mg/L $CaCO_3$ = <u>0.2 meq/L</u>

MgNCH = 30 mg/L as $CaCO_3$ = <u>0.6 meq/L</u>

The carbon dioxide concentration in meq/L is: (7.61 mg/L)/(22 mg/meq) = 0.346 meq/L

From the discussion above:

Lime Dosage = CO_2 + CaCH + CaNCH

Substituting values:

<u>Lime Dosage = 0.346 + 2.2 + 0.2 meq/L = <u>2.75 meq/L</u></u>

Also from the discussion above:

Soda Ash Dosage = CaNCH

Substituting values:

<u>Soda Ash Dosage = 0.2 <u>meq/L</u></u>

CO_2 dosage = (fraction of residual $CO_3^=$ to be converted to HCO_3^-)*(lower limit for calcium hardness residual)

Substituting values:

<u>CO_2 dosage = (0.5)(0.8 meq/L) = <u>0.4 meq/L</u></u>

A screenshot of the "Selective Ca Removal" worksheet in the course spreadsheet is shown in Figure 6 below on the next page. It illustrates a spreadsheet layout for calculating chemical dosages for a single stage selective calcium removal water softening process and shows the solution to Example #11.

The screenshot in Figure 6 also shows the results for daily chemical requirements and daily solids production which will be covered in the next two sections.

Lime Soda Softening Calculations - U.S. or S.I. Units

Selective Calcium Removal (Suitable for Mg Hardness ≤ 40 mg/L CaCO₃)

Instructions: Enter values in blue boxes. Spreadsheet calculates values in yellow boxes

Inputs

% CaO in Quicklime:	90%	
% Na₂CO₃ in Soda Ash =	99%	
Fraction of Resid. CO₃⁼		
to convert to HCO₃⁻ =	0.5	

Type of Lime used - **Click on choice below:**

⊙ Quicklime
○ Slaked Lime   **Quicklime**

Click on the blue cell below and on the arrow to the right of it. Then use the drop down list to select the units you want to use:

U.S. Units

Calculations

Lime reqmt, QKLIME:	76.9	mg/L CaO	Lime reqmt, **LIME** =	2.75	meq/L
Soda Ash reqmt =	10.6	mg/L Na₂CO₃	Soda Ash reqmt =	0.2	meq/L
Recarb. CO₂ needed =	8.8	mg/L CO₂	Recarb. CO₂ needed =	0.40	meq/L

Daily Chemical Requirements:

Daily lime requirement as CaO:	2886	lb CaO/day
Daily requirement of 90% Quicklime:	3206	lb/day
Daily soda ash requirement:	398	lb Na2CO3/day
Daily requirement of 99% Soda Ash	402	lb/day
Carbon dioxide requirement:	330	lb CO2/day

Daily Solids Production:

Daily calcium solids produced:	7405	lb/day
Daily magnesium solids produced:	0	lb/day
Total daily solids produced:	7405	lb/day

Figure 6. Course Spreadsheet showing calculation of Chemical Dosages for a Single Stage Selective Calcium Removal Process

11. Calculation of Daily Chemical Requirements

Introduction: The calculations thus far have centered on chemical dosages needed in meq/L. The daily chemical requirement in lb/day or kg/day can readily be calculated for any of the chemicals with the equation:

Daily requirement in lb/day = (dosage of chemical in meq/L)(Equiv. Wt. of chemical)[8.34 lb/MG/(mg/L)](plant flow in MGD)

Or Daily requirement in kg/day = (dosage of chemical in meq/L)(Equiv. Wt. of chemical)(plant flow in m3/d)(1000 g/kg)

Equivalent weights from Table 1 on page 9 of this course are: quicklime (CaO) - 28 mg/meq; slaked lime [$Ca(OH)_2$] - 37 mg/meq; soda ash (Na_2CO_3) - 53 mg/meq; and carbon dioxide - 22 mg/meq

Daily Chemical Requirements Calculations: Equations for calculating the daily requirements for quicklime, slaked lime, soda ash and carbon dioxide, in lb/day from dosages in meq/L, are as follows:

Daily quicklime requirement:

(in lb/day of CaO) = (Lime dosage in meq/L)(28 mg/meq)
[8.34 lb/MG/(mg/L)](design flow rate in MGD)

(in kg/day of CaO) = (Lime dosage in meq/L)(28 mg/meq)
(design flow rate in m^3/d)/(1000 g/kg)

Daily slaked lime requirement:

(in lb/day of $Ca(OH)_2$) = (Lime dosage in meq/L)(37 mg/meq)
[8.34 lb/MG/(mg/L)](design flow rate in MGD)

(in kg/day of $Ca(OH)_2$) = (Lime dosage in meq/L)(37 mg/meq)
(design flow rate in m^3/d)/(1000 g/kg)

Daily soda ash requirement:

(in lb/day of Na_2CO_3) = (soda ash dosage in meq/L)(53 mg/meq)
[8.34 lb/MG/(mg/L)](design flow rate in MGD)

(in kg/day of Na_2CO_3) = (soda ash dosage in meq/L)(53 mg/meq)
(design flow rate in m^3/d)/(1000 g/kg)

Daily carbon dioxide requirement:

(in lb/day of CO_2) = (carbon dioxide dosage in meq/L)(22 mg/meq)
[8.34 lb/MG/(mg/L)](design flow rate in MGD)

(in kg/day of CO_2) = (carbon dioxide dosage in meq/L)(22 mg/meq)
(design flow rate in m^3/d)/(1000 g/kg)

Example #12: Calculate the daily requirements for lime, soda ash, and carbon dioxide (all in lb/day) for the selective calcium removal lime soda softening process described in Example #11, which has the following chemical dosage requirements

- Lime dosage = 2.62 meq/L
- Soda Ash dosage = 0.2 meq/L
- Carbon dioxide dosage = 0.4 meq/L

Make the calculations for a design plant flow rate of 2.5 MGD, using slaked lime as the chemical for lime addition.

Solution: These calculations can be made using the equations just presented above in this section:

<u>Daily lime requirement</u> = (2.62 meq/L)(28 mg/meq)[8.34 lb/MG/(mg/L)](2.5 MGD)

= **<u>1530 lb CaO/day</u>**

<u>Daily soda ash requirement</u> = (0.2 meq/L)(53 mg/meq)[8.34 lb/MG/(mg/L)](2.5 MGD)

= **<u>221 lb Na_2CO_3/day</u>**

Daily CO$_2$ requirement = (0.4 meq/L)(22 mg/meq)[8.34 lb/MG/(mg/L)](2.5 MGD)

= **183 lb CO$_2$/day**

12. Calculation of Daily Solids Production

Introduction: As a byproduct of chemical precipitation to remove components from water, there will be production of solids (sludge) for disposal. The calcium removed from the water will be precipitated as calcium carbonate (CaCO$_3$) and the magnesium removed from the water will be precipitated as magnesium hydroxide (Mg(OH)$_2$) A projection of the quantity of calcium solids produced per day can be calculated as follows for each of the lime soda softening processes.

Two Stage Excess Lime Softening Process: The daily production of calcium and magnesium solids from the two stage excess lime softening process can be estimated from the following equations. Note that the equations are the same for U.S. units or S.I. units except for a different conversion factor needed for each one. Both U.S. and S.I. versions of the equations are shown.

Daily calcium solids in lb/day (U.S. units) = (**CaCH** + **CaNCH** + **LimeDose** - **CaHResid**)(**50** mg/meq)(**8.34**)(**design flow rate** in MGD)

Daily calcium solids in kg/day (S.I. units) = (**CaCH** + **CaNCH** + **LimeDose** - **CaHResid**)(**50** mg/meq)(**design flow rate** in m^3/d)/(**1000** g/kg)

Where:

- **CaCH** = the calcium carbonate hardness in the raw water in meq/L

- **CaNCH** = the calcium noncarbonate hardness in the raw water in meq/L

- **LimeDose** = the lime dosage used in meq/L

- **CaHResid** = the residual calcium hardness in the treated water in meq/L

Daily magnesium solids in lb/day (U.S. units) = (**MgCH** + **MgNCH** - **MgHResid**)(**29.2** mg/meq)(**8.34**)(**design flow rate** in MGD)

Daily magnesium solids in kg/day (S.I. units) = (**MgCH** + **MgNCH** - **MgHResid**)(**29.2** mg/meq)(**design flow rate** in m^3/d)/(**1000** g/kg)

Where:

- **MgCH** = the magnesium carbonate hardness in the raw water in meq/L

- **MgNCH** = the magnesium noncarbonate hardness in the raw water in meq/L

- **MgHResid** = the residual Magnesium hardness in the treated water in meq/L

Selective Calcium Removal Lime Soda Softening Process: The daily production of calcium and magnesium solids from the selective calcium removal lime soda softening process can be estimated from the following equations.

Daily calcium solids in lb/day (U.S. units) = (**CaCH** + **CaNCH** + **LimeDose** - **CaHResid**)(**50** mg/meq)(**8.34**)(**design flow rate** in MGD)

Daily calcium solids in kg/day (S.I. units) = (**CaCH** + **CaNCH** + **LimeDose** - **CaHResid**)(**50** mg/meq)(**design flow rate** in m^3/d)/(**1000** g/kg)

Where:

- **CaCH** = the calcium carbonate hardness in the raw water in meq/L

- **CaNCH** = the calcium noncarbonate hardness in the raw water in meq/L

- **LimeDose** = the lime dosage used in meq/L

- **CaHResid** = the residual calcium hardness in the treated water in meq/L

Daily magnesium solids in lb/day = 0 (Since magnesium is not removed in the process variation, no magnesium hydroxide solids are produced.)

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Split Treatment Lime Soda Softening Process: The daily production of calcium and magnesium solids from the split treatment lime soda softening process can be estimated from the following equations.

Daily calcium solids in lb/day (U.S. units) = (**CaCH** - **CaHResid**)(**50** mg/meq)(**8.34)** **(design flow rate** in MGD) + (**Daily Lime Requirement**)(**50**/**equiv wt for lime**)

Daily calcium solids in kg/day (S.I. units) = (**CaCH** - **CaHResid**)(**50** mg/meq) (**design flow rate** in m^3/d)/(**1000** g/kg) + (**Daily Lime Requirement**) (**50**/**equiv wt for lime**)

Where:

- **CaCH** = the calcium carbonate hardness in the raw water in meq/L

- **CaHResid** = the residual calcium hardness in the treated water in meq

- **T**he **Daily Lime Requirement** is in lb/day for U.S. units or kg/day for S.I. units

- The **equiv wt for lime** is 28 for quicklime or 37 for slaked lime

Daily magnesium solids in lb/day (U.S. units) = (**MgCH** + **MgNCH** - **MgHResid**) (**29.2** mg/meq)(**8.34**)(**design flow rate** in MGD)

Daily magnesium solids in kg/day (S.I. units) = (**MgCH** + **MgNCH** - **MgHResid**) (**29.2** mg/meq)(**design flow rate** in m^3/d)/(**1000** g/kg)

Where:

- **MgCH** = the magnesium carbonate hardness in the raw water in meq/L

- **MgNCH** = the magnesium noncarbonate hardness in the raw water in meq/L

- **MgHResid** = the residual Magnesium hardness in the treated water in meq/L

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Example #13: Calculate an estimate of the daily production rates of calcium solids, magnesium solids, and total solids, for two stage excess lime softening of the water described in Example #4, which has the following analysis?

- Total hardness = 150 mg/L as $CaCO_3$
- Calcium hardness = 100 mg/L as $CaCO_3$
- Alkalinity = 120 mg/L as $CaCO_3$

The design flow rate to be treated is 2.5 MGD. The carbon dioxide concentration of the raw water is 4.85 mg/L. Use 0.7 meq/L excess lime dosage. Use 0.5 as the fraction of carbonate ion to be converted to bicarbonate ion in the first stage recarbonation. Use 0.8 meq/L as the design magnesium hardness residual and use 0.8 meq/L as the lower limit for calcium hardness residual.

Solution: These calculations can be made using the equations just presented above in this section. The equation for daily calcium solids production rate is:

Daily calcium solids in lb/day = (**CaCH** + **CaNCH** + **LimeDose** - **CaHResid**)(**50** mg/meq)(**8.34**)(**design flow rate** in MGD)

As calculated in Example #4, the CaCH and CaNCH in this water are:

CaCH = 100 mg/L as $CaCO_3$ = <u>2 meq/L</u>

CaNCH = 0 mg/L $CaCO_3$ = <u>0 meq/L</u>

As calculated in Example #9, the lime dosage for this water is:

LimeDose = 4.421 meq/L

As given in the problem statement use 0.8 meq/L as the calcium hardness residual (**CaHResid**)

Substituting values into the equation gives:

Daily calcium solids in lb/day = (2 + 0 + 4.421 - 0.8)(50)(8.34)(2.5) = **<u>5860 lb/day</u>**

The equation for daily calcium solids production rate is:

Daily magnesium solids in lb/day = (**MgCH** + **MgNCH** - **MgHResid**)(**29.2** mg/meq)(**8.34**)(**design flow rate** in MGD)

As calculated in Example #4, the MgCH and MgNCH in this water are

MgCH = 20 mg/L $CaCO_3$ = <u>0.4 meq/L</u>

MgNCH = 30 mg/L as $CaCO_3$ = <u>0.6 meq/L</u>

As given in the problem statement use 0.8 meq/L as the design magnesium hardness residual (**MgHResid**)

Substituting values into the equation gives:

Daily magnesium solids in lb/day = (0.4 + 0.6 + 0.8)(29.2)(8.34)(2.5) = **<u>1096 lb/day</u>**

The total solids production rate will be simply the sum of the rate of production of calcium solids and the rate of production of magnesium solids. Thus:

Total solids production rate = 5860 + 1096 = **<u>6956 lb/day</u>**

13.   Summary

The lime soda water softening process uses addition of lime, soda ash and carbon dioxide to remove the diavalent cations, Ca^{++} and Mg^{++}, which cause hardness in water. The calcium is precipitated as calcium carbonate and the magnesium is precipitated as magnesium hydroxide. This course presented information about calculating the concentrations of different types of hardness and the carbon dioxide concentration in a water sample based on values for the hardness, calcium hardness, alkalinity, and pH. Also information was presented on three different lime soda water softening process alternatives, i) two stage excess lime softening, ii) split treatment lime soda softening, and iii) selective calcium removal lime soda softening. For each of these process alternatives, equations and worked examples were presented for calculating i) the dosages of lime, soda ash and carbon dioxide required in mg/L $CaCO_3$ and in meq/L; ii)

daily chemical requirements of lime, soda ash, and carbon dioxide in lb/day; and iii) the daily production rate of calcium solids and of magnesium solids.

14. References

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