

Lesson 14:

Lime Softening

Objective

In this lesson we will answer the following questions:

- What is hardness and why is hard water problematic?
- What methods can be used to soften water?
- What are the advantages and disadvantages of softening?

Reading Assignment

Read the online lecture.

Lecture

Hardness

Hard water is usually defined as water which contains a *high concentration of calcium and magnesium*. Measurements of hardness are given in terms of the *calcium carbonate equivalent (CaCO₃)*, which is an expression of the concentration of hardness ions in water in terms of their equivalent value of calcium carbonate.

The hardness in water is the result of water flowing over and through different geologic formation and dissolving calcium and magnesium. Calcium comes from limestone. Magnesium primarily comes from dolomite. Groundwater tends to be harder than surface water.

Let's take a look at the range of hardness values:

Soft	0-60 mg/L as CaCO ₃
Moderate	61-120 mg/L as CaCO ₃
Hard	121-180 mg/L as CaCO ₃
Very hard	> 180 mg/L as CaCO ₃
Target	50-85 mg/L as CaCO₃

Hardness of water is an issue due to scale formation of calcium carbonate and magnesium hydroxide and the reaction with soap, causing a ring around the tub or cause an excessive use of soap.

Lesson 14:

Lime Softening Calculations

Objective

In this part of the lesson we will perform the following calculations

- determining calcium hardness
- determining magnesium hardness
- determining total hardness
- carbonate/noncarbonate hardness
- lime dosage
- recarbonation
- feed rates

Softening Process Calculations

There are certain process calculations that may need to be performed pertaining to hardness and lime dosage for removal of carbonate hardness. Let's look at the process calculations that affect the softening process.

Calcium Hardness as CaCO_3

The hardness, in mg/L as CaCO_3 for any given metallic ion is calculated with the following equation: (Remember to look up the equivalent weights under the hardness section above to save yourself some time.)



Example:

A water sample has calcium content of 51 mg/L. What is the calcium hardness expressed as CaCO_3 ?

$$\frac{\text{calcium hardness, mg/L as CaCO}_3}{\text{equivalent weight of CaCO}_3} = \frac{\text{calcium, mg/L}}{\text{equivalent weight of calcium}}$$

$$\frac{\text{calcium hardness, mg/L as CaCO}_3}{50.045} = \frac{51 \text{ mg/L}}{20.04}$$

$$\text{calcium hardness, mg/L as CaCO}_3 = \frac{51 \text{ mg/L} \times 50.045}{20.04}$$

$$\text{calcium hardness, mg/L as CaCO}_3 = 127 \text{ mg/L as CaCO}_3$$

Calculating Magnesium Hardness as CaCO₃

To calculate magnesium hardness, use the following equation:

<p>Lime Compounds</p> <p>Quicklime - CaO Another name for <i>calcium oxide</i> (CaO) it is used for water softening and water stabilization.</p> <p>Hydrated Lime - Ca(OH)₂ Quicklime that has been combined with water. Also called <i>slaked lime</i> or <i>calcium hydroxide</i>.</p> <p>Reduces Carbonate Hardness</p>	<p>Soda Ash</p> <p>Soda Ash - Na₂CO₃ The minerals that cause noncarbonate calcium hardness are precipitated using Soda Ash.</p> <p>Reduces Noncarbonate Hardness</p>
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Example:

A sample of water contains 24 mg/L magnesium. Express this magnesium hardness as CaCO₃.

$$\frac{\text{magnesium hardness, mg/L as CaCO}_3}{\text{equivalent weight of CaCO}_3} = \frac{\text{magnesium, mg/L}}{\text{equivalent weight of magnesium}}$$

$$\frac{\text{magnesium hardness, mg/L as CaCO}_3}{50.045} = \frac{24 \text{ mg/L}}{12.15}$$

$$\text{magnesium hardness, mg/L as CaCO}_3 = \frac{24 \text{ mg/L} \times 50.045}{12.15}$$

$$\text{magnesium hardness, mg/L as CaCO}_3 = 98.9 \text{ mg/L as CaCO}_3$$

Calculating Total Hardness

Calcium and magnesium ions are the primary cause of hardness in water. To find total hardness, we simply add the concentrations of calcium and magnesium ions, expressed in terms of calcium carbonate (CaCO₃):

$$\text{Total hardness, mg/L as CaCO}_3 = \text{calcium hardness, mg/L as CaCO}_3 + \text{magnesium hardness, mg/L as CaCO}_3$$

Example:

Determine the total hardness as CaCO₃, of a sample of water that has calcium content of 28 mg/L and magnesium content of 9 mg/L.

The first step is to determine the calcium hardness as CaCO₃:

$$\frac{\text{calcium hardness, mg/L as CaCO}_3}{\text{equivalent weight of CaCO}_3} = \frac{\text{calcium, mg/L}}{\text{equivalent weight of calcium}}$$

$$\frac{\text{calcium hardness, mg/L as CaCO}_3}{50.045} = \frac{28 \text{ mg/L}}{20.04}$$

$$\text{calcium hardness, mg/L as CaCO}_3 = \frac{28 \text{ mg/L} \times 50.045}{20.04}$$

$$\text{calcium hardness, mg/L as CaCO}_3 = 69.9 \text{ mg/L as CaCO}_3$$

Now determine the magnesium hardness as CaCO₃:

$$\frac{\text{magnesium hardness, mg/L as CaCO}_3}{\text{equivalent weight of CaCO}_3} = \frac{\text{magnesium, mg/L}}{\text{equivalent weight of magnesium}}$$

$$\frac{\text{magnesium hardness, mg/L as CaCO}_3}{50.045} = \frac{9 \text{ mg/L}}{12.15}$$

$$\text{magnesium hardness, mg/L as CaCO}_3 = \frac{9 \text{ mg/L} \times 50.045}{12.15}$$

$$\text{magnesium hardness, mg/L as CaCO}_3 = 37.1 \text{ mg/L as CaCO}_3$$

Now you can determine the total hardness:

$$\text{Total hardness, mg/L as CaCO}_3 = \text{calcium hardness, mg/L as CaCO}_3 + \text{magnesium hardness, mg/L as CaCO}_3$$

$$\text{Total hardness, mg/L as CaCO}_3 = 69.9 \text{ mg/L as CaCO}_3 + 37.1 \text{ mg/L as CaCO}_3$$

$$\text{Total hardness, mg/L as CaCO}_3 = 107 \text{ mg/L as CaCO}_3$$

Calculating Carbonate and Noncarbonate Hardness

As mentioned, total hardness is comprised of calcium and magnesium hardness. Once total hardness has been calculated, it is sometimes used to determine another expression of hardness - carbonate and noncarbonate. When hardness is numerically greater than the sum of bicarbonate and carbonate alkalinity, that amount of hardness equivalent to the total alkalinity (both in units of mg/L as CaCO₃) is referred to as the carbonate hardness; the amount of hardness in excess of this is the noncarbonate hardness. When the hardness is numerically equal to or less than the sum of carbonate and noncarbonate alkalinity, all hardness is carbonate hardness, and noncarbonate hardness is absent. Again, the total hardness is comprised of carbonate hardness and noncarbonate hardness:

$$\text{Total hardness} = \text{carbonate hardness} + \text{noncarbonate hardness}$$

When the *alkalinity* (as CaCO₃) is **greater** than the *total hardness*, all the **hardness** is *carbonate hardness*:

$$\text{Total hardness, mg/L as CaCO}_3 = \text{carbonate hardness, mg/L as CaCO}_3$$

When the *alkalinity* (as CaCO₃) is **less** than the *total hardness*, then the **alkalinity** represents *carbonate hardness* and the *balance* of the hardness is *noncarbonate hardness*:

$$\text{Total hardness, mg/L as CaCO}_3 = \text{carbonate hardness, mg/L as CaCO}_3 + \text{noncarbonate hardness, mg/L as CaCO}_3$$

When *carbonate hardness* is represented by the *alkalinity*:

$$\text{Total hardness, mg/L as CaCO}_3 = \text{alkalinity, mg/L as CaCO}_3 + \text{noncarbonate hardness, mg/L as CaCO}_3$$

Example 1:

A water sample contains 110 mg/L alkalinity as CaCO₃ and 105 mg/L total hardness as CaCO₃. What is the carbonate and noncarbonate hardness of the sample?

Because the alkalinity is greater than the total hardness, all the hardness is carbonate hardness:

$$\text{Total hardness, mg/L as CaCO}_3 = \text{carbonate hardness, mg/L as CaCO}_3$$

$$105 \text{ mg/L as CaCO}_3 = \text{carbonate hardness, mg/L as CaCO}_3$$

No noncarbonate hardness is present in this water.

Example 2:

The alkalinity of a water sample is 80 mg/L as CaCO₃. If the total hardness of the water sample is 112 mg/L as CaCO₃, what is the carbonate and noncarbonate hardness, in mg/L as CaCO₃?

Alkalinity is less than total hardness; therefore, both carbonate and noncarbonate hardness will be present in the hardness of the sample.

Total hardness, mg/L as CaCO₃ = carbonate hardness, mg/L as CaCO₃ + noncarbonate hardness, mg/L as CaCO₃

112 mg/L as CaCO₃ = 80 mg/L as CaCO₃ + noncarbonate hardness, mg/L as CaCO₃

112 mg/L as CaCO₃ - 80 mg/L as CaCO₃ = noncarbonate hardness, mg/L as CaCO₃

noncarbonate hardness, mg/L as CaCO₃ = 32 mg/L as CaCO₃

Lime Dosage Calculation for Carbonate Hardness Removal

The lime-soda ash water softening process uses lime (Ca(OH)₂), and soda ash (Na₂CO₃), to precipitate hardness from solution. Carbonate hardness (calcium and magnesium bicarbonates) is complexed by lime. Noncarbonate hardness (calcium and magnesium sulfates or chlorides) requires the addition of soda ash for precipitation. The molecular weights of various chemicals and compounds used in lime-soda ash softening calculations are as follows:

Chemical or Compound	Molecular Weight
Qucklime (CaO ₂)	56
Hydrated Lime (Ca(OH) ₂)	74
Magnesium (Mg)	24.3
Carbon dioxide (CO ₂)	44
Magnesium hydroxide (Mg(OH) ₂)	58.3
Soda ash (Na ₂ CO ₃)	100
Alkalinity (as CaCO ₃)	100
Hardness (as CaCO ₃)	100

To calculate quicklime or hydrated lime dosage, mg/L, use the following equation:

$$\text{Quicklime feed, mg/L} = \frac{(A + B + C + D) \times 1.15}{\text{Lime purity, decimal}}$$

Where:

A = CO₂ in source water (mg/L as CO₂ x 56/44)

B = bicarbonate alkalinity removed in softening (mg/L as CaCO₃ x 56/100)

C = hydroxide alkalinity in softener effluent (mg/L as CaCO₃ x 56/100)

D = magnesium removed in softening (mg/L as Mg x 56/24.3)

1.15 = excess lime dosage (using 15% excess)

Note: For hydrated lime dosage, use the same equation as above, except substitute 74 for 56 when calculating A, B, C and D.

Example:

A water sample has a carbon dioxide content of 4 mg/L as CO₂, total alkalinity of 130 mg/L as CaCO₃, and magnesium content of 26 mg/L as Mg. Approximately how much quicklime (CaO x 90% purity) will be required for softening? (Assume 15% excess lime.)

Now determine how much hydrated lime will be required for softening a water with the same characteristics. First, calculate the A through D factors for quicklime:

A = CO₂, mg/L x (56/44)

A = 4 mg/L x (1.27)

A = 5 mg/L

B = Bicarbonate alkalinity, mg/L x (56/100)

B = 130 mg/L x (0.56)

B = 73 mg/L

C = Hydroxide alkalinity, mg/L x (56/100)

C = 0 mg/L

D = Mg, mg/L x (56/24.3)

D = 26 mg/L x (2.30)

D = 60 mg/L

Now calculate the quicklime dosage:

$$\text{Quicklime feed, mg/L} = \frac{(A + B + C + D) \times 1.15}{\text{Lime purity, decimal}}$$

$$\text{Quicklime feed, mg/L} = \frac{(5 \text{ mg/L} + 73 \text{ mg/L} + 0 \text{ mg/L} + 60 \text{ mg/L}) \times 1.15}{0.90}$$

$$\text{Quicklime feed, mg/L} = 176 \text{ mg/L CaO}$$

Now determine the estimated hydrated lime dosage required for softening the same water:

First, calculate the A through D factors for hydrated lime. Remember it's the same formulas, just substitute 74 for 56 in the calculations:

$$A = \text{CO}_2, \text{ mg/L} \times (74/44)$$

$$A = 4 \text{ mg/L} \times (1.68)$$

$$A = 7 \text{ mg/L}$$

$$B = \text{Bicarbonate alkalinity, mg/L} \times (74/100)$$

$$B = 130 \text{ mg/L} \times (0.74)$$

$$B = 96 \text{ mg/L}$$

$$C = \text{Hydroxide alkalinity, mg/L} \times (74/100)$$

$$C = 0 \text{ mg/L}$$

$$D = \text{Mg, mg/L} \times (74/24.3)$$

$$D = 26 \text{ mg/L} \times (3.05)$$

$$D = 79 \text{ mg/L}$$

Now calculate the hydrated lime dosage:

$$\text{Hydrated lime dosage, mg/L} = \frac{(A + B + C + D) \times 1.15}{\text{Lime purity, decimal}}$$

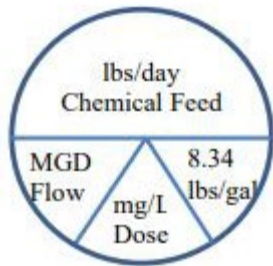
$$\text{Hydrated lime dosage, mg/L} = \frac{(7 \text{ mg/L} + 96 \text{ mg/L} + 0 \text{ mg/L} + 79 \text{ mg/L}) \times 1.15}{0.90}$$

$$\text{Hydrated lime dosage, mg/L} = 233 \text{ mg/L Ca(OH)}_2$$

As you can see, it takes more hydrated lime (233 mg/L) than quicklime (176 mg/L) to soften the same water.

Now you can determine the feed rate for the hydrated lime or quicklime by:

$$\text{Feed rate, lb/day} = \frac{\text{Dosage, mg/L} \times \text{Flow, MGD} \times 8.34 \text{ lb/gal}}{\text{Purity, decimal}}$$



Davidson Pie Chart:

- To find the quantity above the horizontal line: multiply the pie wedges below the line together and divide by the purity, as a decimal.
- To solve for one of the pie wedges below the horizontal line: cover that pie wedge, then divide the remaining pie wedges into the quantity above the horizontal line and multiply by the purity, as a decimal.
- The given units must match the units shown in the pie wheel.

Example:

Determine the feed rate for both the hydrated lime and quicklime dosages calculated above if the flow to the plant is 3.32 MGD:

Quicklime:

$$\text{Quicklime feed rate, lb/day} = \frac{\text{Dosage, mg/L} \times \text{Flow, MGD} \times 8.34 \text{ lb/gal}}{\text{Purity, decimal}}$$

$$\text{Quicklime feed rate, lb/day} = \frac{176 \text{ mg/L} \times 3.32 \text{ MGD} \times 8.34 \text{ lb/gal}}{0.90}$$

$$\text{Quicklime feed rate, lb/day} = 5415 \text{ lb/day}$$

Hydrated Lime:

$$\text{Hydrated lime feed rate, lb/day} = \frac{\text{Dosage, mg/L} \times \text{Flow, MGD} \times 8.34 \text{ lb/gal}}{\text{Purity, decimal}}$$

$$\text{Hydrated lime feed rate, lb/day} = \frac{233 \text{ mg/L} \times 3.32 \text{ MGD} \times 8.34 \text{ lb/gal}}{0.90}$$

$$\text{Hydrated lime feed rate, lb/day} = 7168 \text{ lb/day}$$

Calculation for Removal of Noncarbonate Hardness

Soda ash is used for precipitation and removal of noncarbonate hardness. To calculate the soda ash dosage required, we use a combination of the following formulas:

Total hardness, mg/L as CaCO_3 = carbonate hardness, mg/L as CaCO_3 + noncarbonate hardness, mg/L as CaCO_3

Soda ash, mg/L as Na_2CO_3 = noncarbonate hardness, mg/L as CaCO_3 x (106/100)

Example:

A water sample has a total hardness of 250 mg/L as CaCO_3 and a total alkalinity of 180 mg/L. What soda ash

dosage will be required to remove the noncarbonate hardness, mg/L?

First calculate the noncarbonate hardness:

Total hardness, mg/L as CaCO_3 = carbonate hardness, mg/L as CaCO_3 + noncarbonate hardness, mg/L as CaCO_3

250 mg/L as CaCO_3 = 180 mg/L + noncarbonate hardness, mg/L as CaCO_3

noncarbonate hardness, mg/L as CaCO_3 = 250 mg/L - 180 mg/L

noncarbonate hardness, mg/L as CaCO_3 = 70 mg/L

Now calculate the soda ash required:

Soda ash, mg/L as Na_2CO_3 = noncarbonate hardness, mg/L as CaCO_3 x (106/100)

Soda ash, mg/L as Na_2CO_3 = 70 mg/L as CaCO_3 x (1.06)

Soda ash, mg/L as Na_2CO_3 = 74.2 mg/L soda ash

Recarbonation Calculation

Recarbonation involves the *reintroduction of carbon dioxide into the water*, either *during or after lime softening*, lowering the pH of the water to about 10.4. After the addition of soda ash, recarbonation lowers the pH of the water to about 9.8, promoting better precipitation of calcium carbonate and magnesium hydroxide. The following equations are used to estimate carbon dioxide dosage.

Excess lime, mg/L = (A + B + C + D) x 0.15

Total CO_2 dosage, mg/L = [$\text{Ca}(\text{OH})_2$ excess mg/L x (44/74)] + [Mg residual, mg/L x (44/24.3)]

Example:

The A, B, C and D factors of the excess lime equation have been calculated as:

A = 10mg/L

B = 87 mg/L

C = 0 mg/L

$$D = 111 \text{ mg/L}$$

If the residual magnesium is 5 mg/L, what carbon dioxide dosage would be required for recarbonation?

The excess lime is:

$$\text{Excess lime, mg/L} = (A + B + C + D) \times 0.15$$

$$\text{Excess lime, mg/L} = (10 \text{ mg/L} + 87 \text{ mg/L} + 0 \text{ mg/L} + 111 \text{ mg/L}) \times 0.15$$

$$\text{Excess lime, mg/L} = 208 \text{ mg/L} \times 0.15$$

$$\text{Excess lime, mg/L} = 31 \text{ mg/L}$$

The required carbon dioxide dosage for recarbonation is:

$$\text{Total CO}_2 \text{ dosage, mg/L} = [\text{Ca(OH)}_2 \text{ excess mg/L} \times (44/74)] + [\text{Mg residual, mg/L} \times (44/24.3)]$$

$$\text{Total CO}_2 \text{ dosage, mg/L} = [31 \text{ mg/L} \times (44/74)] + [5 \text{ mg/L} \times (44/24.3)]$$

$$\text{Total CO}_2 \text{ dosage, mg/L} = 18 \text{ mg/L} + 9 \text{ mg/L}$$

$$\text{Total CO}_2 \text{ dosage, mg/L} = 27 \text{ mg/L CO}_2$$

Calculating Feed Rates

The appropriate chemical dosage for various unit processes is typically determined by laboratory or pilot-scale testing (i.e. jar testing), monitoring, and historical experience. Once the chemical dosage is determined, the feed rate can be calculated using the following equation. Once the chemical feed rate is known, this value must be translated into a chemical feeder setting.

$$\text{Feed rate, lb/day} = \text{Chemical dose, mg/L} \times \text{Flow rate, MGD} \times 8.34 \text{ lb/gal}$$

To calculate the lb/min chemical required:

$$\text{Chemical, lb/min} = \frac{\text{Chemical, lb/day}}{1440 \text{ min/day}}$$

Example:

Jar tests indicate that the optimum lime dosage is 200 mg/L. If the flow to be treated is 4.0 MGD, what should be the chemical feeder setting in lb/day and lb/min?

First calculate the lb/day feed rate:

$$\text{Feed rate, lb/day} = \text{Chemical dose, mg/L} \times \text{Flow rate, MGD} \times 8.34 \text{ lb/gal}$$

$$\text{Feed rate, lb/day} = 200 \text{ mg/L} \times 4.0 \text{ MGD} \times 8.34 \text{ lb/gal}$$

$$\text{Feed rate, lb/day} = 6672 \text{ lb/day}$$

Now convert this feed rate to lb/min:

$$\text{Chemical, lb/min} = \frac{\text{Chemical, lb/day}}{1440 \text{ min/day}}$$

$$\text{Chemical, lb/min} = \frac{6672 \text{ lb/day}}{1440 \text{ min/day}}$$

$$\text{Chemical, lb/min} = 4.6 \text{ lb/min}$$

Summary

- Water that has a hardness concentration >180 mg/L as CaCO_3 is considered very hard.
- Water that has a hardness concentration ranging from 121 - 180 mg/L as CaCO_3 is considered hard.
- Water that has a hardness concentration ranging from 61 - 120 mg/L as CaCO_3 is considered moderately hard.
- Water that has a hardness concentration ranging from 0 - 60 mg/L as CaCO_3 is considered soft.
- Raw water can usually be softened by only using lime when it contains little or no noncarbonate hardness.
- Calcium and magnesium are the two main constituents of water hardness.
- When softening water using the lime-soda ash softening process, soda ash dosage is based on the amount of noncarbonate hardness to be removed.
- Ion exchange softening processes can be used for direct groundwater treatment as long as turbidity and iron levels are not too high.
- The double-stage process in excess-lime softening is designed to achieve greater magnesium removal.
- Recarbonation is required to stabilize the water following the lime softening process to prevent CaCO_3 from precipitating out on the filters.
- Another name for noncarbonated hardness is permanent hardness.
- Soda Ash will produce a cake that is both difficult and hazardous to handle when it comes into contact with moisture.
- Water that is too soft will cause your skin to feel slippery after washing with soap due to a soap scum feeling on your skin.
- Raw water requires both lime and soda ash when there are nominal amounts of magnesium hardness in the water.
- The lime softening processes can cause the formation of THMs due to the high pH levels required since THM formation increases as pH increases.

- It takes about 20-30 minutes to slake lime in a detention-time lime slaker.
- The slaking process should be maintained at 160° F or higher for best results.
- The sludge blanket in a softening plant's contact clarifier should have a solids concentration in the range of 5-15% total solids.

Assignment

Please complete the [assignment](#) for this lesson. You must be logged into Canvas to complete this assignment.

Quiz

Answer the questions in the [lesson quiz](#). You will need to log into Canvas to take the quiz. You may take the quiz 3 times, if needed, and an average will be taken from your attempts for final grade calculation.



Hard water causes bathtub rings.



Calcium carbonate scale on a piece of pipe.

Excessively hard water will nearly always have to be softened in order to protect the water treatment plant equipment and piping systems.

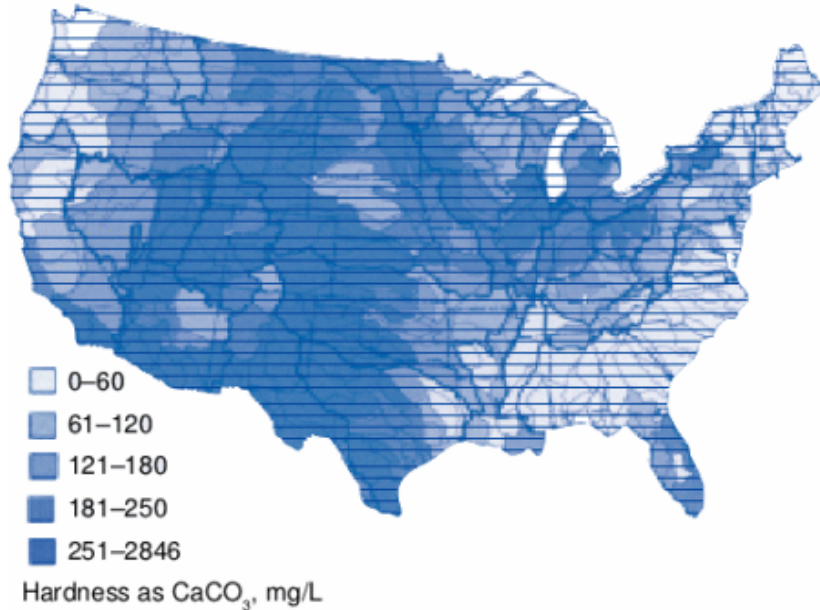
The two primary constituents of water that determine the hardness of water are calcium and magnesium. If the concentration of these elements in the water is known, the total hardness of the water can be calculated. To make this calculation, the equivalent weights of calcium, magnesium, and calcium carbonate must be known. The equivalent weights are given below:

Element	Equivalent Weight
Calcium (Ca)	20.04
Magnesium (Mg)	12.15
Calcium Carbonate (CaCO ₃)	50.045

Sources of Hardness

Hardness generally enters groundwater as the water percolates through minerals containing calcium or magnesium. The most common sources of hardness are limestone (which introduces calcium into the water) and dolomite (which introduces magnesium.) Since hardness enters water in this manner, groundwater generally has a greater hardness than surface water. There are also regional variations in hardness, shown by the map below.

Average Water Hardness in the Continental United States



Courtesy of the U.S. Geological Survey, Report 78-200

Types of Hardness

As mentioned above, hardness in water is caused by a variety of divalent cations, primarily calcium and magnesium. These cations have a tendency to combine with anions (negatively charged ions) in the water to form stable compounds known as salts. The type of anion found in these salts distinguishes between the two types of hardness - carbonate and noncarbonate hardness.

Carbonate hardness compounds	Noncarbonate hardness compounds
Calcium carbonate (CaCO_3)	Calcium sulfate (CaSO_4)
Magnesium carbonate (MgCO_3)	Magnesium sulfate (MgSO_4)
Calcium bicarbonate ($\text{Ca}(\text{HCO}_3)_2$)	Calcium chloride (CaCl_2)
Magnesium bicarbonate ($\text{Mg}(\text{HCO}_3)_2$)	Magnesium chloride (MgCl_2)
Calcium hydroxide ($\text{Ca}(\text{OH})_2$)	
Magnesium hydroxide ($\text{Mg}(\text{OH})_2$)	

As you can see in the table above, **carbonate hardness** is caused by *metals combined with a form of alkalinity*. As you may remember, **alkalinity** is the *capacity of water to neutralize acids* and is *caused by* compounds such as *carbonate, bicarbonate, hydroxide*, and sometimes borate, silicate, and phosphate. In contrast, **noncarbonate hardness** forms when *metals combine with anything other than alkalinity*.

Carbonate hardness is sometimes called *temporary hardness* because it can be removed by boiling water. **Noncarbonate hardness** cannot be broken down by boiling the water, so it is also known as *permanent hardness*. In general, it is important to distinguish between the two types of hardness because the removal method differs for the two.

When measuring hardness, we typically consider **total hardness** which is the *sum of all hardness compounds in water, expressed as a calcium carbonate equivalent*. Total hardness includes both temporary and permanent hardness caused by calcium and magnesium compounds.

Alkalinity

Alkalinity is a measure of water's ability to neutralize acids. It results primarily from dissolving limestone or dolomite minerals in the aquifer. Alkalinity and total hardness are usually nearly equal in concentration (when they are both reported in mg/L as CaCO₃ because they form from the same minerals).

If alkalinity is much greater than total hardness, it may indicate that your water has passed through a water softener. If alkalinity is much less than total hardness it may signify elevated levels of chloride, nitrate or sulfate.

Water with low levels of alkalinity (less than 150 mg/L) is more likely to be corrosive.

High alkalinity water (greater than 150 mg/L) may contribute to scaling.

There are no health concerns related to alkalinity. The value should be roughly 75 - 100% of the total hardness value in an unsoftened sample.

Alkalinity Relationships				
IF	Then measured alkalinity is due to:			
<i>Result of Titration</i>		<i>Hydroxide Alkalinity</i>	<i>Carbonate Alkalinity</i>	<i>Bicarbonate Concentration</i>
P = 0	Bicarbonates	0	0	T
P < ½ T	Carbonates and bicarbonates	0	2P	T - 2P
P = ½ T	Carbonates	0	2P	0
P > ½ T	Hydroxides and carbonates	2P - T	2(T - P)	0
P = T	Hydroxides	T	0	0

To Soften or Not to Soften?

Since softening is not a required treatment process, each treatment plant must decide whether or not to soften its water. This decision should be made after carefully weighing the advantages and disadvantages of softening.

Softening will deal with the problems caused by hard water - excessive soap use and scaling being the most troublesome. In addition, depending on the type of softening process used, softening may also aid in other water treatment processes. Softening often removes iron and manganese, reduces tastes and odors, reduces total solids content, and removes radioactivity. The high pH associated with lime softening can aid in disinfection. Finally, when water is stabilized using recarbonation at the end of the lime softening process, corrosion in the distribution system is avoided.

Softening processes all carry a certain monetary expense. In addition, softening can cause several other problems. The high pH associated with lime softening tends to favor the formation of hypochlorite as the dominant free chlorine residual, and hypochlorite is a less powerful disinfectant than other free chlorine residuals. The high pH may also increase trihalomethane levels in the water. If the water is not properly stabilized after treatment, then corrosive water may be produced which will corrode the distribution system. Ion exchange softening, as noted above, can also cause problems due to the high levels of sodium in the treated water. Both lime softening and ion exchange softening create waste disposal problems.

Large Scale Softening Processes

Softened water should have a hardness of about 80 to 90 mg/L as calcium carbonate. If the water is softened further (as in the ion exchange process) then the hard water must be mixed with the softened water to achieve the desired hardness. Excessively soft water can be nearly as problematic as excessively hard water since it causes corrosion of pipes.

The softening process does have a few disadvantages. For example, the process produces large quantities of sludge, requires careful operation, and if the pH is not properly adjusted, may create operational problems downstream of the process.

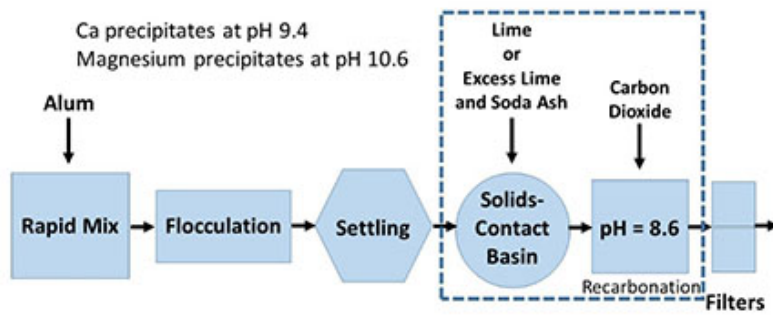
Chemical Precipitation

In chemical precipitation, it is necessary to **adjust pH**. To precipitate the calcium and magnesium ions, the pH must be raised to about **9.4 for calcium** and about **10.6 for magnesium**. To **raise the pH** to the required levels, *lime is added*. There are a few variations of this type of softening process, including:

- lime softening
- lime-soda ash softening
- excess-lime treatment
- split treatment
- caustic soda treatment

Caustic soda is too expensive and not likely used, though it does produce less sludge than the other processes.

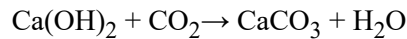
If the hardness present in the water is primarily due to **calcium**, **lime** may be the only treatment needed to *raise the pH* in the contact basin to **9.4**.



Single-Stage Process

Once the softening occurs, carbon dioxide is added to lower the pH back to a stable range of 8.6. This step is called recarbonation. This process stabilizes the water so that calcium carbonate doesn't precipitate out and collect on the filters or in the distribution system.

Lime + Carbon dioxide → Calcium carbonate + Water



Soda ash is added to remove *non-carbonate hardness*. **Lime** is added to remove *carbonate hardness*. This type of softening process is the most commonly used.

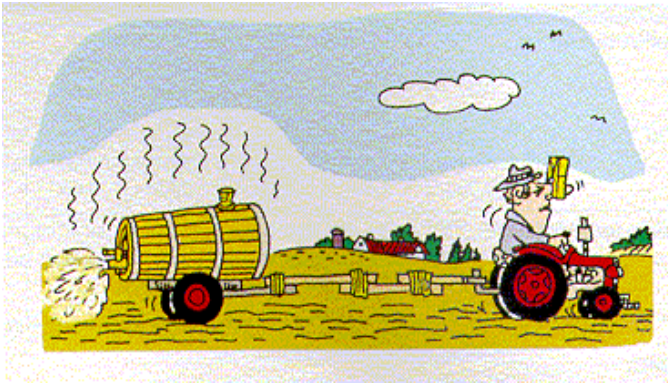
Lime softening produces large quantities of sludge. In fact, for every pound of lime used, about two pounds of sludge are formed.



Lime sludge

The softening process usually requires two sedimentation basins, each with a detention time of 1.5 to 3 hours, to deal with the large quantities of sludge. One sedimentation basin handles the sludge resulting from lime and soda ash softening and the other sedimentation basin deals with the sludge resulting from recarbonation. Sludge may be disposed of through any number of the methods. Landfill disposal is the most common, although sludge may sometimes be sent to sanitary sewers. Lime sludge has a high

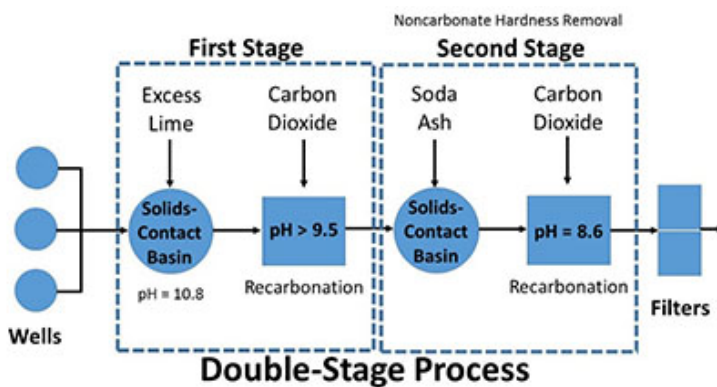
pH and has increasingly been disposed of by applying it to agricultural land to increase the pH of acidic soils.



If softening problems are discovered, the cause usually lies in either chemical feeder malfunctions or source water quality changes. A variety of water characteristics can influence lime-soda ash softening:

- **Water hardness** will determine the quantity of chemicals which must be added to soften the water.
- **pH** influences the chemical reactions in the softening process. A higher pH makes the process more efficient.
- **Alkalinity** determines whether the hardness in the water is carbonate or noncarbonate hardness.
- **Temperature** influences the rate of the reaction and the amount of hardness which the water will hold.

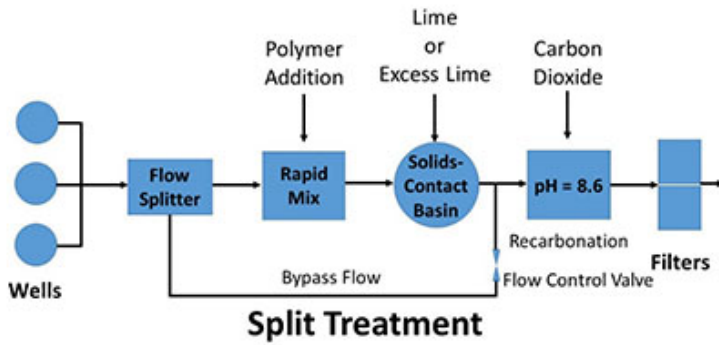
If the hardness in the water is **also due to magnesium**, a **double stage process** may be required. Magnesium hardness would be removed in the first stage by bringing the *pH up to 10.8* in the solids contact basin. *Recarbonate* to help *bring the pH down* to the range needed for calcium removal, which is *9.5*.



Designed to achieve greater Magnesium removal than the single stage process

During the second stage, **soda ash** is added to help *precipitate the calcium*. This process *removes the non-carbonate hardness*. Recarbonate again to lower the pH to 8.6 before it enters the system. This type of process is designed to achieve a greater magnesium removal than the single-stage process.

By using **split treatment**, it allows the water to bypass the rapid mix and contact basin, treating only a portion of the flow, while maintaining the hardness and alkalinity of the water. Both flow portions meet up for recarbonation with carbon dioxide and a pH of 8.6. This type of process is used to help reduce chemical costs by only treating a portion of the total flow.



In general, soda ash is added to remove non-carbonate hardness and lime is added to remove carbonate hardness.

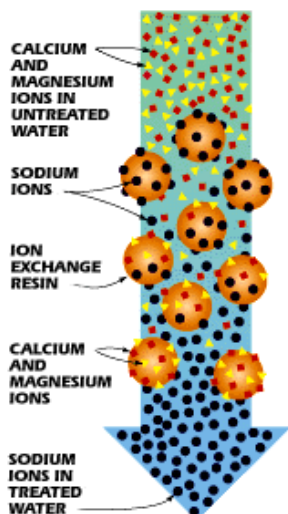
Small Scale Softening Processes

Softening can occur on a small scale through ion exchange, nanofiltration, electrodialysis or distillation.

Ion Exchange Softening

Hardness can be removed by ion exchange. In water softening, the ion exchange process "exchanges" non-hardness ions like sodium and potassium for the hardness ions calcium and magnesium by passing through an "ion exchanger". During this process, calcium and magnesium are removed while sodium or potassium is added to the water. This may cause an issue with dialysis machines, so caution needs to be taken when using ion exchange softeners on your home. This process can be used for direct groundwater treatment as long as the turbidity and iron levels are not too high.

The ion exchange resin can be regenerated by using a saturated Sodium chloride (NaCl) brine solution. By exposing the resin beads to a high concentration of sodium, the process reverses and the calcium and magnesium ions are released, while the sodium ions are attached to the resin, making it ready for use.



When all of the exchange sites have been utilized, hardness begins to appear in the influent, known as **breakthrough**. Breakthrough requires the regeneration of the medium by bringing it into contact with a concentrated solution of sodium chloride. Ion exchange used in water softening has both advantages and disadvantages. One of its major advantages is that it produces a softer water than does chemical precipitation.

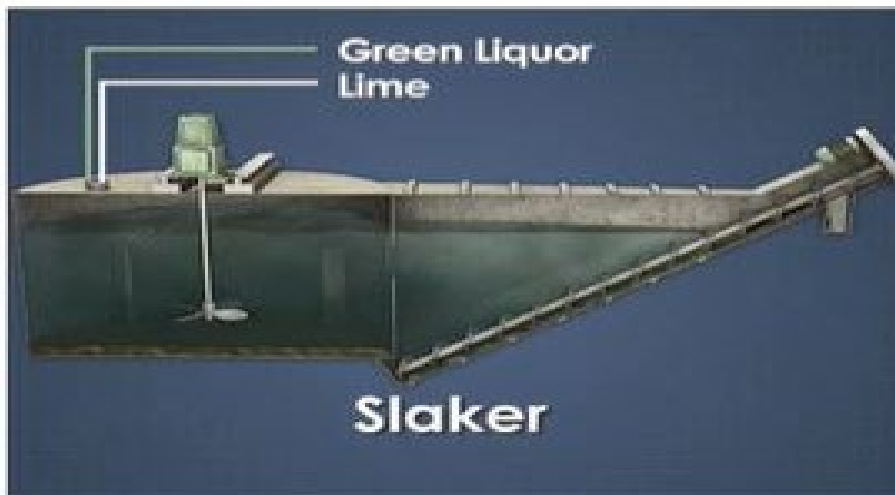
Additionally, ion exchange does not produce the large quantity of sludge encountered in the lime-soda ash process. One disadvantage is that, although it does not produce sludge, ion exchange does produce concentrated brine. Moreover, the water must be free of turbidity and particulate matter or the resin might function as a filter and become plugged. Ion-exchange is used extensively in small water systems and individual homes.

Lime Softeners

The lime used for softening comes in two forms - **hydrated lime** and **quicklime**. Both types of lime soften water in the same way, but the equipment required for the two types of lime is different.

Hydrated lime ($\text{Ca}(\text{OH})_2$) is also known as *calcium hydroxide* or *slaked lime*. Hydrated lime can be added to water as it is without requiring any special equipment, so it is a popular choice for small water treatment plants.

In contrast, **quicklime** (CaO), also known as *calcium oxide* or *unslaked lime*, must be slaked before it is used. The lime is fed with a dry chemical feeder and mixed with water in the slaking compartment. The **slaker** makes a mixture of the calcium oxide and water called "*milk of lime*", which is fed as a liquid. This process generates a lot of heat.



Slaking is the process of converting quicklime to hydrated lime by adding water. Slaking requires specialized equipment. The cost of equipment and the operator time required to run the equipment usually make quicklime use uneconomical in small plants. However, since the chemical cost of quicklime is less than the cost of hydrated lime, quicklime is often used in large plants.

In a *detention* type of slaker, the water to lime ratio is 4 or 5:1 by weight.

In a *paste* type of slaker, the water to lime ratio is 2 or 2.5:1 by weight.

Once the lime is added to the water, it takes 20-30 minutes for it to dissolve into solution. To help ensure complete contact, continuous mixing is required in the slaking compartment. The heat that is generated is transferred to the incoming water, maintaining a temperature of $> 160^\circ\text{F}$.

Above the top portion, the milk of lime flows over and goes through a classifier so it doesn't have any of the impurities in the solution. The slurry discharge doesn't allow any impurities to go into the system.

Process Equipment

The softening process is very similar to the conventional treatment process, but has some special equipment as well, including:

- Rapid-mix basin
- Flocculation basin
- Sedimentation basin
- Solids-contact clarifiers
- Pellet reactors
- Recarbonation
- Filtration

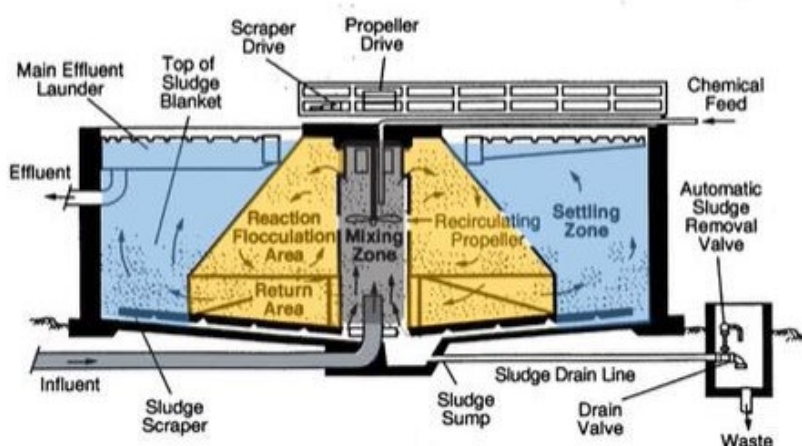
Rapid-Mix Basin

Just like in a conventional treatment plant, coagulant is added and mixed rapidly to ensure good coagulation. Alum is commonly used at the front end of a softening plant. Other coagulants may be used as part of the softening process to help gather the fine calcium and magnesium precipitates and aid in their settling. These coagulants are added to the solids-contact clarifier and not at the front end of the plant.

The main coagulants used for the softening process include:

- Alum
- Ferric chloride
- Ferric sulfate
- Polymers

Solids-Contact Basin



There are two distinct zones in a solids contact clarifier:

- Mixing and reaction zone (yellow and gray in the image above)
- Settling zone (blue in the image above)

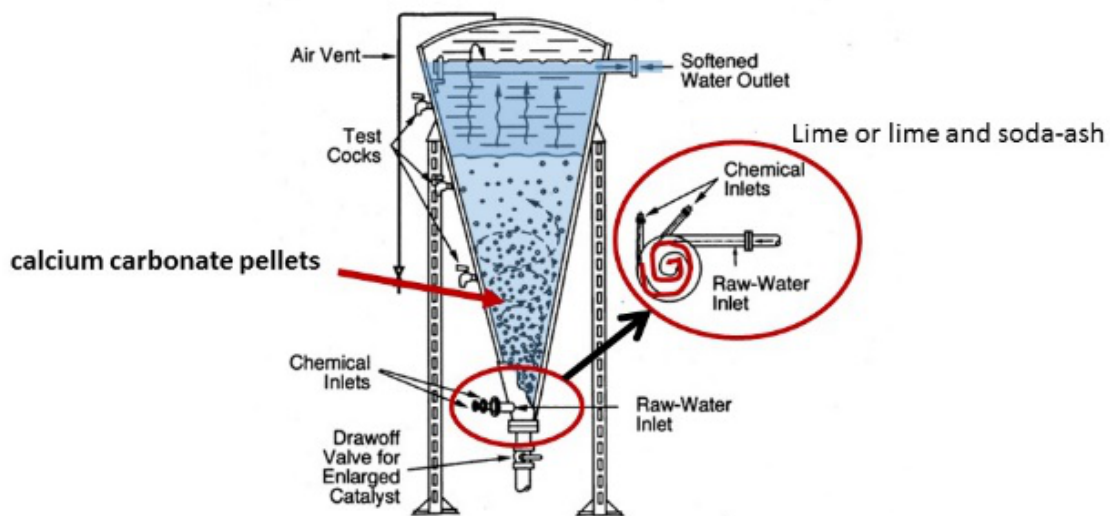
The **mixing zone** of the solids-contact basin is where the *lime or lime and soda ash is added*. The reaction area is also called the mixing zone and flows upward. The softened water flows up and over the effluent launder.

The **settling zone** is where the *sludge will collect after it settles*. You want a sludge with 5-15% total solids concentration in your *sludge blanket*. Some of this blanket gets recirculated into the mixing zone.

Pellet Reactors

Pellet reactors can be used if the hardness is primarily calcium, with minimum magnesium.

Detention Time = 5 - 10 minutes
Not effective for removing magnesium hardness



Pellet Reactor

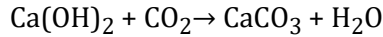
Pellets enter at the same location as the raw water inlet. They enter on a tangent, which causes it to spiral, flowing from the bottom of the reactor, upward. The combination of lime and soda ash with calcium and magnesium will form the precipitate that settles onto the calcium carbonate pellets. These pellets will grow in size as the precipitate settles. As they get larger, they settle towards the bottom, and the water flows up and over the weir.

Pellet reactors are much faster at lime softening than solids-contact clarifiers, with a normal detention time of 5-10 minutes. This process is not effective, however, at removing magnesium hardness. This is only effective for calcium hardness.

Recarbonation

Carbon dioxide is added to the water during the **recarbonation** process to *lower the pH* to a range of 8.6 - 8.7. The recarbonation process stabilizes the water so that calcium carbonate doesn't precipitate out, settling on the filters or in the distribution system.

Lime + Carbon dioxide → Calcium carbonate + Water



Backwashing

Backwashing

Backwashing the softener is very similar to backwashing a pressure filter and the purpose is the same. Although the purpose of a softener is not to filter out particulate matter, some particles inevitably get caught in the softener. By sending water backwards through the softener, this particulate matter is removed. After backwashing, the softener is ready to be regenerated. This is the part of the process in which the magnesium and calcium ions on the resin become replaced with sodium so that the softener can be used to treat more hard water. In order to regenerate the resin, a salt solution, known as brine, is allowed to flow through the softener for about an hour. During regeneration, calcium chloride, magnesium chloride, and excess sodium chloride flow to waste

After the brine has been given a sufficient contact time, it must be rinsed out of the softener. During the rinse cycle, fresh water is passed through the unit as it would be during treatment, but with the effluent going to waste. Rinse usually takes about 20 to 40 minutes. Both the spent brine from regeneration and from the rinse must be disposed of carefully since the calcium, magnesium, and sodium salts are corrosive and toxic to the environment. Spent brine is sometimes discharged in sewers or into streams at very high dilutions. Alternatively, the brine can be disposed of in a landfill.

Safety Precautions

Operators should observe safety procedures while handling both hydrated lime and quicklime. Lime dust can be harmful when it comes in contact with the eyes, nose, or mouth, and skin contact can cause burns. As a result, operators should wear goggles and dust masks as well as protective clothing. Both hydrated lime and quicklime can deteriorate in quality over time while in storage. In addition, storing quicklime can cause safety problems. If quicklime comes in contact with water, it begins to slake, a process which produces a great deal of heat and can cause explosions when uncontrolled. Quicklime should never be stored with alum since the quicklime will absorb water away from the alum and cause an explosion.

Soda ash (Na_2CO_3) comes in only one form and does not require any treatment before it is added to the water. Safety issues resemble those for lime handling. Soda ash dust irritates the eyes and mucous membranes of the nose, so the operator should wear protective clothing, goggles, and a dust mask. In addition, areas in which soda ash is used should be equipped with a ventilation system to deal with the dust.

Caustic soda (NaOH), also known as sodium hydroxide, can replace soda ash and some of the lime in the treatment process. The treatment process using caustic soda follows the same steps as that of lime-soda ash softening. First, carbon dioxide reacts with the caustic soda to make sodium carbonate and water. The remaining caustic soda can react with calcium bicarbonate and magnesium bicarbonate. Caustic soda has the advantages of stability in storage, lower sludge formation, and easy handling. However, safety issues still apply. Caustic soda is dangerous to the operator and can cause severe burns to the skin. As a result, rubber gloves, dusk

masks, goggles, and a rubber apron should be worn while handling the chemical.

Alkalinity and Hardness Relationship

I guess you are wondering why we are learning about alkalinity and hardness when the lesson is about softening. That's because alkalinity and hardness play a large role in how well a plant can soften the water. Let's dive in to their relationship to softening.

The reason you balance alkalinity, pH, then calcium hardness is that adjusting alkalinity often affects pH. Adjusting both alkalinity and pH often affects your calcium hardness, as adding sodium bicarbonate (baking soda) and sodium carbonate (soda ash) can increase the hardness. Alkalinity often reaches 200-300 mg/L and hardness can be much higher. In natural water systems calcium carbonate is usually present and responsible for different characteristics of the water. Both hardness and alkalinity are expressed as a concentration of calcium carbonate

(CaCO₃) for convenience of reporting a single number to represent multiple chemicals and for ease in calculating a solution's carbonate and noncarbonate hardness. Hardness is the sum of the multivalent metal ions in solution, whereas alkalinity is a measure of the solution's ability to neutralize acids (sum of hydroxide, carbonate and bicarbonates).

Alkalinity and hardness are related through common ions formed in aquatic systems. As a result, the carbonate fraction of hardness is chemically equivalent to the bicarbonate of alkalinity present in water in areas where the water interacts with limestone. Any hardness greater than the alkalinity represents noncarbonate hardness. Alkalinity is important because it buffers the pH of water within the system. Without this buffering capacity, small additions of acids or bases would result in significant changes of pH, which could be detrimental for aquatic life. Hardness can also affect the utility of water for industrial purposes. Hard water is often the source of scale formed in hot water heaters and industrial systems where water is heated. This scale results from the precipitation of calcium carbonate, which becomes less water soluble as the temperature increases. In these situations, water is usually softened by precipitating the calcium carbonate or by using ion exchange softening methods.

Total hardness, mg/L as CaCO₃ = Calcium hardness, mg/L as CaCO₃ + Magnesium hardness, mg/L as CaCO₃

IF alkalinity > Total hardness:

Carbonate hardness, mg/L as CaCO₃ = Total hardness, mg/L as CaCO₃ and

Noncarbonate hardness, mg/L as CaCO₃ = 0

IF alkalinity < Total hardness:

Carbonate hardness, mg/L as CaCO₃ = Alkalinity, mg/L as CaCO₃ and

Noncarbonate hardness, mg/L as CaCO₃ = Total hardness removed, mg/L as CaCO₃ - Alkalinity removed, mg/L as CaCO₃

[Part 2: Softening Calculations](#)