

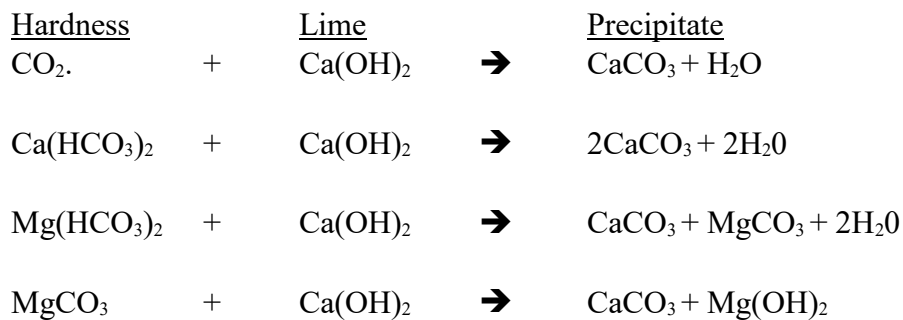


Lime Softening

Chemical precipitation is one of the more common methods used to soften water. Chemicals normally used are lime (calcium hydroxide, $\text{Ca}[\text{OH}]_2$) and soda ash (sodium carbonate, Na_2CO_3). Lime is used to remove chemicals that cause carbonate hardness. Soda ash is used to remove chemicals that cause non-carbonate hardness.

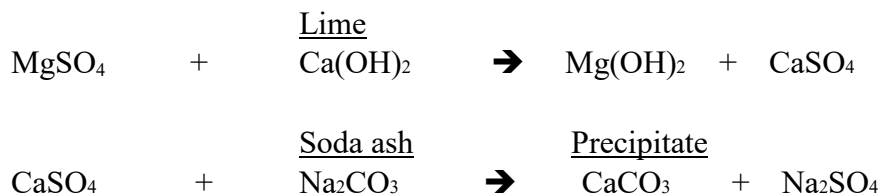
When lime and soda ash are added, hardness-causing minerals form nearly insoluble precipitates. Calcium hardness is precipitated as calcium carbonate (CaCO_3). Magnesium hardness is precipitated as magnesium hydroxide ($\text{Mg}[\text{OH}]_2$). These precipitates are then removed by conventional processes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

LIME ADDITION



CO_2 does not contribute to the hardness, but it reacts with the lime, and therefore uses up some lime before the lime can start removing the hardness.

LIME AND SODA ASH ADDITION



CO_2 = carbon dioxide, $\text{Ca}(\text{OH})_2$ = calcium hydroxide or hydrated lime, CaCO_3 = calcium carbonate, $\text{Ca}(\text{HCO}_3)_2$ = calcium bicarbonate, $\text{Mg}(\text{HCO}_3)_2$ = magnesium bicarbonate, MgCO_3 = magnesium carbonate, $\text{Mg}(\text{OH})_2$ = magnesium hydroxide, MgSO_4 = magnesium sulfate, CaSO_4 = calcium sulfate, H_2O = water, Na_2CO_3 = sodium carbonate or soda ash



For each molecule of calcium bicarbonate hardness removed, one molecule of lime is used. For each molecule of magnesium bicarbonate hardness removed, two molecules of lime are used. For each molecule of non-carbonate calcium hardness removed, one molecule of soda ash is used. For each molecule of non-carbonate magnesium hardness removed one molecule of lime plus one molecule of soda ash is used.

CONVENTIONAL LIME-SODA ASH TREATMENT

When water has minimal magnesium hardness, only calcium needs to be removed. Only enough lime and soda ash are added to water to raise pH to between 10.3 and 10.6, and calcium hardness will be removed from the water (but minimal magnesium hardness will be removed).

EXCESS LIME TREATMENT

When magnesium hardness is more than about 40 milligrams per liter (mg/l) as CaCO_3 , magnesium hydroxide scale deposits in household hot-water heaters operated at normal temperatures of 140 to 150° F. To reduce magnesium hardness, more lime must be added to the water. Extra lime will raise pH above 10.6 to help magnesium hydroxide precipitate out of the water.

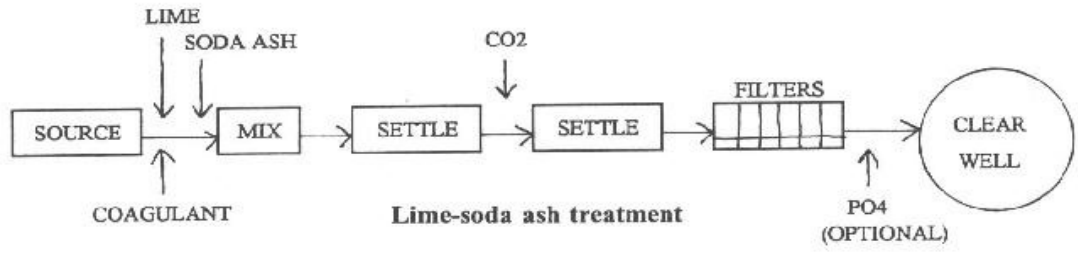
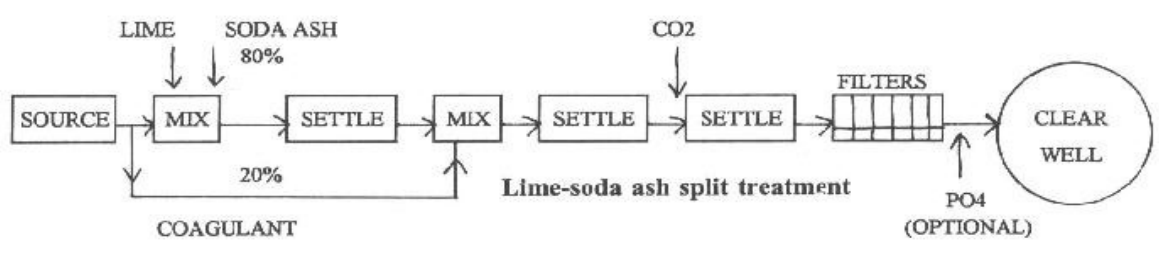
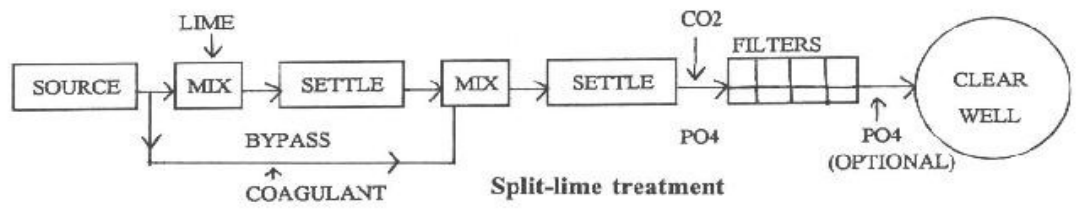
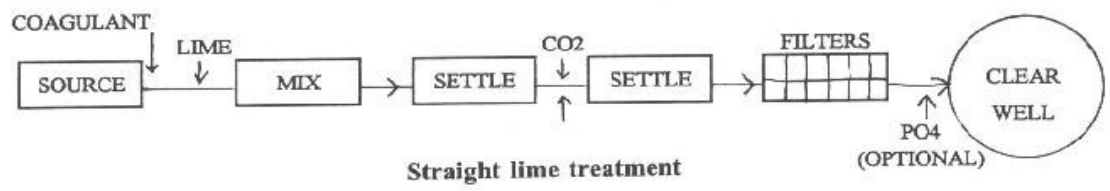
SPLIT TREATMENT

When water contains high amounts of magnesium hardness, split treatment may be used. Approximately 80 percent of the water is treated with excess lime to remove magnesium at a pH above 11, after which it is blended with 20 percent of the source water. Split treatment can reduce the amount of carbon dioxide required to re-carbonate the water as well as offer a savings in lime feed.

Since the fraction of the water that is treated contains an excess lime dose, magnesium is almost completely removed from this portion. When this water is mixed with the water that does not undergo softening, the carbon dioxide and bicarbonate in that water re-carbonates the final blend. Split treatment reduces the amount of chemical needed to remove hardness from water by 20 to 25 percent (a significant savings).

DESIGN CONSIDERATIONS

In lime soda-ash softening plants, the softening process may be carried out by a sequence of rapid mix, flocculation, and sedimentation or in a solids contactor. In the solids contactor the rapid mix, flocculation, and sedimentation occur in a single unit. The process begins with the mixing of the chemicals into the water, followed by violent agitation, termed rapid mixing. This allows chemicals to react with, and precipitate calcium or magnesium hardness in the water.



Flocculation allows flocs to contact other flocs and grow large enough to settle in the sedimentation stage. Water is mixed gently with a small amount of energy. Most flocculators are compartmentalized, allowing for a tapered mix, so less energy must be applied as the flocs grow in size.

Detention time in the flocculator is important to allow particles to come in contact with each other. The minimum time recommended is 30 minutes for conventional water softening.

Sludge returned to the head of the flocculator reduces the amount of chemical needed and provides seed flocs for the precipitation. The estimated return sludge is 10 to 25 percent of the source water.

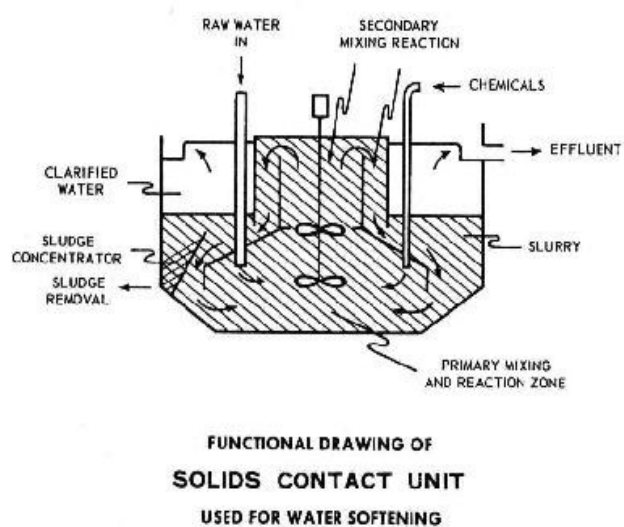
Sedimentation follows flocculation. Settling rates for these tanks are a function of particle size and density. Detention times in the settling basins range from 1.5 hours to 3.0 hours, and they can be rectangular, square, or circular (some designs incorporate inclined tube settlers).

Sedimentation can also occur in the solids-contact unit, in which the water is mixed with chemicals and flocculated in the center of the basin, then forced down and trapped for removal in a sludge blanket in the bottom of the tank.

Sludge Removal

Residue created from lime-soda ash softening is normally very high in calcium carbonate or a mixture of calcium carbonate, and magnesium hydroxide. Calcium carbonate sludges are normally dense, stable inert, and dewater readily. Solids content in the sludge range from 5 to 30 total solids with a pH greater than 10.5.

Lime-soda ash sludges may be treated with lagooning, vacuum filtration, centrifugation, pressure filtration, recalcination, or land application. The most common method is storage of sludge in lagoons and application to farmland or landfills disposal.



Calculations

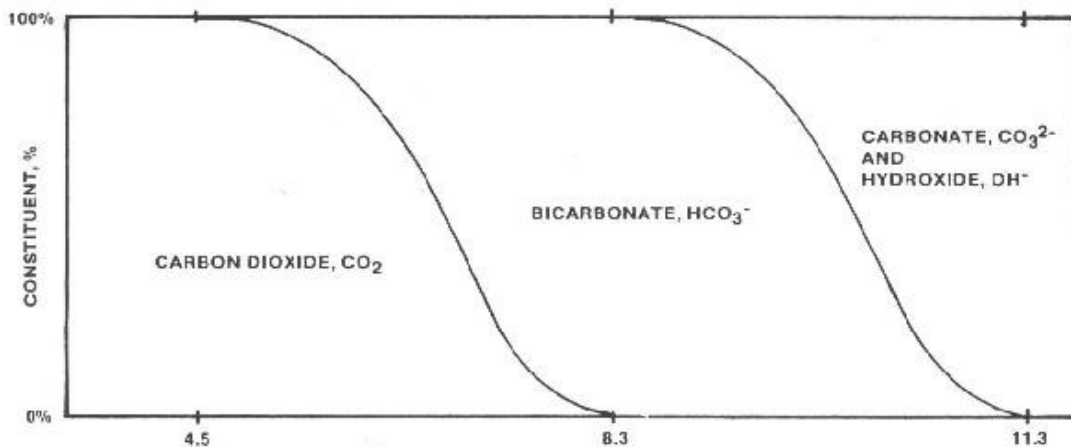
There are two methods for calculating lime and soda ash dosages: conventional dosage method and conversion factor method. The conventional method, although much longer, is helpful in understanding the chemical and mathematical relationships involved in softening. The conversion factor method is simpler, quicker, and more practical for daily operations.

In both calculation methods, lime and soda ash dosages depends on carbonate and non-carbonate hardness in the water. Lime is used to remove carbonate hardness, and both lime and soda ash are used to remove non-carbonate hardness. If total hardness is less than or equal to total alkalinity, there is no non-carbonate hardness (only carbonate hardness). If total hardness is greater than total alkalinity, non-carbonate hardness equals the difference between total hardness and total alkalinity (and carbonate hardness equals total alkalinity).

If total hardness is equal to or less than total alkalinity, then:

Lime Dosage = the carbon dioxide concentration [CO₂] + the total hardness concentration [Total Hardness] + the magnesium concentration [Mg] + [Excess]

Optimum chemical dosages can be evaluated with a jar test.



Relationship between pH and alkalinity (HCO₃⁻, CO₃²⁻ and OH⁻)

Alkalinity (mg/l as CaCO₃) is the capacity of water to neutralize acids. This is determined by the content of carbonate, bicarbonate and hydroxide. Alkalinity is a measure of how much acid can be added to a liquid without causing any significant change in pH.

When pH is less than 8.3, all alkalinity is in the bicarbonate form and is commonly referred to as natural alkalinity. When pH is above 8.3, alkalinity may consist of bicarbonate, carbonate, and hydroxide. As pH increases the alkalinity progressively shifts to carbonate and hydroxide forms. Total alkalinity is the sum of bicarbonate, carbonate, and hydroxide alkalinity. Various chemicals effect water differently:

Lowers Alkalinity:

- Aluminum sulfate
- Carbon dioxide
- Chlorine gas
- Ferric Chloride
- Ferric Sulfate
- Sulfuric acid

Increases Alkalinity:

- Calcium hypochlorite
- Caustic soda
- Hydrate lime
- Soda ash
- Sodium Aluminate



The following table gives molecular weights for common chemicals:

Quicklime (CaO).....	56
Hydrate Lime (CaOH).....	74
Magnesium (Mg).....	24.3
Carbon Dioxide (CO ₂).....	44
Magnesium Hydroxide (Mg(OH) ₂)... 58.3	
Soda Ash (NaCO ₃).....	106
Alkalinity (as CaCO ₃).....	100
Hardness (as CaCO ₃).....	100

Quicklime dosage can be calculated with the following formula:

$$\text{Quicklime (CaO) mg/l} = \frac{(\text{A} + \text{B} + \text{C} + \text{D}) + \% \text{ EXCESS}}{\text{purity of lime as a decimal}}$$

A = Carbon Dioxide in source water

$$\begin{aligned} &= \text{mg/l CO}_2 \times \left(\frac{\text{CaO}}{\text{CO}_2}\right) \\ &= \text{mg/l CO}_2 \times 56/44 \\ &= \text{mg/l CO}_2 \times 1.27 \end{aligned}$$

B = Bicarbonate alkalinity removed

$$\begin{aligned} &= \text{mg/l as CaCO}_3 \times \left(\frac{\text{CaO}}{\text{CaCO}_3}\right) \\ &= \text{mg/l} \times 56/100 \\ &= \text{mg/l alkalinity} \times .56 \end{aligned}$$

C = Hydroxide alkalinity in softener effluent

$$\begin{aligned} &= \text{mg/l hydroxide alkalinity} \times \left(\frac{\text{CaO}}{\text{CaCO}_3}\right) \\ &= \text{mg/l hydroxide alkalinity} \times 56/100 \\ &= \text{mg/l hydroxide alkalinity} \times .56 \end{aligned}$$

D = Magnesium removed in softening

$$\begin{aligned} &= \text{Mg/l as Mg}^{2+} \times \left(\frac{\text{CaO}}{\text{Mg(OH)}_2}\right) \\ &= \text{Mg/l as Mg}^{2+} \times 56/24.3 \\ &= \text{Mg/l as Mg}^{2+} \times 2.30 \end{aligned}$$

If hydrated lime (CaOH) is used in place of quicklime, the molecular weight of quicklime of 56 should be replaced with the weight of hydrated lime (74).



When treating water that contains non-carbonate hardness, soda ash is required. The amount of soda ash can be estimated by using the following formula:

$$\begin{aligned}\text{Soda Ash (NaCO}_3\text{) mg/l} &= \text{mg/l Non Carbonate Hardness as CaCO}_3 \times \text{Na}^2\text{CO}_3/\text{CaCO}_3 \\ &= \text{mg/l Non-Carbonate Hardness as CaCO}_3 \times 106/100 \\ &= \text{mg/l Non-Carbonate Hardness as CaCO}_3 \times 1.06\end{aligned}$$

After softening, pH of the water is generally above 10. If left at this pH, water will plate filter sand and cause problems in the distribution system. Carbon dioxide (through re-carbonation), is added to lower the pH. The amount of carbon dioxide (CO₂) required can be estimated:

$$\begin{aligned}\text{Total CO}_2\text{ (mg/l)} &= \text{Ca(OH)}_2\text{ (mg/l)} \times \frac{\text{CO}_2}{\text{Ca(OH)}_2} + \text{Mg(OH)}_2\text{ residual} \times \frac{\text{CO}_2}{\text{Mg(OH)}_2} \\ \text{Total CO}_2 &= \text{Ca(OH)}_2\text{ mg/l} \times 44/74 + \text{Mg(OH)}_2\text{ residual} \times 44/58.3 \\ \text{Total CO}_2 &= \text{Ca(OH)}_2\text{ mg/l} \times .59 + \text{Mg(OH)}_2\text{ residual} \times .75\end{aligned}$$

Conversion Method

Equivalent weight conversions required in the conventional method have been combined into single factors shown in the table below. These factors, multiplied by the concentration of the corresponding material, will give the lime or soda ash dosage needed to remove material in units of milligrams per liter or pounds per million gallons. The total dosage is the sum of all material removed from the water, such as the carbon dioxide, bicarbonate alkalinity, and the magnesium, plus the amount of excess that is required to reduce the hardness in the water. The total soda-ash dosage is found in the same manner by finding the sum of the amounts needed to remove the non-carbonate material from the water. An additional calculation is needed to adjust for the purity of the lime or soda-ash used.



	Converting to:			
	Lime (CaO)		Soda Ash	
	mg/l	lb/MG	mg/l	lb/MG
Carbon Dioxide (mg/l as CaCO ₃)	1.27	10.63	---	---
Bicarbonate Alkalinity (mg/l as CaCO ₃)	0.56	4.67	---	---
Magnesium as Mg (mg/l as CaCO ₃)	2.31	19.24	---	---
Excess as CaCO ₃ (mg/l as CaCO ₃)	0.56	4.67	---	---
Non-carbonate Hardness (mg/l as CaCO ₃)	---	---	1.06	8.83
Excess Soda ash (mg/l as CaCO ₃)	---	---	1.06	8.83

Example:

The following test results were provided by the laboratory:

CO ₂ concentration	25 mg/l as CO ₂
HCO ₃ (bicarbonate) concentration	205 mg/l as CaCO ₃
Mg (magnesium) concentration	9 mg/l as Mg
non-carbonate hardness concentration	95 mg/l as CaCO ₃

Assuming no excess lime is added, find correct dosages for lime (containing 90% pure CaO) and soda ash (containing 99% pure Na₂CO₃) required to remove all hardness.

CO ₂	25 mg/l x 1.27	=	31.75 mg/l as CaO
HCO ₃	205 mg/l x 0.56	=	114.80 mg/l as CaO
Mg	9 mg/l x 2.31	=	20.79 mg/l as CaO
TOTAL		=	167.34 mg/l as CaO

Then adjust lime dosage for purity:

$$\text{Actual Lime Dose} = \frac{167.34 \text{ mg/l}}{.90} = 185.93 \text{ mg/l}$$

Next, find soda ash dosage:

$$\text{Soda Ash Dosage} = 95 \text{ mg/l} \times 1.0 = 100.7 \text{ mg/l as Na}_2\text{CO}_3$$

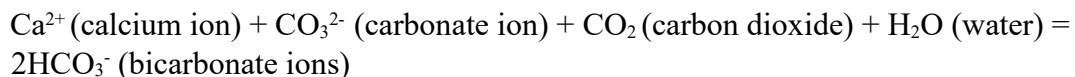
$$\text{Actual Dosage} = \frac{100.7 \text{ mg/l}}{.99} = 101.7 \text{ mg/l as Na}_2\text{CO}_3$$



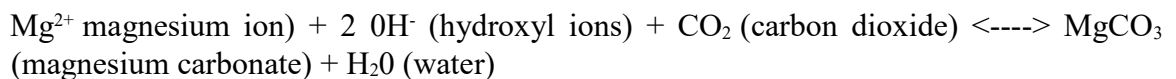
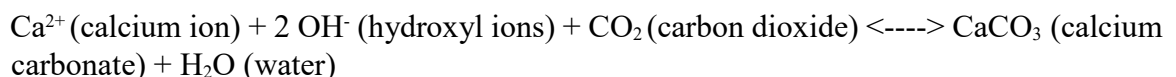
Recarbonation

After adding lime and/or soda ash, treated water will generally have a pH greater than 10. It is necessary to lower the pH to stabilize the water and prevent deposition of carbonate scale on filter sand and distribution piping. Recarbonation is the most common process used to reduce pH. This procedure adds carbon dioxide to water after softening. Generally, enough carbon dioxide is added to reduce the pH of the water to less than 8.7. The amount of carbon dioxide added is determined using a saturation index. The Langelier Index is the most common stabilization index used, but some plants instead use the Rizner Index, (reciprocal of the Langelier Index). The Langelier Index is expressed as pH of stabilization (pHs) minus actual pH measured (pHs - pH). When the Langelier Index is positive, pipes tend to become coated with scale. When it is negative, the water tends to be corrosive.

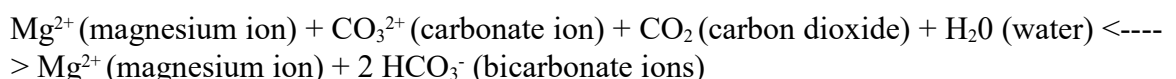
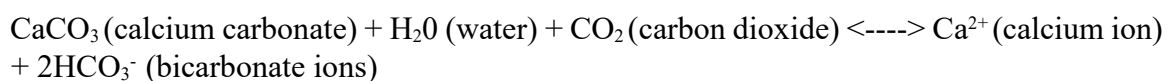
When low magnesium water is softened, no excess lime needs to be added. After softening, water becomes supersaturated with calcium carbonate and has a pH between 10.0 and 10.6. When carbon dioxide is added, the excess calcium carbonate is converted back to permanent hardness or calcium bicarbonate by the following formula:



When high magnesium water is softened, excess lime needs to be added to raise the pH above 11, and magnesium hydroxide precipitates out. After treatment, enough carbon dioxide must be added to neutralize the excess hydroxide ions, as well as convert carbonate ions to bicarbonate ions. The first stage of this reaction reduces the pH to between 10.0 and 10.5. In this range, calcium carbonate is formed and magnesium hydroxide that did not precipitate, or did not settle out, is converted to magnesium carbonate.



Additional carbon dioxide needs to be added to lower the pH to between 8.4 and 8.6. The previously formed calcium carbonate re-dissolves and carbonate ions are converted to bicarbonate ions as shown below:





For treatment of low magnesium water (where excess-lime addition is not required) single-stage recarbonation is used. The water is mixed with lime or soda ash in the rapid-mix basin, resulting in a pH of 10.2 to 10.5. If non-carbonate hardness removal is required, soda ash will also be added at this step. After rapid mixing, the resulting slurry is mixed gently for a period of 30 to 50 minutes to allow the solids to flocculate. After flocculation, the water is allowed to flow into a sedimentation basin where the solids will be removed by sedimentation. Following sedimentation the clear water flows to the recarbonation basin where carbon dioxide is added to reduce the pH to between 8.3 and 8.6. Any particles remaining in suspension after recarbonation are removed by filtration.

Two-Stage Softening

Two-stage softening is sometimes used for treatment of high magnesium water (where excess lime is required). Excess lime is added in the first stage to raise pH to 11.0 or higher for magnesium removal. Following first stage treatment, carbon dioxide is added to reduce the pH to between 10.0 and 10.5, the best value for removal of calcium carbonate. If non-carbonate hardness removal is needed, soda ash will be added at this point. After second stage treatment, the water flows to a secondary recarbonation tank, where pH is reduced to between 8.3 and 8.6.

Single-Stage Softening

Single-stage recarbonation is the one most commonly practiced (Because of the high capital cost for building this type of two-stage treatment train). There are some benefits to using the twostage method, including reduced operating cost since less carbon dioxide is needed. Better finished water quality is usually obtained through the two-stage process.