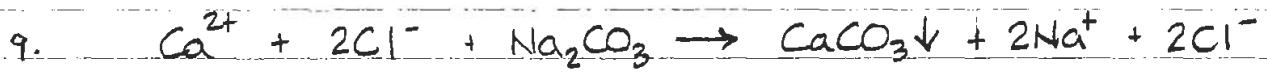
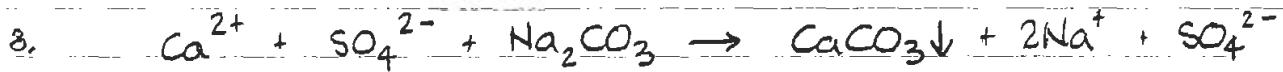


## Lecture 9 - Lime-soda ash softening, Part 2

For waters with non-carbonate hardness, single-stage softening is insufficient. Leftover hardness is removed by addition of soda ash ( $\text{Na}_2\text{CO}_3$ )



Practical limits of lime-soda ash softening are dictated by solubility of precipitates:  $\text{CaCO}_3 \rightleftharpoons \text{Mg}(\text{OH})_2$

Ca = 30 mg/L as  $\text{CaCO}_3$

Mg = 10 mg/L as  $\text{CaCO}_3$

Total hardness = 40 mg/L as  $\text{CaCO}_3$

In practice, residual hardness = 50 to 80 mg/L

This water has high pH and needs to be recarbonated

Lime-soda ash treatment is usually treated by "two-stage softening" also called "excess-lime treatment" and "split recarbonation treatment"

See Lecture 8, page 10

Split treatment is similar, except only part of water is treated with lime. Other part by-passes lime treatment and gets soda-ash treatment along with lime-treated water

The  $\text{CO}_2$  in untreated water neutralizes high pH in lime-treated water and recarb. is not needed

Water split is computed such that enough Mg is removed in lime-treated water to meet target Mg level in combined finished water

Computing chemical doses for lime soda ash softening - Example 11.4  
from Viessman and Hammer, pg. 445 - pg 3 and 4

$$\text{CO}_2 = 8.8 \text{ mg/L as CO}_2$$

$$\text{Ca}^{2+} = 70 \text{ mg/L}$$

$$\text{Mg}^{2+} = 9.7 \text{ mg/L}$$

$$\text{Na}^+ = 6.9 \text{ mg/L}$$

$$\text{Alk} = 115 \text{ mg/L as CaCO}_3$$

$$\text{SO}_4^{2-} = 96 \text{ mg/L}$$

$$\text{Cl}^- = 10.6 \text{ mg/L}$$

Easiest method is to construct a table that converts all concentrations to equivalent concentrations, and then to equivalents of  $\text{CaCO}_3$

Also use chart from VH Fig 11.8, pg 446

	conc (mg/L)	MW (gm/mole)	equiv (eq/molecule)	eq wt (gm/mole-eq)	meg/L	mg/L as $\text{CaCO}_3$
$\text{CO}_2$	8.8	44.0	2	22.0	0.4	20.0
$\text{Ca}^{2+}$	70	40.0	2	20.0	3.5	175.
$\text{Mg}^{2+}$	9.7	24.4	2	12.2	0.80	39.8
$\text{Na}^+$	6.9	23.0	1	23.0	0.30	15.0
					4.6	229.8
Alk	115	100	2	50.0	2.3	115.0
$\text{SO}_4^{2-}$	96	96.0	2	48.0	2.0	100.0
$\text{Cl}^-$	10.6	35.5	1	35.5	0.30	14.9
					4.6	229.9

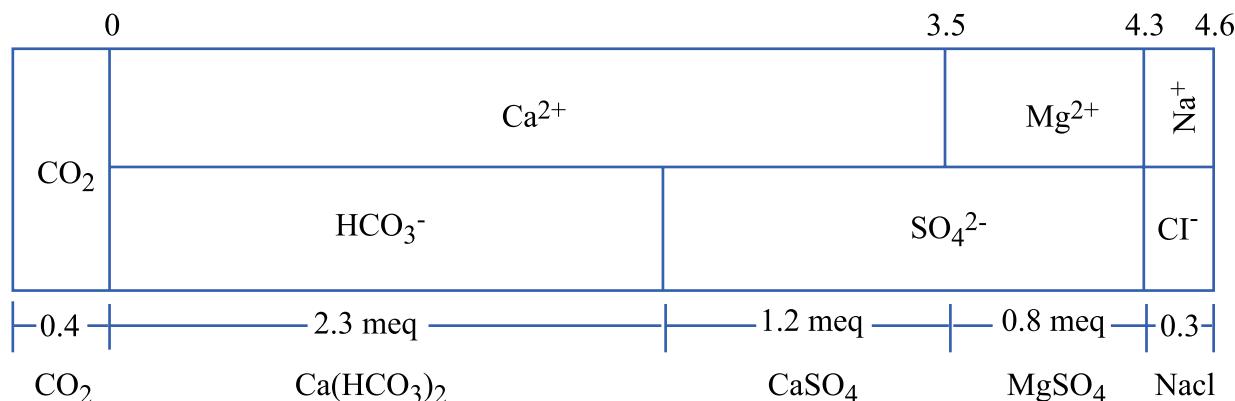
$$\text{Total hardness} = \text{Ca}^{2+} + \text{Mg}^{2+} = 175 + 39.8 = 214.8 \text{ mg/L as } \text{CaCO}_3$$

$$\text{Carbonate hardness} = [\text{Alk}] = 115 \text{ mg/L as } \text{CaCO}_3$$

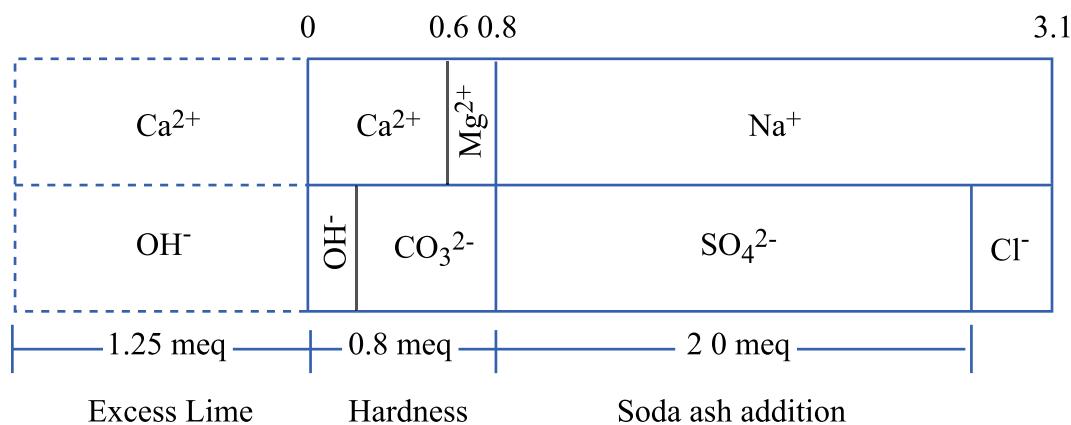
$$\text{Noncarbonate hardness} = \text{TH} - \text{CH} = 99.8 \text{ mg/L as } \text{CaCO}_3$$

$$\text{Mg noncarbonate hardness} = 39.8 \text{ mg/L as } \text{CaCO}_3$$

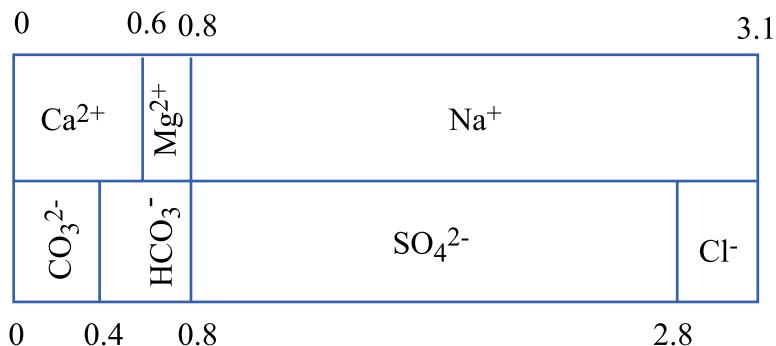
Milliequivalent Bar Graph for Example 11.4



(A) Bar graph & hypothetical chemical combinations in the raw water



(B) Bar graph of the water after lime & soda ash additions & settling but before recarbonation.



(C) Bar Graph of the water after two-stage recarbonation & final filtration

Figure by MIT OCW.

Adapted from: Viessman, W., Jr., and M. J. Hammer. *Water Supply and Pollution Control*. 7th ed. Upper Saddle River, NJ: Pearson Education, Inc., 2005, p. 446.

**Before treatment:**

0.4	0	Ca <sup>2+</sup>	3.5	4.3	4.6
CO <sub>2</sub>		HCO <sub>3</sub> <sup>-</sup>		Mg <sup>2+</sup>	Na <sup>+</sup>
			2.3 meq Ca(HCO <sub>3</sub> ) <sub>2</sub> Carbonate hardness	1.2 meq CaSO <sub>4</sub> Non-carb. hardness	0.8 meq MgSO <sub>4</sub> NCH 0.3 NaCl

**After treatment with lime Ca(OH)<sub>2</sub> and intermediate reaction to remove carbonate hardness:**  
**(chemical equations 1, 2, & 3)**

1.25	0	1.2	2.0	2.3
Ca <sup>2+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	
OH <sup>-</sup>		SO <sub>4</sub> <sup>2-</sup>		Cl <sup>-</sup>

1.25 meq excess lime	2.0 meq NCH	0.3 NaCl
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**After treatment with lime and intermediate reaction to remove noncarbonate Mg hardness:**  
**(chemical equations 4 & 5)**

1.25	0	1.8	2.0	2.3
Ca <sup>2+</sup>	Ca <sup>2+</sup>	Mg	Na <sup>+</sup>	
OH <sup>-</sup>		SO <sub>4</sub> <sup>2-</sup>		Cl <sup>-</sup>

1.25 meq excess lime	2.0 meq NCH	0.3 NaCl
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**After treatment with soda ash Na<sub>2</sub>CO<sub>3</sub>:**  
**(chemical equations 8 & 9)**

1.25	0	0.6	0.8	2.8	3.1
Ca <sup>2+</sup>	Ca <sup>2+</sup>	Mg	Na <sup>+</sup>		
OH <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>		SO <sub>4</sub> <sup>2-</sup>		Cl <sup>-</sup>

1.25 meq excess lime	residual 0.8 meq hardness	2.0 meq added soda ash	0.3 NaCl
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**After recarbonation:**  
**(chemical equations 6 & 7)**

0	0.6	0.8	2.8	3.1
Ca <sup>2+</sup>	Mg	Na <sup>+</sup>		
HCO <sub>3</sub> <sup>-</sup>		SO <sub>4</sub> <sup>2-</sup>		Cl <sup>-</sup>

residual 0.8 meq hardness	2.0 meq added soda ash	0.3 NaCl
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Lime required

For  $\text{CO}_2$  - 20.0 mg/L as  $\text{CaCO}_3$

For carbonate hardness - 115.0

For Mg noncarbonate hardness - 39.8

174.8 mg/L as  $\text{CaCO}_3$   
(3.5 meq)

Convert from  $\text{CaCO}_3$  to  $\text{CaO}$

$$\frac{\text{CaO}}{\text{CaCO}_3} = \frac{40+16}{40+12+3\times16} = \frac{56}{100} = \frac{28}{50}$$

$$174.8 \text{ mg/L as } \text{CaCO}_3 = 97.9 \text{ mg/L as } \text{CaO}$$

Include excess lime of 35 mg/L

$$\text{Req'd lime} = 133 \text{ mg/L}$$

Soda Ash for noncarbonate hardness

$$\text{NCH} = 99.8 \text{ mg/L as } \text{CaCO}_3 \quad (2.0 \text{ meq})$$

(recall that Mg NCH was treated with lime  
but simply swaps Ca for Mg, so still  
needs treatment with soda ash)

$$\text{Req'd Soda Ash} = 99.8 \text{ mg/L as } \text{CaCO}_3$$

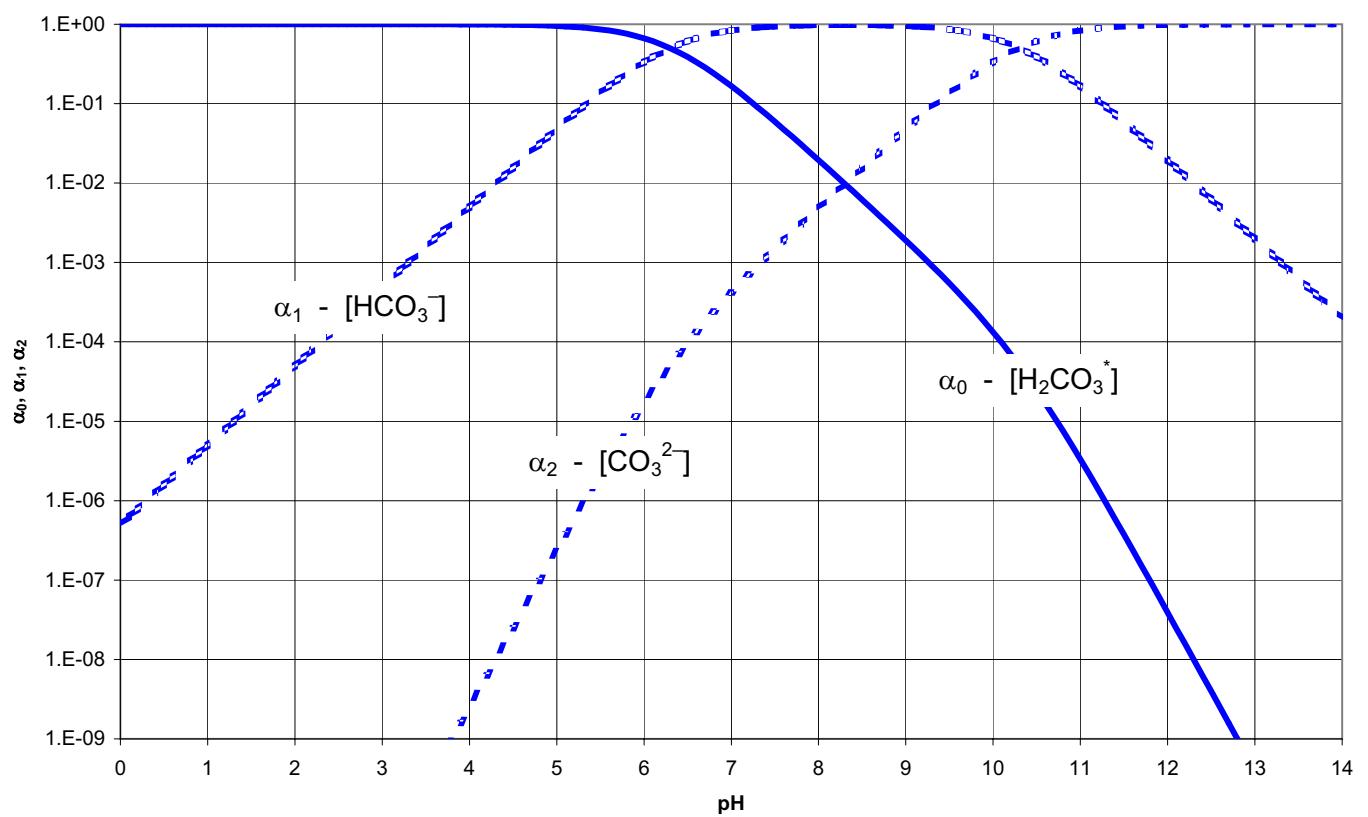
Convert to  $\text{Na}_2\text{CO}_3$ :

$$\frac{\text{Na}_2\text{CO}_3}{\text{Ca CO}_3} = \frac{2\times23+12+3\times16}{40+12+3\times16} = 1.06$$

$$\text{Req'd soda ash} = 1.06 \times 99.8 = 106 \text{ mg/L}$$

Note that pg 14 shows  $\text{HCO}_3^-$  but will actually be an equilibrium between  $\text{CO}_2$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  depending on pH per pg 6

### Carbonate system equilibrium



Summary of chemical dosage calculations required for lime & lime-soda ash softening\*

PROCESS	REQUIRED CHEMICAL DOSAGE CALCULATIONS
<b>Single-Stage Lime:</b> For waters with high calcium, low magnesium, & carbonate hardness	<p><b>Lime addition for softening:</b>  <math>\text{CaO} = \{\text{carbonic acid concentration}\} + \{\text{calcium carbonate hardness}\}</math></p> <p><b>Soda ash addition for softening:</b>  <math>\text{Na}_2\text{CO}_3 = \text{none}</math></p> <p><b>Carbon dioxide for pH adjustment after softening:</b></p> $\text{CO}_2 = \left\{ \begin{array}{l} \text{estimated carbonate} \\ \text{alkalinity of softened water} \end{array} \right\} = \left\{ \begin{array}{l} \text{source water} \\ \text{alkalinity} \end{array} \right\} - \left\{ \begin{array}{l} \text{source water} \\ \text{calcium hardness} \end{array} \right\}$ $+ \left\{ \begin{array}{l} \text{estimated residual} \\ \text{calcium hardness} \\ \text{of softened water} \end{array} \right\}$
<b>Excess Lime:</b> For waters with high calcium, high magnesium, and carbonate hardness; process may be one or two stages	<p><b>Lime addition for softening:</b>  <math>\text{CaO} = \left\{ \begin{array}{l} \text{carbonic acid} \\ \text{concentration} \end{array} \right\} + \left\{ \begin{array}{l} \text{total alkalinity} \end{array} \right\} + \left\{ \begin{array}{l} \text{magnesium} \\ \text{hardness} \end{array} \right\} + \left\{ \begin{array}{l} \text{excess lime} \\ \text{dose} \end{array} \right\}</math></p> <p><b>Soda ash addition for softening:</b>  <math>\text{Na}_2\text{CO}_3 = \text{none}</math></p> <p><b>Carbon dioxide for pH adjustment after softening:</b></p> $\text{CO}_2 = \left\{ \begin{array}{l} \text{source water} \\ \text{alkalinity} \end{array} \right\} - \left\{ \begin{array}{l} \text{source water} \\ \text{total hardness} \end{array} \right\} - \left\{ \begin{array}{l} \text{excess lime} \\ \text{dose} \end{array} \right\} + \left\{ \begin{array}{l} \text{estimated residual} \\ \text{calcium hardness} \\ \text{of softened water} \end{array} \right\}$ $+ 2 \left\{ \begin{array}{l} \text{excess lime} \\ \text{dose} \end{array} \right\} + \left\{ \begin{array}{l} \text{estimated residual} \\ \text{magnesium hardness} \\ \text{of softened water} \end{array} \right\}$
<b>Single-Stage Lime Soda Ash:</b> For water with high calcium, low magnesium, & carbonate and noncarbonate hardness	<p><b>Lime addition for softening:</b>  <math>\text{CaO} = \{\text{carbonic acid concentration}\} + \{\text{calcium carbonate hardness}\}</math></p> <p><b>Soda ash addition for softening:</b>  <math>\text{Na}_2\text{CO}_3 = \{\text{calcium noncarbonate hardness}\} \text{ and/or } \{\text{magnesium noncarbonate hardness}\}</math></p> <p><b>Carbon dioxide for pH adjustment after softening:</b></p> $\text{CO}_2 = \left\{ \begin{array}{l} \text{source water} \\ \text{alkalinity} \end{array} \right\} + \left\{ \begin{array}{l} \text{soda ash} \\ \text{dose} \end{array} \right\} - \left\{ \begin{array}{l} \text{source water} \\ \text{calcium hardness} \end{array} \right\} + \left\{ \begin{array}{l} \text{estimated residual} \\ \text{calcium hardness} \\ \text{of softened water} \end{array} \right\}$
<b>Excess Lime - Soda Ash:</b> For waters with high calcium, high magnesium, and carbonate and noncarbonate hardness; process may be one or two stages	<p><b>Lime addition for softening:</b>  <math>\text{CaO} = \left\{ \begin{array}{l} \text{carbonic acid} \\ \text{concentration} \end{array} \right\} + \left\{ \begin{array}{l} \text{calcium carbonate} \\ \text{concentration} \end{array} \right\} + 2 \left\{ \begin{array}{l} \text{magnesium} \\ \text{carbonate} \\ \text{hardness} \end{array} \right\} + \left\{ \begin{array}{l} \text{magnesium} \\ \text{noncarbonate} \\ \text{hardness} \end{array} \right\}</math> <math>+ \left\{ \begin{array}{l} \text{excess lime} \\ \text{requirement} \end{array} \right\}</math></p> <p><b>Soda ash addition for softening:</b>  <math>\text{Na}_2\text{CO}_3 = \left\{ \begin{array}{l} \text{calcium} \\ \text{noncarbonate} \\ \text{hardness} \end{array} \right\} + \left\{ \begin{array}{l} \text{magnesium} \\ \text{noncarbonate} \\ \text{hardness} \end{array} \right\}</math></p> <p><b>Carbon dioxide for pH adjustment after softening:</b></p> $\text{CO}_2, \text{ first stage} = \left\{ \begin{array}{l} \text{estimated hydroxide} \\ \text{alkalinity of softened water} \end{array} \right\} - \left\{ \begin{array}{l} \text{excess lime} \\ \text{dose} \end{array} \right\} + \left\{ \begin{array}{l} \text{estimated residual} \\ \text{magnesium hardness} \\ \text{of softened water} \end{array} \right\}$ $\text{CO}_2, \text{ second stage} = \left\{ \begin{array}{l} \text{estimated hydroxide} \\ \text{alkalinity of softened water} \end{array} \right\} = \left\{ \begin{array}{l} \text{source water} \\ \text{alkalinity} \end{array} \right\} + \left\{ \begin{array}{l} \text{soda ash} \\ \text{dose} \end{array} \right\} - \left\{ \begin{array}{l} \text{source} \\ \text{water total} \\ \text{hardness} \end{array} \right\}$ $+ \left\{ \begin{array}{l} \text{estimated residual} \\ \text{hardness of softened water} \end{array} \right\}$

\* All quantities are expressed as mg/L as  $\text{CaCO}_3$

Figure by MIT OCW.

Adapted from: MWH, J. C. Crittenden, R. R. Trussell, D. W. Hand, K. J. Howe, and G. Tchobanoglous. *Water Treatment: Principles and Design*. 2nd ed. Hoboken, NJ: John Wiley & Sons, 2005, pp. 1610-1611.