Lecture 8 - Chemical Removal - Lime-Soda Ash Softening

Often necessary to remove certain chemicals from water and wastewater:

Water: iron and manganese
arsenic
hardness
nitrate
radionuclides
organic chemicals

Industrial wastewater: virtually any chemical, but especially
metals
organic chemicals

Hardness

A water is "hard" if:

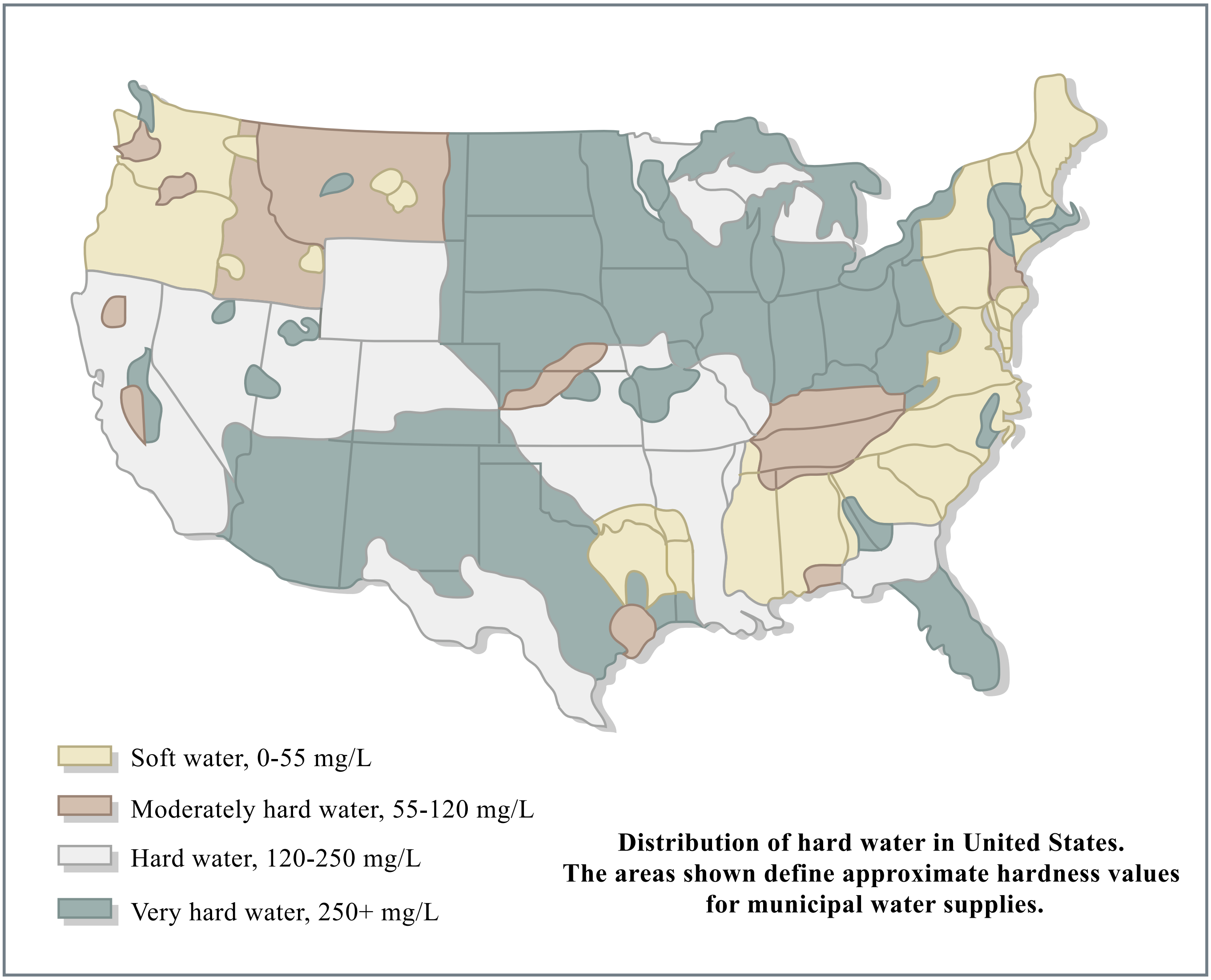
1. soap does not easily form a foam or lather
2. the water leaves scale in hot-water pipes, boilers, etc.

Hardness arises from divalent metal ions in the water:

Ca^{++}
Mg^{++}
Sr^{++}
Fe^{++}
Mn^{++}

} come from natural rocks in source area, especially: limestones:
calcite $CaCO_3$
dolomite $CaMg(CO_3)_2$

Prevalence of hard water nationwide reflects geology - see Figure 19-8 from MWH, 2005



Distribution of hard water in United States.
The areas shown define approximate hardness values for municipal water supplies.

Figure by MIT OCW.

Adapted from: Dekker, Marcel. *Water and Water Pollution Handbook*. Edited by L. Ciaccio. New York, NY: 1971.

Different definitions of hardness

Total hardness = $\sum [M^{++}] \times \frac{50}{\text{eq. wt. of } M^{++}}$

Hardness is expressed in equivalents of $CaCO_3$

Ca	–	MW = 40	× 1	=	40
C	–	MW = 12	× 1	=	12
O	–	MW = 16	× 3	=	48
					100 = MW

Since Ca^{++} and $CO_3^{=}$
have valence of 2,
equivalent weight of $CaCO_3$ = 100/2 = 50

Example water: (Ex 11.4, pg. 445 of Y & H):

CO_2 = 8.8 mg/L as CO_2
Ca^{2+} = 70 mg/L
Mg^{2+} = 9.7 mg/L
Na^{+} = 6.9 mg/L

Alk (HCO_3^-) = 115 mg/L as $CaCO_3$
SO_4^{2-} = 96 mg/L
Cl^- = 10.6 mg/L

M^{++}	conc (mg/L)	MW	eq. wt.	hardness
Ca^{2+}	70	40	20	175
Mg^{2+}	9.7	24.4	12.2	39.8
				214.8

pretty hard water!

Most hardness is due to Ca and Mg

Ca hardness = that due to Ca
Mg hardness = that due to Mg

Total hardness ≅ Ca hardness + Mg hardness

carbonate hardness = part of total hardness equivalent to carbonate plus bicarbonate alkalinity

Refresher on alkalinity [Alk]:

Alk = capacity for solutes to neutralize a strong acid

$= \Sigma[\text{strong bases}] - \Sigma[\text{strong acids}]$
in equivalents be liter

Strong acids are those that completely dissociate in water: HCl, H_2SO_4, HNO_3, HBr, HI, $HClO_4$

Strong bases completey dissociate: $NaOH$, KOH, $Ca(OH)_2$, $Mg(OH)_2$, $LiOH$, $RbOH$, $Sr(OH)_2$, $Ba(OH)_2$

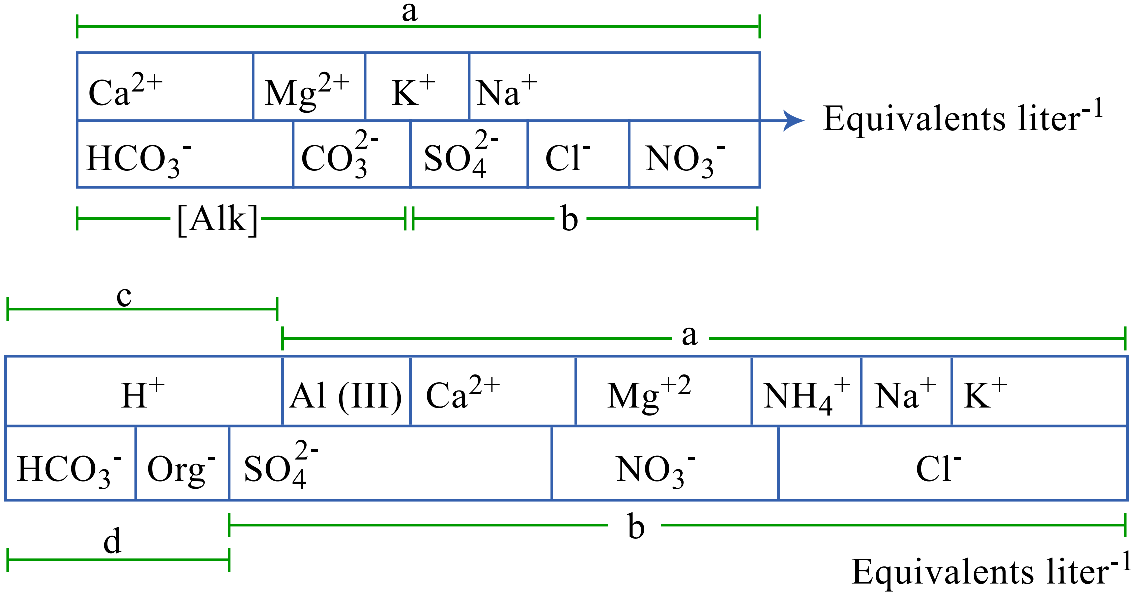
$$[Alk] = [Na^+] + [K^+] + 2[Ca^{++}] + 2[Mg^{++}] - [Cl^-] - 2[SO_4^{=}] - [NO_3^-]$$

$$= \Sigma[SB] - \Sigma[SA]$$

Can also find charge balance assuming carbonates dominate system

$$\Sigma[SB] + [H^+] = \Sigma[SA] + [OH^-] + 2[CO_3^{=}] + [HCO_3^-]$$

$$\Sigma[SB] - \Sigma[SA] = [Alk]$$
$$= [OH^-] - [H^+] + 2[CO_3^{=}] + [HCO_3^-]$$



Natural water charge balance for an alkaline system (Alk = a-b) and an acid system (Alk = a-b = d-c).

Figure by MIT OCW.

Adapted from: Schnoor, J. L. *Environmental Modeling:fate and transport of pollutants in water, air, and soil*. New York, NY: John Wiley & Sons. 1996.

Carbonate hardness (for [Alk] in terms of $CaCO_3$)

If [Alk] < total hardness,

then carbonate hardness = [Alk]

If [Alk] > total hardness,

then carbonate hardness = total hardness

Carbonate hardness causes scaling at high temps:

$$Ca^{++} + 2\,HCO_3^- \xrightarrow{\Delta} CaCO_3\downarrow + CO_2 + H_2O$$

Noncarbonate hardness = total hardness − carbonate hardness

For water treatment, carbonate hardness is removed by adding lime $Ca(OH)_2$:

First lime reacts with any CO_2:

1. $CO_2 + Ca(OH)_2 \rightarrow CaCO_3\downarrow + H_2O$

Then lime reacts to remove carbonate hardness

2. $Ca^{2+} + 2HCO_3^- + Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O$

3. $Mg^{2+} + 2HCO_3^- + 2Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + Mg(OH)_2\downarrow + 2H_2O$

And finally to remove non-carbonate Mg hardness

4. $Mg^{2+} + SO_4^= + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + Ca^{2+} + SO_4^=$

5. $Mg^{2+} + 2Cl^- + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + Ca^{2+} + 2Cl^-$

Reactions 4. and 5. simply swap Mg noncarbonate hardness for Ca noncarbonate hardness

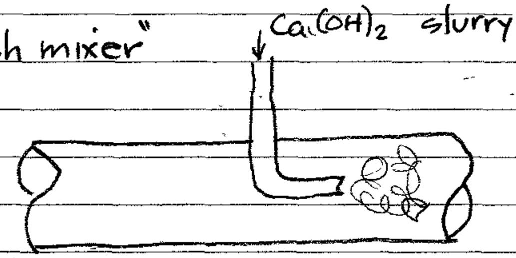
Reactions 1 - 5 remove magnesium hardness and calcium carbonate hardness. Calcium noncarb hardness in original solution plus that created removing Mg hardness remain.

For waters low in Mg and with carbonate Ca hardness, this would be sufficent treatment – called "Single - stage lime treatment", "single-stage softening", or "undersoftening"

Typical process in water-treatment plant:

$CaCO_3$ added in "flash mixer"

Water →



Water/lime mix goes into flocculator, then clarifier to precipitate and remove $CaCO_3$ (T_R = 1-2 hrs)

Water is then "recarbonated"

Recarbonation is needed because addition of $Ca(OH)_2$ raises pH of water to 10.2 to 10.5

Recarbonation consists of bubbling CO_2 through treated water, lowering pH to 8.7 to 9.0:

6. $Ca(OH)_2 + CO_2 \rightarrow CaCO_3\downarrow + H_2O$

7. $CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$

Recarbonation is also done to "stabilize" the water

If water is supersaturated with $CaCO_3$, it will precipitate as "scale"

If water is undersaturated, water can be "aggressive" and cause pipe corrosion

Ideal is to keep water slightly oversaturated to maintain thin protective coat of $CaCO_3$ on inside of pipe

Scale precipitation involves two chemical reactions:

$$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3(s) \qquad 1/K_s$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad K_2$$

$$K_s = \frac{[Ca^{2+}][CO_3^{2-}]}{[CaCO_3(s)]}$$

($[CaCO_3(s)] \rightarrow 1$)

$$K_2 = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]}$$

Overall reaction:

$$Ca^{2+} + HCO_3^- \rightleftharpoons CaCO_3(s) + H^+$$

$$K = \frac{[Ca^{2+}][HCO_3^-]}{[H^+]} = \frac{K_s}{K_2}$$

Rearrange to get: $[H^+] = \dfrac{[Ca^{2+}][HCO_3^-]}{K}$

$$[H^+] = \frac{[Ca^{2+}][HCO_3^-]}{K}$$

$$\log[H^+] = \log[Ca^{2+}] + \log[HCO_3^-] - \log K$$

$$-\log[H^+] = -\log[Ca^{2+}] - \log[HCO_3^-] + \log(K_s/K_2)$$

$$pH_{eq} = pCa + pHCO_3^- + \log(K_s/K_2)$$
$$\approx pCa \quad p[Alk] + \log(K_s/K_2)$$

↑ to denote this is pH at $CaCO_3$ equilibrium

$I = pH_{actual} - pH_{eq} \equiv SI$

Langlier Stability Index

$I > 0 \rightarrow$ $CaCO_3$ precipitates ($pH_{actual} > pH_{eq}$)

$I = 0 \rightarrow$ stable

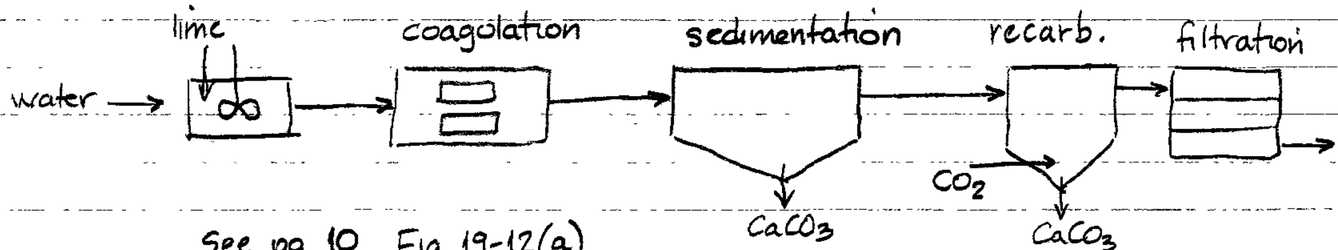
$I < 0 \rightarrow$ $CaCO_3$ dissolves

$I = 0.2$ is desirable – carbonation steps seeks to set $I \hat{=} 0.2$

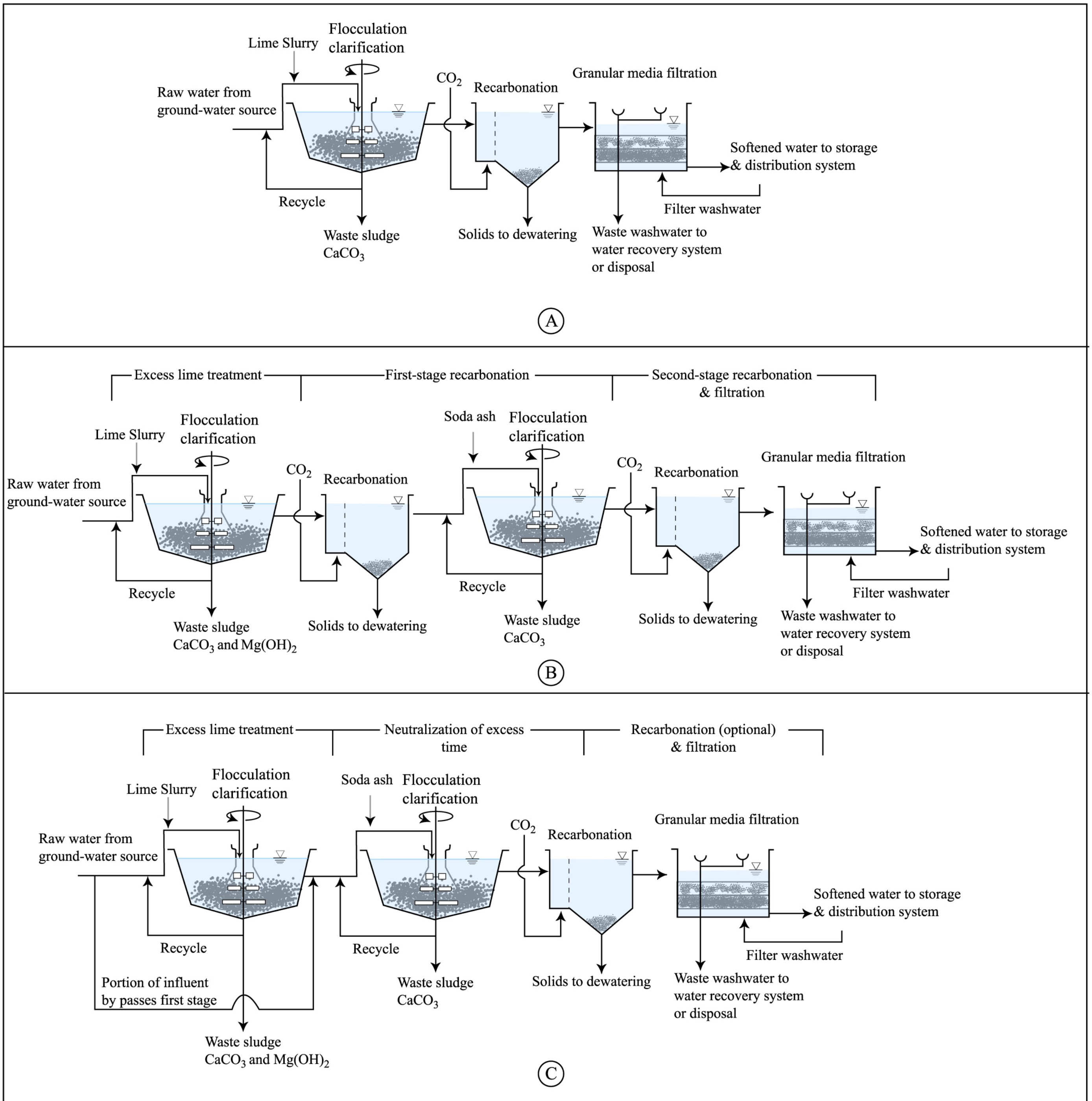
K_2, K_s are functions of temp.

$pK_s = 8.4$ $pk_2 = 10.4$ at $T = 15C$

conventional lime treatment process looks like:



See pg 10 Fig 19-12(a)



Process flow diagram of common softening treatment techniques: (a) Single- stage lime treatment; (b) two-stage excess lime-soda treatment; (c) split-flow lime treatment

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, p. 1601.

For waters with non-carbonate hardness, single-stage softening is insufficient. Leftover hardness is removed by addition of soda ash (NO_2CO_3) NaX

8. $Ca^{2+} + SO_4^{2-} + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2Na^+ + SO_4^{2-}$

9. $Ca^{2+} + 2Cl^- + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2Na^+ + 2Cl^-$

Practical limits of lime-soda ash softening are dictated by solubility of precipitates: $CaCO_3$ & $Mg(OH)_2$

Ca: 30 mg/L as $CaCO_3$
Mg: 10 mg/L as $CaCO_3$
Total hardness = 40 mg/L as $CaCO_3$

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 pg 10 Fig 19-12 (b) from MWH

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 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 13 and 14

CO_2 = 8.8 mg/L as CO_2
Ca^{++} = 70 mg/L
Mg^{++} = 9.7 mg/L
Na^{+} = 6.9 mg/L

Alk = 115 mg/L as $CaCO_3$
SO_4^{2-} = 96 mg/L
Cl^{-} = 10.6 mg/L

Easiest method is to construct a table that converts all concentrations to equivalent concentrations, and then to equivalents of $CaCO_3$
Also use chart from VH Fig 11.8, pg 446

	mg/L	MW	equiv	eq wt	meq/L	mg/L as $CaCO_3$
CO_2	8.8	44.0	2	22.0	0.4	20.0
Ca^{2+}	70	40.0	2	20.0	3.5	175.
Mg^{2+}	9.7	24.4	2	12.2	0.80	39.8
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
SO_4^{2-}	96	96.0	2	48.0	2.0	100.0
Cl^{-}	10.6	35.5	1	35.5	0.30	14.9
					4.6	229.9

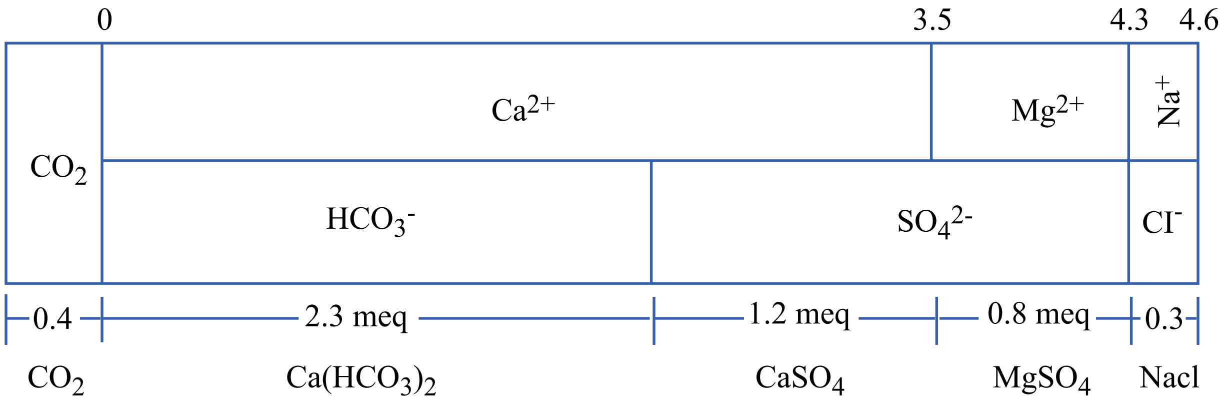
Total hardness = Ca^{2+} + Mg^{2+} = 175 + 39.8 = 214.8 mg/L as $CaCO_3$

Carbonate hardness = [Alk] = 115 mg/L as $CaCO_3$

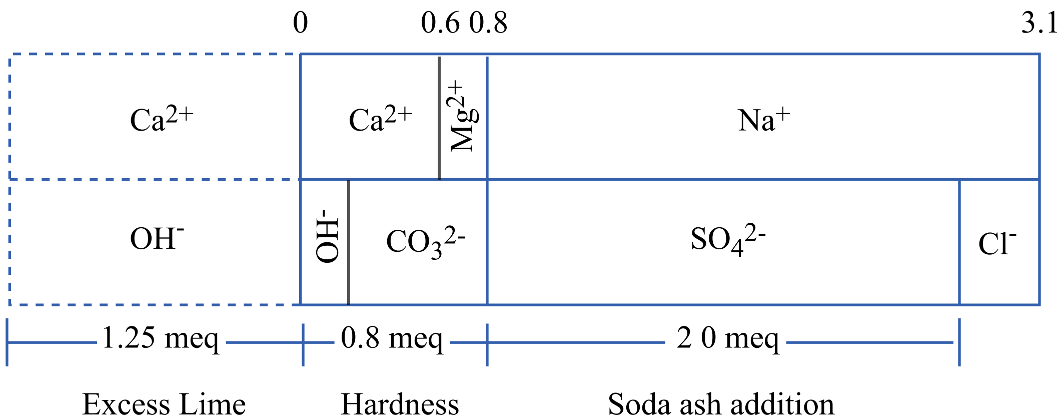
Noncarbonate hardness = TH - CH = 99.8 mg/L as $CaCO_3$

Mg noncarbonate hardness = 39.8 mg/L as $CaCO_3$

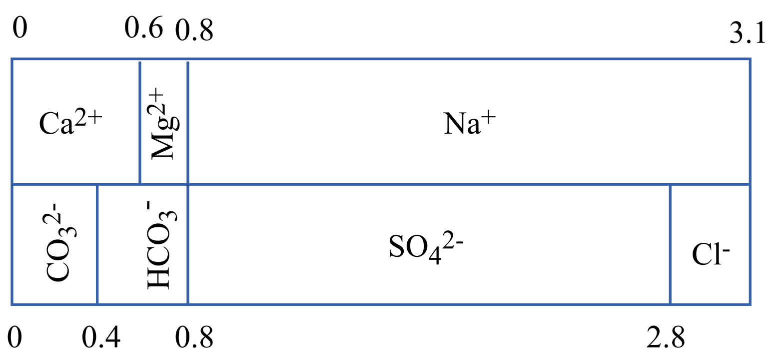
Milliequivalent Bar Graph for Example 11.4



(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.

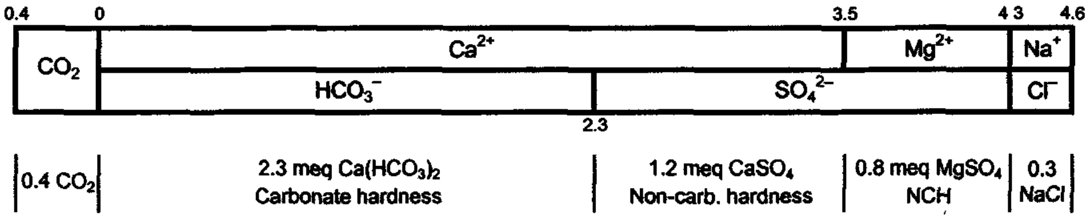


(C) Bar Graph of the water after two-stage recarbonation & final filtration

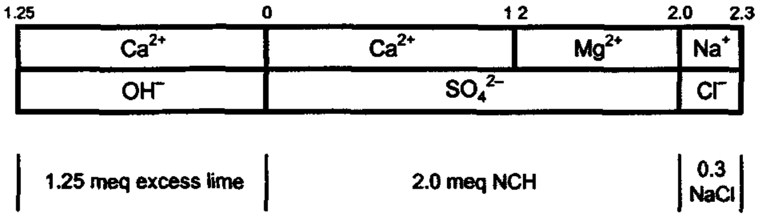
Figure by MIT OCW.

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.

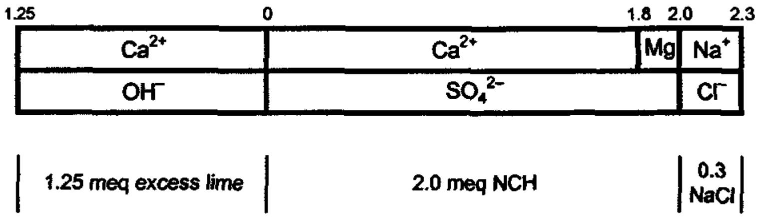
Before treatment:



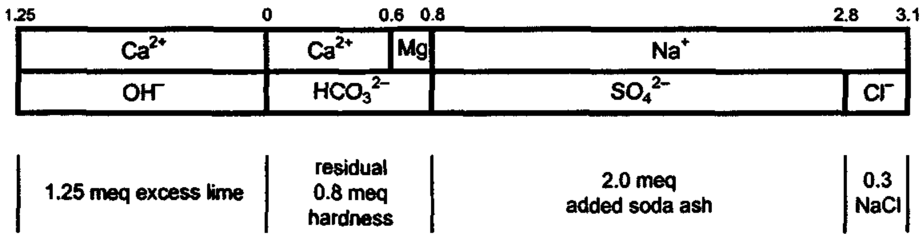
After treatment with lime $Ca(OH)_2$ and intermediate reaction to remove carbonate hardness:
(chemical equations 1, 2, & 3)



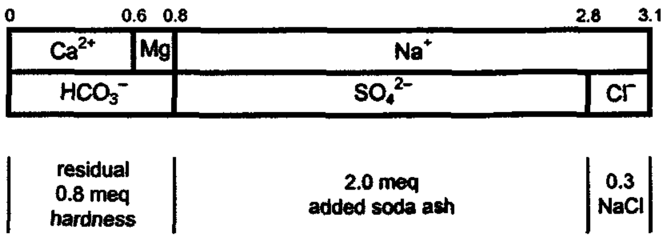
After *treatment* with lime and intermediate reaction to remove noncarbonate Mg hardness:
(chemical equations 4 & 5)



After treatment with soda ash Na_2CO_3:
(chemical equations 8 & 9)



After recarbonation:
(chemical equations 6 & 7)



Lime required

For CO_2 - 20.0 mg/L as $CaCO_3$

For carbonate hardness - 115.0

For Mg noncarbonate hardness - 39.8

174.8 mg/L as $CaCO_3$ (3.5 meq)

Convert from $CaCO_3$ to CaO

$$\frac{CaO}{CaCO_3} = \frac{40+16}{40+12+3\times16} = \frac{56}{100} = \frac{28}{50}$$

174.8 mg/L as $CaCO_3$ = 97.9 mg/L as CaO

Include excess lime of 35 mg/L

Req'd lime = 133 mg/L

Soda Ash for noncarbonate hardness

NCH = 99.8 mg/L as $CaCO_3$ (2.0 meq)

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

Reqd Soda Ash - 99.8 mg/L as $CaCO_3$

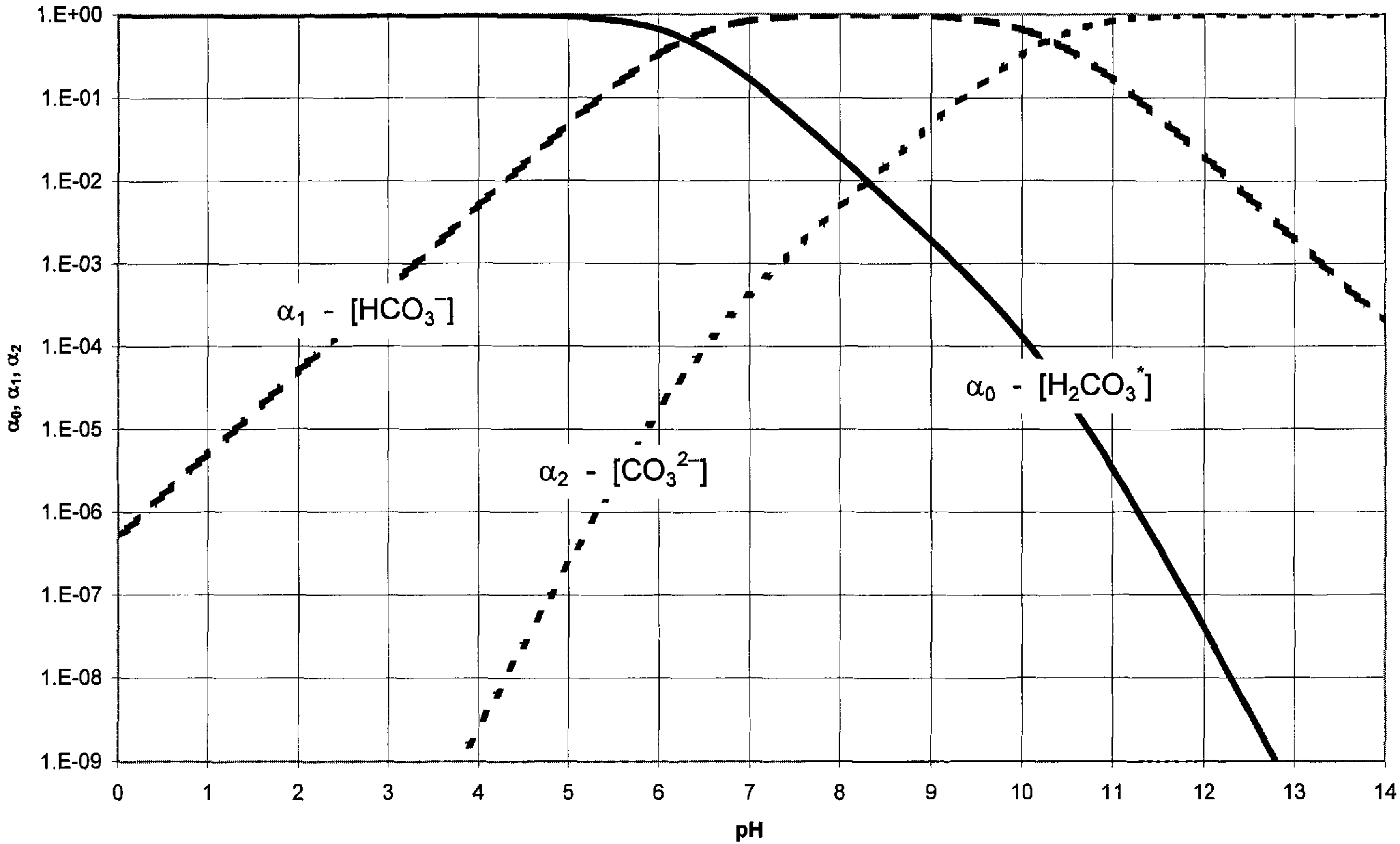
Convert to Na_2CO_3:

$$\frac{Na_2CO_3}{CaCO_3} = \frac{2\times23+12+3\times16}{40+12+3\times16} = 1.06$$

Reqd soda ash = 1.06 × 99.8 = 106 mg/L

Note that pg 14 shows HCO_3^- but will actually be an equilibrium between CO_2, HCO_3^-, CO_3^{2-} depending on pH per pg 16

Carbonate system equilibrium



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

PROCESS	REQUIRED CHEMICAL DOSAGE CALCULATIONS
Single-Stage Lime: For waters with high calcium, low magnesium, & carbonate hardness	**Lime addition for softening:** CaO = {carbonic acid concentration} + { calcium carbonate hardness} **Soda ash addition for softening:** Na_2CO_3 = none **Carbon dioxide for pH adjustment after softening:** CO_2 = {estimated carbonate alkalinity of softened water} = {source water alkalinity} – {source water calcium hardness} + {estimated residual calcium hardness of softened water}
Excess Lime: For waters with high calcium, high magnesium, and carbonate hardness; process may be one or two stages	**Lime addition for softening:** CaO = {carbonic acid concentration} + {total alkalinity} + {magnesium hardness} + {excess lime dose} **Soda ash addition for softening:** Na_2CO_3 = none **Carbon dioxide for pH adjustment after softening:** CO_2 = {source water alkalinity} – {source water total hardness} – {excess lime dose} + {estimated residual calcium hardness of softened water} + 2 {excess lime dose} + {estimated residual magnesium hardness of softened water}
Single-Stage Lime Soda Ash: For water with high calcium, low magnesium, & carbonate and noncarbonte hardness	**Lime addition for softening:** CaO = {carbonic acid concentration} + { calcium carbonate hardness} **Soda ash addition for softening:** Na_2CO_3 = {calcium noncarbonate hardness} and /or {magnesium noncarbonate hardness} **Carbon dioxide for pH adjustment after softening:** CO_2 = {source water alkalinity} + {soda ash dose} – {source water calcium hardness} + {estimated residual calcium hardness of softened water}
Excess Lime - Soda Ash: For waters with high calcium, high magnesium, and carbonate and noncarbonate hardness; process may be one or two stages	**Lime addition for softening:** CaO = {carbonic acid concentration} + {calcium carbonate concentration} + 2 {magnesium carbonate hardness} + {magnesium noncarbonate hardness} + {excess lime requirement} **Soda ash addition for softening:** Na_2CO_3 = {calcium noncarbonate hardness} + {magnesium noncarbonate hardness} **Carbon dioxide for pH adjustment after softening:** CO_2, first stage = {estimated hydroxide alkalinity of softened water} = {excess lime dose} + {estimated residual magnesium hardness of softened water} CO_2, second stage = {estimated hydroxide alkalinity of softened water} = {source water alkalinity} + {soda ash dose} – {source water total hardness} + {estimated residual hardness of softened water}

* All quantities are expressed as mg/L as $CaCO_3$

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.