

## Lecture 8 - Lime-soda ash softening, Part 1

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:

$\text{Ca}^{++}$   
 $\text{Mg}^{++}$   
 $\text{Sr}^{++}$   
 $\text{Fe}^{++}$   
 $\text{Mn}^{++}$

} come from natural rocks  
in source area,  
especially: limestones:  
calcite  $\text{CaCO}_3$   
dolomite  $\text{CaMg}(\text{CO}_3)_2$

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

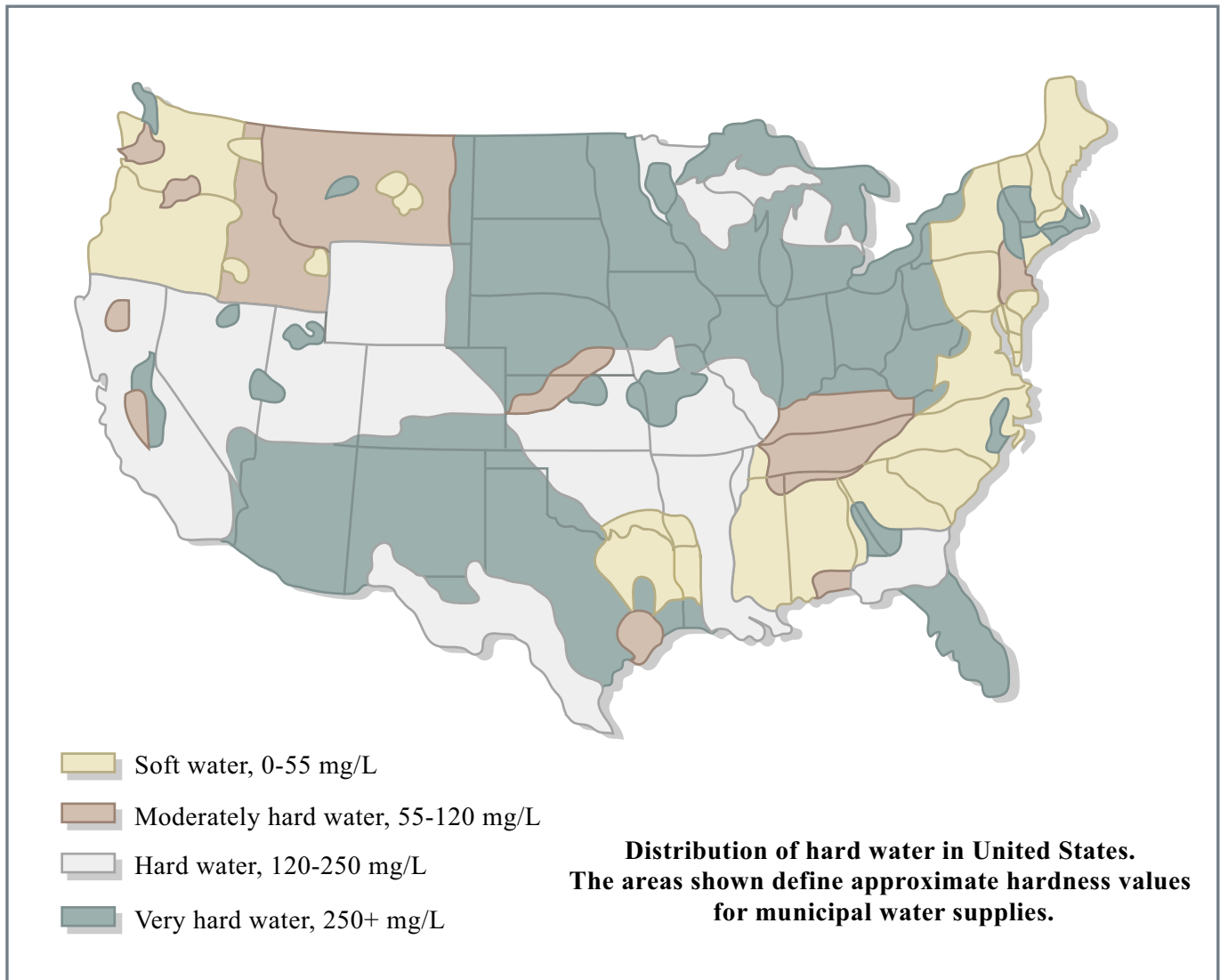


Figure by MIT OCW.

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

## Different definitions of hardness

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

Hardness is expressed in equivalents of  $\text{CaCO}_3$

$$\begin{array}{rcl} \text{Ca} & - & \text{MW} = 40 \times 1 = 40 \\ \text{C} & - & \text{MW} = 12 \times 1 = 12 \\ \text{O} & - & \text{MW} = 16 \times 3 = 48 \\ & & \hline & & 100 = \text{MW} \end{array}$$

Since  $\text{Ca}^{++}$  and  $\text{CO}_3^{--}$  have valence of 2,  
equivalent weight of  $\text{CaCO}_3 = 100/2 = 50$

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

$$\begin{array}{ll} \text{CO}_2 = 8.8 \text{ mg/L as CO}_2 & \text{Alk (HCO}_3^-) = 115 \text{ mg/L} \\ \text{Ca}^{2+} = 70 \text{ mg/L} & \text{as CaCO}_3 \\ \text{Mg}^{2+} = 9.7 \text{ mg/L} & \text{SO}_4^{2-} = 96 \text{ mg/L} \\ \text{Na}^+ = 6.9 \text{ mg/L} & \text{Cl}^- = 10.6 \text{ mg/L} \end{array}$$

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

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  $\approx$  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

$$= \sum [\text{strong bases}] - \sum [\text{strong acids}]$$

in equivalents per liter

Strong acids are those that completely dissociate  
in water: HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, HBr, HI, HClO<sub>4</sub>

Strong bases completely dissociate = NaOH, KOH,  
Ca(OH)<sub>2</sub>, Mg(OH)<sub>2</sub>, LiOH, RbOH, Sr(OH)<sub>2</sub>,  
Ba(OH)<sub>2</sub>

$$[\text{Alk}] = [\text{Na}^+] + [\text{K}^+] + 2[\text{Ca}^{++}] + 2[\text{Mg}^{++}]$$

$$- [\text{Cl}^-] - 2[\text{SO}_4^{2-}] - [\text{NO}_3^-]$$

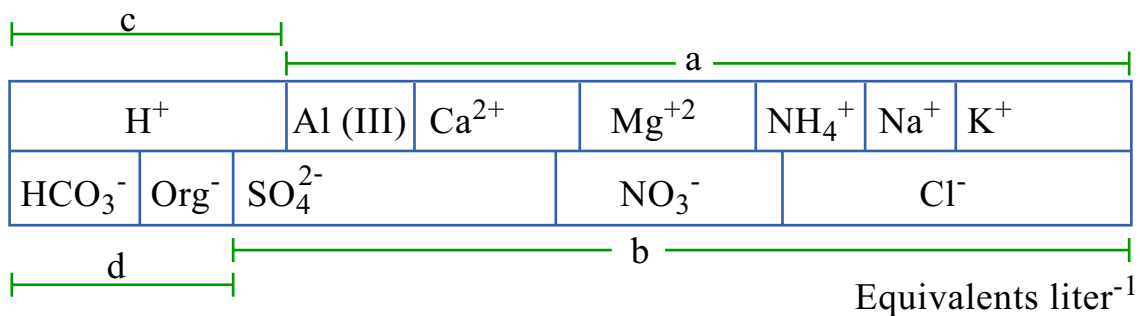
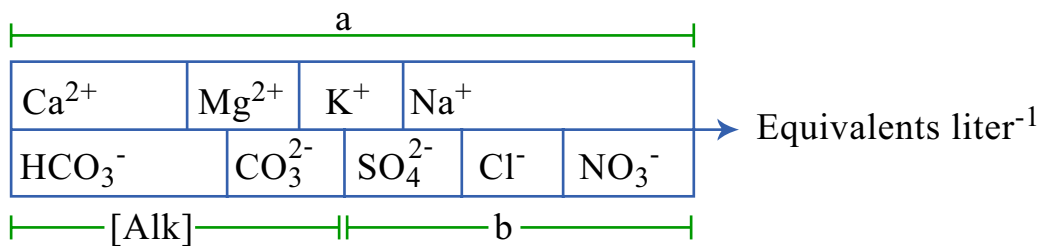
$$= \sum [\text{SB}] - \sum [\text{SA}]$$

Can also find charge balance assuming carbonates  
dominate system

$$\sum [\text{SB}] + [\text{H}^+] = \sum [\text{SA}] + [\text{OH}^-] + 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-]$$

$$\sum [\text{SB}] - \sum [\text{SA}] = [\text{Alk}]$$

$$= [\text{OH}^-] - [\text{H}^+] + 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-]$$



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  $CaCO_3$ )

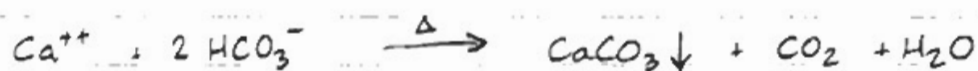
If  $[Alk] < \text{total hardness}$ ,

then carbonate hardness =  $[Alk]$

If  $[Alk] > \text{total hardness}$ ,

then carbonate hardness = total hardness

Carbonate hardness causes scaling at high temps:



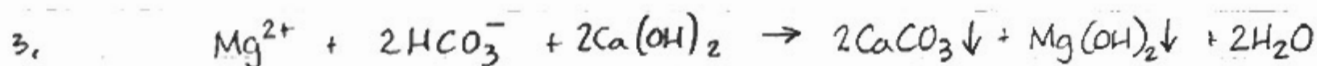
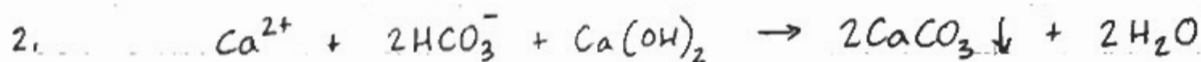
Noncarbonate hardness = total hardness - carbonate hardness

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

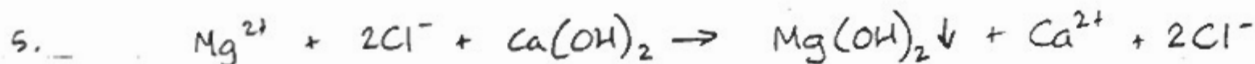
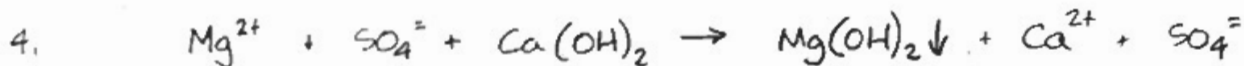
First lime reacts with any  $CO_2$ :



Then lime reacts to remove carbonate hardness



And finally to remove non-carbonate Mg hardness

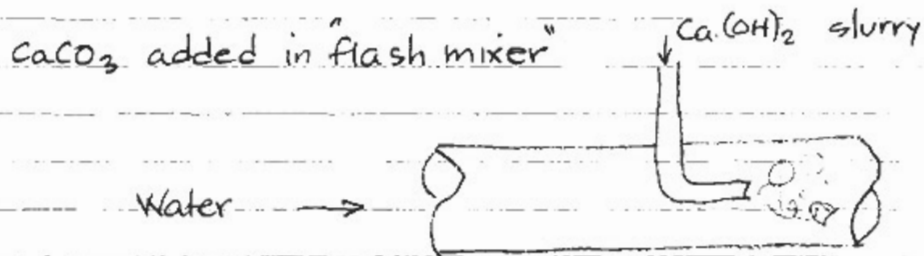


Reactions 4, and 5, simply swap Mg noncarbonate hardness for Ca noncarbonate hardness.

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 sufficient treatment - called "single-stage lime treatment", "single-stage softening", or "undersoftening".

Typical process in water-treatment plant:

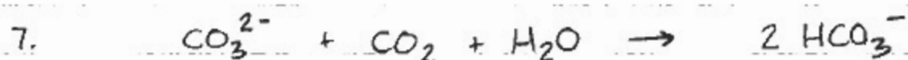
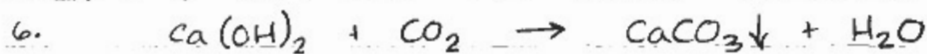


Water/lime mix goes into flocculator, then clarifier to precipitate and remove CaCO<sub>3</sub> (TR = 1-2 hrs)

Water is then "recarbonated"

Recarbonation is needed because addition of Ca(OH)<sub>2</sub> raises pH of water to 10.2 to 10.5

Recarbonation consists of bubbling CO<sub>2</sub> through treated water, lowering pH to 8.7 to 9.0:



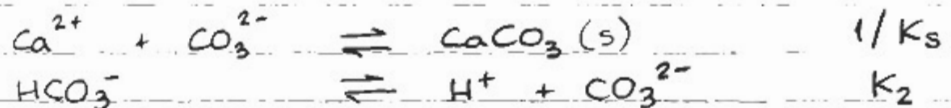
Recarbonation is also done to "stabilize" the water

If water is supersaturated with  $\text{CaCO}_3$ , 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  $\text{CaCO}_3$  on inside of pipe

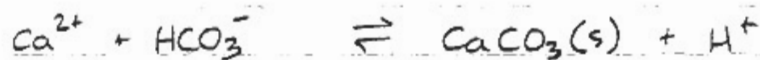
Scale precipitation involves two chemical reactions:



$$K_s = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{[\text{CaCO}_3(s)]}$$

$$K_2 = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]}$$

Overall reaction:



$$K = \frac{[\text{Ca}^{2+}][\text{HCO}_3^-]}{[\text{H}^+]} = \frac{K_s}{K_2}$$

Rearrange to get:

$$[\text{H}^+] = \frac{[\text{Ca}^{2+}][\text{HCO}_3^-]}{K}$$



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

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

$$-\log [H^+] = -\log [Ca^{2+}] - \log [HCO_3^-] + \log (K_1/K_2)$$

$$pH_{eq} = pCa + p[HCO_3^-] + \log (K_1/K_2)$$

$$\approx pCa + p[Alk] + \log (K_1/K_2)$$

↑ to denote this is pH at CaCO<sub>3</sub> 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

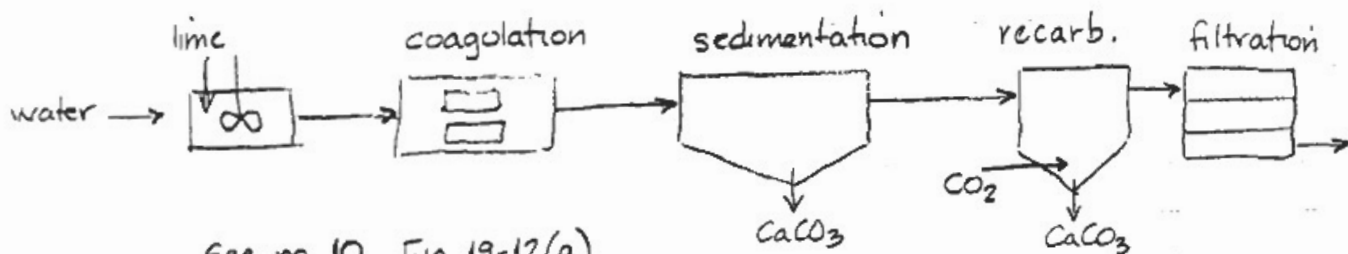
$I < 0 \rightarrow CaCO_3$  dissolves

$I = 0.2$  is desirable - carbonation steps seeks to set  $I \approx 0.2$

$K_1, K_2$  are functions of temp.

$pK_1 = 6.4$       $pK_2 = 10.4$      at  $T = 15^\circ C$

conventional lime treatment process looks like:



See pg 10 Fig 19-12(a)

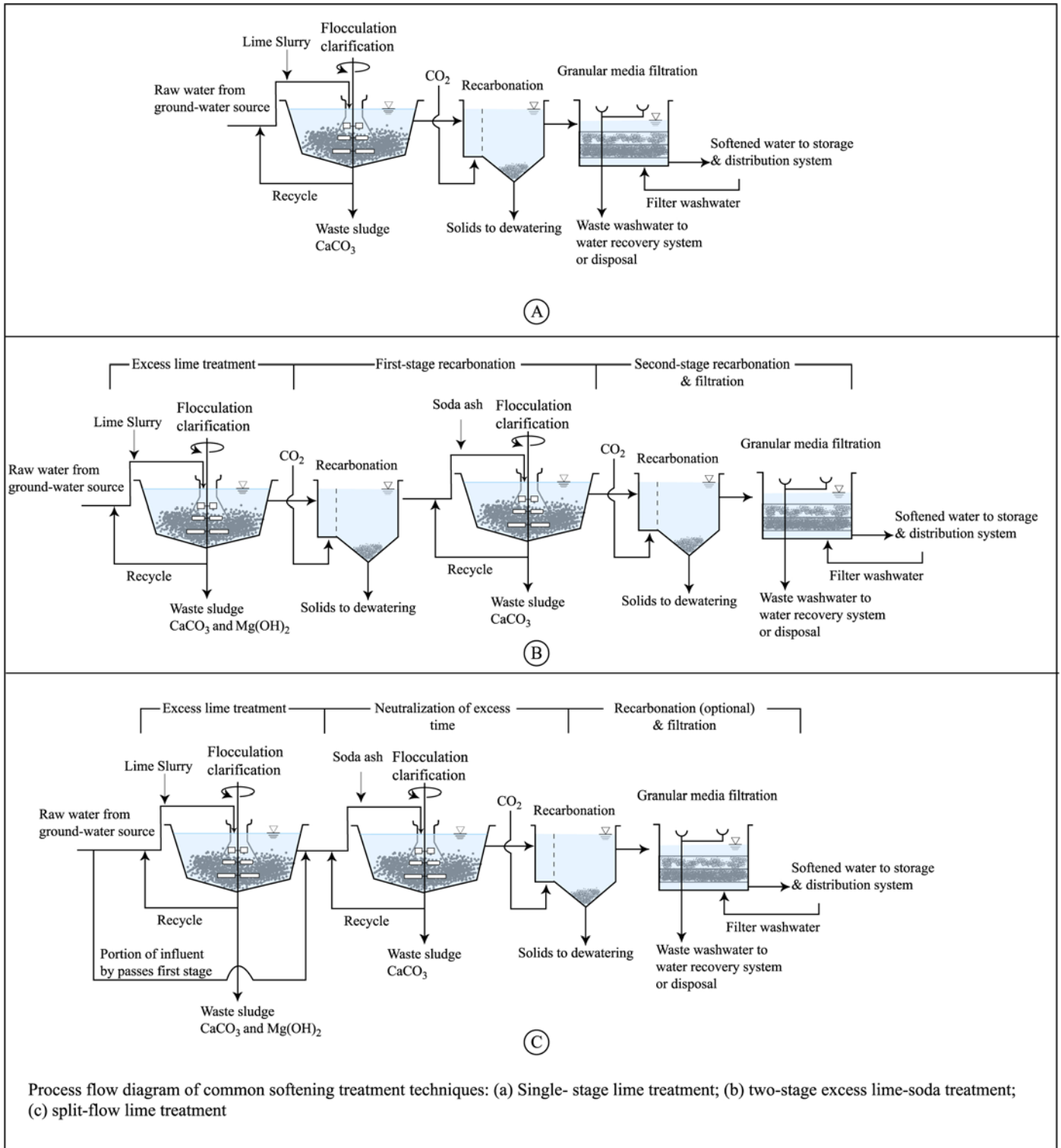


Figure by MIT OCW.

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.