"HARDNESS" IN WATER

Definition:

HARDNESS = $[Ca^{2+}] + [Mg^{2+}]$

What's the problem?

• Lime scale

$$Ca^{2+} + CO_3^{2-} \rightarrow \underline{CaCO_3(s)}$$

Precipitation follows ▸ Heating
▸ Reaeration
} Loss of $CO_2(aq)$

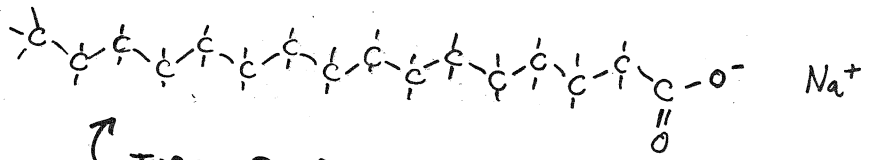
• Mg scale

Magnesium carbonate ~ soluble ($MgCO_3$ not much problem)

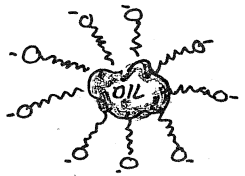
BUT Mg silicates can be problem in BOILERS (>180°F)

$$Mg^{2+} + H_2SiO_3 \rightarrow H^+ + \underline{MgSiO_3}$$ ← VERY HARD SCALE "glassy"

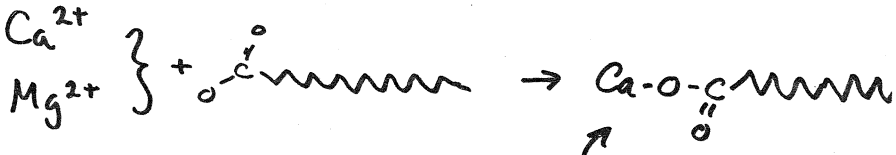
• Precipitation of Soap "Scum"



TYPICAL SOAP INGREDIENT: Na palmitate ($C_{16}H_3O_2^-Na^+$)



← Soap dissolves oil & dirt by emulsifying



INSOLUBLE IN H_2O (used sometimes to make crayons, grease pencils)

SOAP SCUM

- Soap scum build-up
- Failure to lather
- Failure to clean

(But can use this to make napalm)

CONC. UNITS FOR HARDNESS

- $[Ca^{2+}] + [Mg^{2+}]$: mol/L (M)
  - ~ OK, but as we'll see becomes inconvenient in calculations for treatment

- Equivalents/L (eq/L or meq/L etc.)

  "equivalent" = moles × valence #

$$[Ca^{2+}] = 3\times10^{-3}\ mol/L = 6\times10^{-3}\ eq/L$$
$$[Na^{+}] = 3\times10^{-3}\ mol/L = 3\times10^{-3}\ eq/L$$
$$[HCO_3^-] = 3\times10^{-3}\ mol/L = 3\times10^{-3}\ eq/L$$
$$[CO_3^{2-}] = 3\times10^{-3}\ mol/L = 6\times10^{-3}\ eq/L$$

"1 equivalent/L of Ca^{2+} will combine with 1 equivalent/L HCO_3^-": $Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + H_2CO_3$

- mg-$CaCO_3$/L : Defines hardness as # of moles of $CaCO_{3(s)}$ that can ppt. if all due to Ca^{2+}

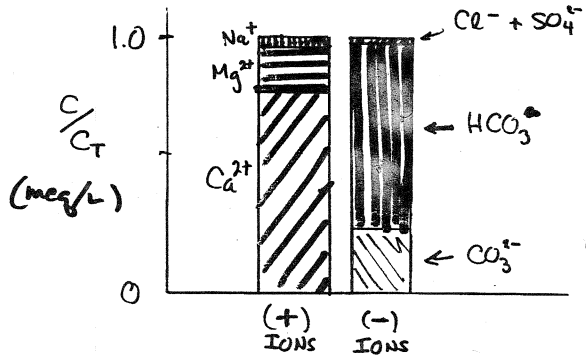
$$1\ \frac{mmol\text{-}Ca^{2+}}{L} \times 100.09\ \frac{mg\text{-}CaCO_3}{mmol\text{-}Ca^{2+}} \cong 100.0\ \frac{mg\text{-}CaCO_3}{L}$$

SOURCES OF HARDNESS

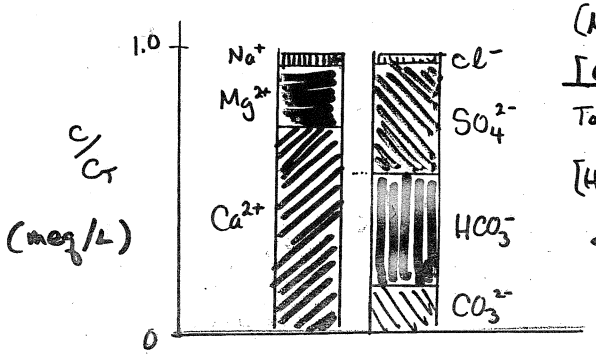
Minerals that the water dissolves (can be surface water or groundwater)

CARBONATE
- CALCITE (Limestone): $CaCO_3$
- DOLOMITE (Dolomitic Limestone): $Ca_x Mg_{(1-x)} (CO_3)$

NON-CARBONATE
- GYPSUM : $CaSO_4$



$[Mg^{2+}] = 1\times10^{-3}$ eq/L
$[Ca^{2+}] = 4\times10^{-3}$ eq/L
Total Hardness = 5×10^{-3} eq/L
"CO_3 HARDNESS" = 5×10^{-3} eq/L



$[Mg^{2+}] < 1\times10^{-3}$ eq/L
$[Ca^{2+}] = 4\times10^{-3}$ eq/L
Total Hardness = 5×10^{-3} eq/L
$[HCO_3^-] + [CO_3] = 3\times10^{-3}$ eq
∴ Carbonate Hardness = 3×10^{-3} eq/L
Noncarbonate Hardness

WHAT ARE PROBLEM LEVELS?

Very subjective. Depends on USE and on local acceptance.

- Cleaning semiconductors: Almost ANY measurable hardness is a problem
- Boiler water for large power plants: Typically want below 40 mg-$CaCO_3$/L
- Boiler water for an old apt. bldg: Can tolerate more with periodic cleanouts
- Drinking water*: No limit other than taste (~ 300 - 500 mg/L)
- Domestic Use: Local custom & acceptance (50 - 200 mg-$CaCO_3$/L)

ROUGH GUIDELINES

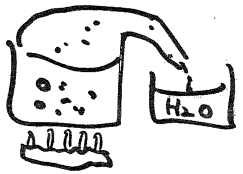
< 50	mg-$CaCO_3$/L	— "Soft" to moderate
50-100	"	— Moderate hardness
100-150	"	— Starts to be significant general problem
150-200	"	— Most domestic users find a nuisance
>200	"	— Very hard

* [illegible]

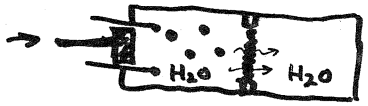
TECHNIQUES FOR SOFTENING WATER

☐ Total ion removal/reduction

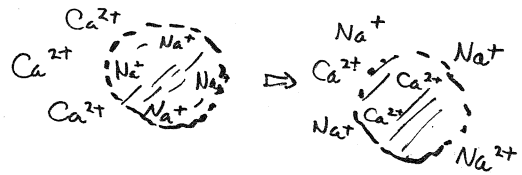
- Distillation



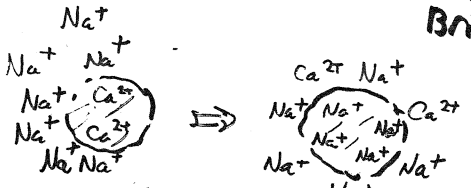
- Reverse osmosis



☐ Ion-exchange Resins (e.g., Dowex™)



REGENERATE: Backwash with strong NaCl Brine



- Good for small applications, homes
- Good for "polishing" water to low levels
- Adds Na^+ to water (health issue?)

PRECIPITATION SOFTENING

Principle: $CaCO_3$ will precipitate out if we raise the pH & shift to mostly carbonate (CO_3^{2-})

$$OH^- + Ca^{2+} + HCO_3^- \rightarrow \underline{CaCO_{3(s)}} + H_2O$$

↖ Could add NaOH (strong base)

BUT QUICKLIME OR HYDRATED LIME is cheaper and SAFER

CaO / $Ca(OH)_2$

$$CaO + H_2O \rightarrow Ca(OH)_2$$

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

We add Ca^{2+} to remove Ca^{2+}!

Can think of sequence:

$$Ca(OH)_2 + H_2CO_3 \rightarrow \underline{CaCO_3} + 2H_2O$$

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2\underline{CaCO_3} + 2H_2O$$

$$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow \underline{CaCO_3} + Mg^{2+} + CO_3^{2-}\ (aq)$$

"EXCESS LIME":

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow 2CaCO_3 + Mg(OH)_2 + 2H_2O$$

What about "Noncarbonate Hardness"

$$CaSO_4 + Ca(OH_2) \rightarrow 2Ca^{2+} + SO_4^{2-} + 2OH^-$$

↑ I.e. Ca^{2+} balanced by SO_4^{2-} No go...

USE "SODA ASH" Na_2CO_3

$$Ca^{2+} + SO_4^{2-} + Na_2CO_3 \rightarrow \underline{CaCO_3} + 2Na^+ + SO_4^{2-}$$

Leaves $Na^+ + SO_4^=$ behind but those are not a big problem @ ~ small conc's.

Mg-non-carbonate hardness is removed by the excess-lime method but need to follow with soda ash:

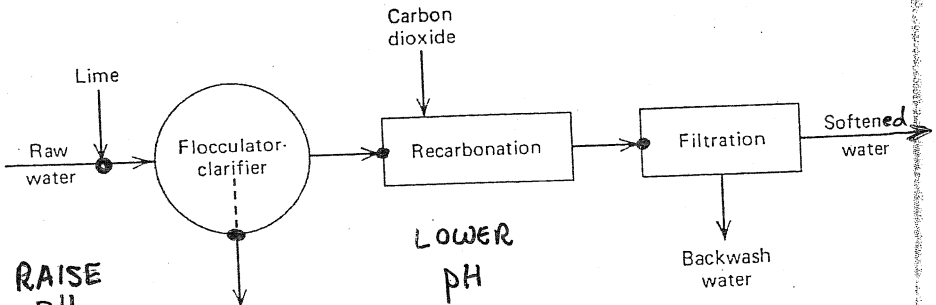
$$Mg^{2+} + SO_4^{2-} + Ca(OH)_2 \rightarrow \underline{Mg(OH)_2} + Ca^{2+} + SO_4^{2-}$$

$$Ca^{2+} + SO_4^{2-} + Na_2CO_3 \rightarrow \underline{CaCO_3} + 2Na + SO_4$$

to get rid of the Ca^{2+} added

LIME SOFTENING

"One-Step" or "Selective" Treatment



RAISE pH WITH $Ca(OH)_2$

Precipitate out $CaCO_3$

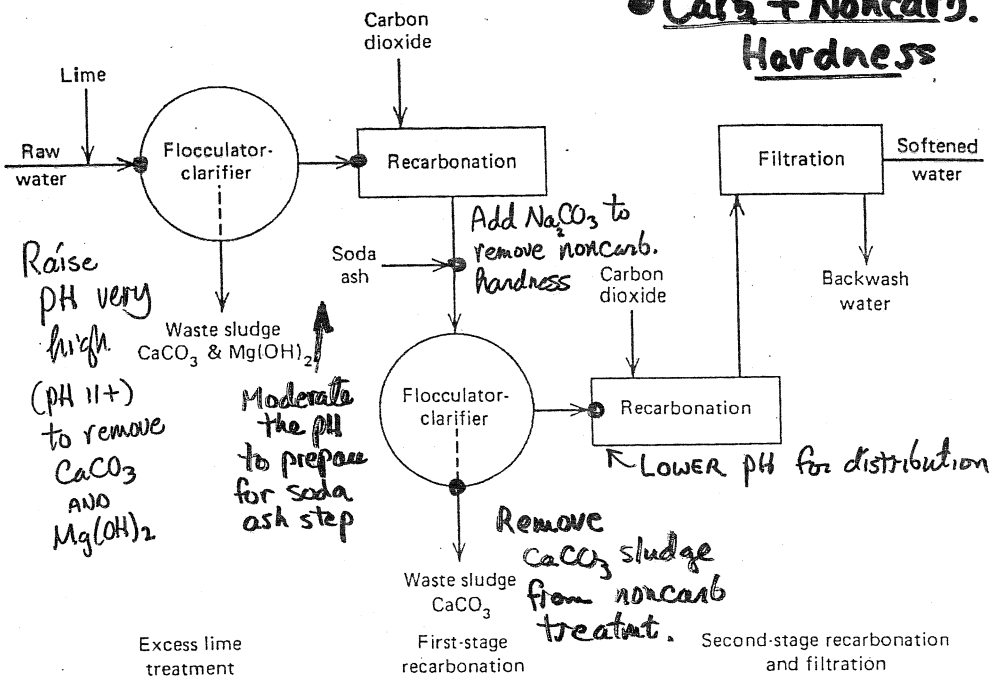
LOWER pH WITH CO_2 (g)

Filter any residual $CaCO_3$

Removes only Ca^{2+} AND only Carbonate hardness

LIME SOFTENING

Two-Step Treatment
- Ca + Mg
- Carb + Noncarb. Hardness



Raise pH very high (pH 11+) to remove $CaCO_3$ AND $Mg(OH)_2$

Add Na_2CO_3 to remove noncarb. hardness

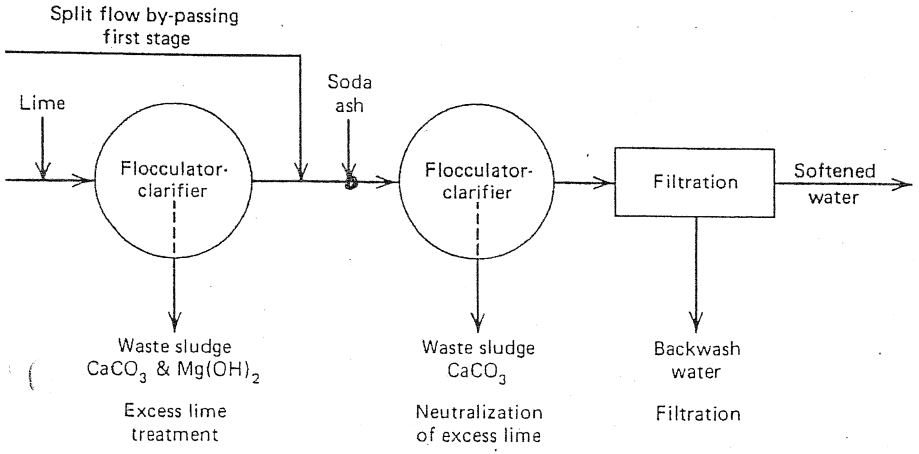
Moderate the pH to prepare for soda ash step

LOWER pH for distribution

Remove $CaCO_3$ sludge from noncarb treatmt.

LIME SOFTENING:

SPLIT-FLOW METHOD (2 step)
Ca + Mg Removal



Excess lime brings pH very high, but only for part of stream

Soda ash Na_2CO_3 added to remove noncarbonate hardness

BAR DIAGRAMS FOR SOFTENING ANALYSIS

REMOVAL ONLY OF Ca^{2+} BY ADDING ONLY LIME ($Ca(OH)_2$)

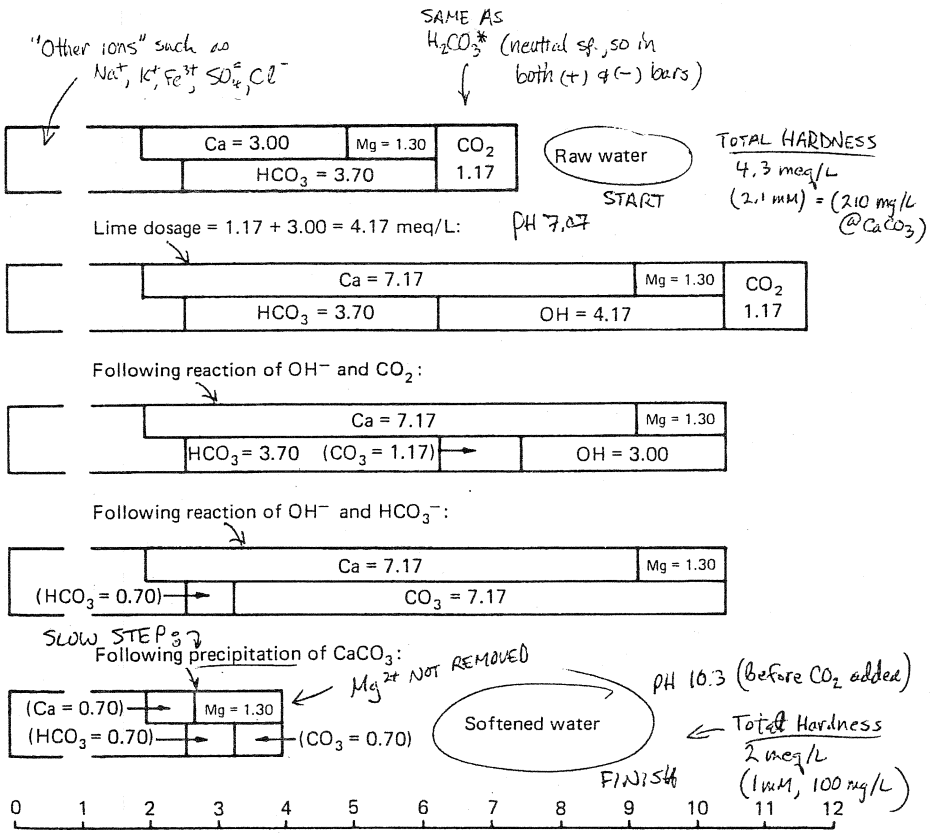


FIGURE 11-2
Bar diagrams for softening analysis. *(Reprinted from Journal of American Water Works Association, 68, by permission of the Association. Copyright 1976 by the American Water Works Association, Inc., 6666 W. Quincy Avenue, Denver, CO. 80235.)*