REVIEW CONC UNITS: HARDNES

$$Ca\text{-}H = [Ca^{2+}]_T \ mol/L$$
$$Mg\text{-}H = [Mg^{2+}]_T \ mol/L$$

$$TH = [Ca^{2+}] + [Mg^{2+}] \ mol/L$$
(TH = Total)

← Inconvenient to keep track of 2+ charge

HENCE USE "EQUIVALENTS/L" (Normality)

$$1 \ eq/L = (Charge) \times 1 \ mol/L$$

Eg $[Ca^{2+}]$: $2 \ eq/L = 1 \ mol/L$ (because $N = 2 \times M$)

OR $100 \ eq/L = 50 \ mol/L$

WHY USE N? Soln. of $Ca(HCO_3)_2$ (calcium bicarbonate)

↙ $1 Ca^{2+}$ ↘ $2 HCO_3^-$

A 1 mmol/L solution yields 1 mmol Ca ($1 \times 2^+$) and 2 mmol HCO_3^- ($2 \times 1^-$)

But, a 1 meq/L solution yields 2 meq/L Ca = 2 meq/L HCO_3

HENCE Ca^{2+}, Mg^{2+} are in consistent stoichiometric w/ CO_3^{2-} & HCO_3^-

COMMON ENG. SYSTEM: "As $CaCO_3$" Use FW of $CaCO_3 = 100.0 \frac{mg}{mol}$

E.g., TAKE 1 mmol of $CaCO_{3(s)}$, dissolve into water, (1 Liter)

$$(1 \ mmol/L)(100.0 \frac{mg}{mol}) = 100 \ mg\text{-}CaCO_3/L$$

Yield Ca-H of 100 mg/L "as $CaCO_3$" = $2 \times 1 \ mM = 2 \ meq/L$

OR $\frac{100 \ mg/L}{2.0} =$ **50 mg/L = 1.0 meq/L**

Now can use "as $CaCO_3$" for anything we'd otherwise use meq/L.

Hence $[Mg^{2+}]$ in mg/L "as $CaCO_3$" (weird, but it does work numerically)

$1\ meq/L\ Mg^{2+} = 50\ mg/L\ Mg^{2+}$ as $CaCO_3$

E.g. $75\ mg/L + 25\ mg/L = 100\ mg/L$
CaH MgH TH

$= 1.5\ meq/L + 0.5\ meq/L = 2.0\ meq/L$

Why? (1) mg/L as $CaCO_3$ = Conc. of lime that dissolved out of rock formation

More usefully:

(2) When we REMOVE X mg/L of hardness (at least Ca-H) we literally produce 2X mg/L of actual $CaCO_{3(s)}$ solids (sludge) (when using lime softening)

Ex: (Simplified)

TH = CaH = 150 mg/L

Want final TH = 75 mg/L

$\Delta TH = (150 - 75) = 75\ mg/L$ (as $CaCO_3$) = 150 mg/L SLUDGE

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

0.75 mM	1.5 mM	0.75 mM	1.5 mM	1.5 mmol ↓
1.5 meq/L	1.5 meq/L	1.5 meq	1.5 meq	3.0 meq/L
75 mg/L	75 mg/L	75 mg/L	75 mg/L	150 mg/L SLUDGE

Alkalinity also in mg/L (as CO_3) (or meq/L)

50 mg/L Alk = 1 meq/L Alk

Quick Review of CO_3 Chemistry

$CO_{2(g)}$

$CO_{2(aq)} + H_2O \rightarrow H_2CO_3$ } $H_2CO_3^* \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$

$K_{a_1} = 10^{-6.3}$ $K_{a_2} = 10^{-10.3}$

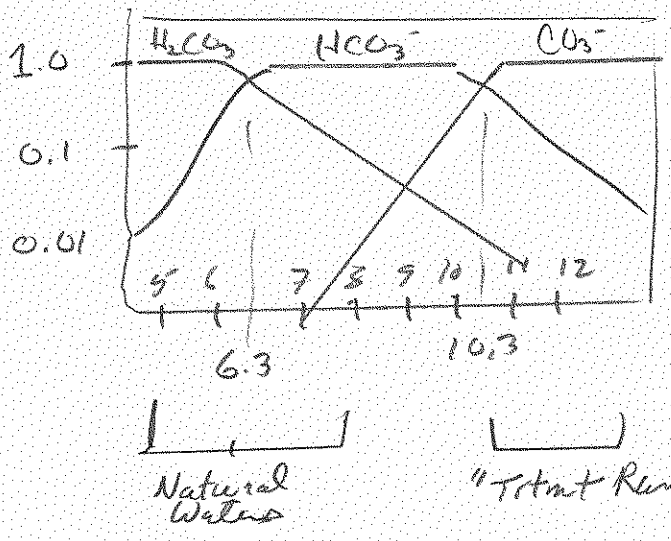
$[H_2CO_3^*] = P_{CO_2} \cdot 10^{-1.5}$ $pK_{a_1} = 6.3$ $pK_{a_2} = 10.3$

$$\frac{(H^+)(HCO_3^-)}{(H_2CO_3)^*} = 10^{-6.3} \qquad \frac{(H^+)(CO_3^{2-})}{HCO_3^-} = 10^{-10.3}$$

AND

$$CaCO_{3(s)} \rightleftharpoons Ca^{2+} + CO_3^{2-}$$

$$K_{sp} = 10^{-8.4} = [Ca^{2+}][CO_3^{2-}]$$



pH < 5 ~All $H_2CO_3^*$

pH 5 - 7 $H_2CO_3^* + HCO_3^-$] Natural water

pH 7 - 9 ~All HCO_3^-]

pH 9 - 11 $CO_3^{2-} + HCO_3^-$] Treat Rang

pH 11 → 14 ~All CO_3^{2-}]

SAY PH 7, HARD WATER

$Ca^{2+} + 2HCO_3^-$

LIME ADDITION

$H_2CO_3^* + OH^-$

HOW MUCH

$Ca^{2+} + CO_3^{2-} + H_2O$

$CaCO_{3(s)}$

(1) $OH^- + H_2CO_3^* \overset{?}{=} HCO_3^- + H_2O$

(2) $OH^- + HCO_3^- = CO_3^{2-} + H_2O$

$[H_2CO_3^*] + 2[HCO_3^-] = \text{Final } [CO_3^{2-}]$

(Already there)

THEN

$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_{3(s)}$

FINAL

$Ca^{2+} + CO_3^{2-} \leftrightharpoons$ 

LEFT BEHIND (OK)

"RESIDUAL CO_3"

↑ ~ 0.6 meq/L

30 mg/L