

Lafayette College
Department of Civil and Environmental Engineering

CE 321: Environmental Engineering and Science

Fall 2013

Homework #12

Due Monday: 12/9/13

SOLUTIONS – Handed out 2013

The town of Easton is considering the use of a Pocono lake as a new water supply during the reconstruction of the main water treatment plant. The new supply will support a 20 million-gallon per day usage. A water analysis has been conducted at a local lab to characterize the lake water; the results are as follows:

Sodium = 55.2 mg/L

Alkalinity = 151.5 mg/L as CaCO₃

Calcium = 51.0 mg/L

Chloride = 28.12 mg/L

Iron (III) = 0.04 mg/L

Fluoride = 0.4 mg/L

Magnesium = 10.68 mg/L

Nitrate = 1.3 mg/L

Potassium = 3.7 mg/L

Sulfate = 102.0 mg/L

The town did not have the CO₂ tested. You, as a well-trained environmental civil engineer, are able to calculate the approximate concentration of CO₂ knowing the pH. Be certain to define Total Hardness (TH), Carbonate Hardness (CH), and Non-Carbonate Hardness (NCH).

Further Information:

pH = 7.9

Cost of CaO = \$0.10/lb

Cost of Soda Ash = \$0.05/lb.

Cost of trucking *sludge* to a landfill = \$20/ton

* Assume the *sludge* after dewatering is 12% solids by weight

Because you are Lafayette College civil engineering student you are well versed in lime/soda softening techniques. For this reason you are given the job of determining the following using the theoretical method of lime/soda ash softening:

- 1) Calculate the amount of CO₂ present in the system.
- 2) Draw a “Milliequivalent Bar Graph.”
- 3) Report the Total Hardness (TH), Carbonate Hardness (CH), and Non-Carbonate Hardness (NCH) as mg/L as CaCO₃.
- 4) How much lime as CaO would be needed considering the theoretical approach to the lime/soda ash softening process?
- 5) How much soda ash (Na₂CO₃) would be needed to complete the lime/soda ash process to remove all of the hardness?
- 6) How much sludge would be produced?
- 7) Total cost of chemicals and sludge disposal per month?
- 8) Total Dissolved Solids (TDS) after treatment?

SOLUTIONS

1) Calculate the amount of CO₂ present in the system

Alkalinity is given as CaCO₃. Most waterways have a pH range of 6 – 9, this one is at 7.9, therefore the predominate form of alkalinity would be bicarbonate (HCO₃⁻). The following calculation is to convert the CaCO₃ to HCO₃⁻. **151.5 (61/50) = 184.83 mg/L**

Cation	Conc mg/L	EW mg/mq	MillE meq/L	CaCO ₃ mg/L	Anion	Conc mg/L	EW mg/mq	MillE meq/L	CaCO ₃ (mg/L)
Na ⁺	55.20	23	2.4	120.0	HCO ₃ ⁻	184.83	61	3.03	151.5
Ca ²⁺	51.00	20	2.55	127.5	Cl ⁻	28.12	35.45	0.79	39.5
Fe ³⁺	0.04	18.61	2.15E-3	0.107	Fl ⁻	0.4	10	2.10E-2	1.05
Mg ²⁺	10.68	12.15	0.87	43.5	NO ₃ ⁻	1.30	62	2.13E-2	1.06
K ⁺	3.70	39.09	9.46E-2	4.73	SO ₄ ²⁻	102.0	48.02	2.12	106.00

pH is give at 7.9, Therefore the hydrogen ion concentration [H⁺] = 10^{-7.9} = **1.26E-8 mole/L**

We have learned that the Molar Concentration of CO₂ = to H₂CO₃. The reason has to do with equilibrium shifts in water. Since the weak acid, Carbonic Acid (H₂CO₃), is pH dependent and we know that typical pH values of waterways range from about 6 to 9 we know that due to speciation of the H₂CO₃ it will be present as bicarbonate (HCO₃⁻). And based on research of how CO₂ speciates as it interacts with the water, researchers have found that the concentration of the intermediate specie, H₂CO₃, is about 0....therefore the forms of the weak acid present are CO₂ and HCO₃⁻. The following stoichiometric sequence demonstrates how CO₂ in the atmosphere enters the water to for an aqueous form of CO₂ and then interacts with water molecules. Therefore, as outlined in this discussion, at equilibrium the two forms of the weak acid (i.e., two factions) that are present are **CO₂ (aq)** and **HCO₃⁻**



We know that pK_{a1} for the equilibrium of H₂CO₃ to HCO₃⁻ is 6.35 (K_{a1} = **4.45E-7**) and the equilibrium relationship is stated as: $K_{a1} = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3]}$

Molar Concentration of [HCO₃⁻] = Conc/MW = 0.18483g/L / 61 g/mole = **3.03E-3 mole/L**

Solving for CO₂ molar concentration

$$[\text{CO}_2] = [\text{H}_2\text{CO}_3] \rightarrow K_{a1} = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3]} \rightarrow \mathbf{4.45E-7 \text{ mole/L}} = \frac{[0.00303 \text{ mole/L}][1.26E-8 \text{ mole/L}]}{[\text{CO}_2]}$$

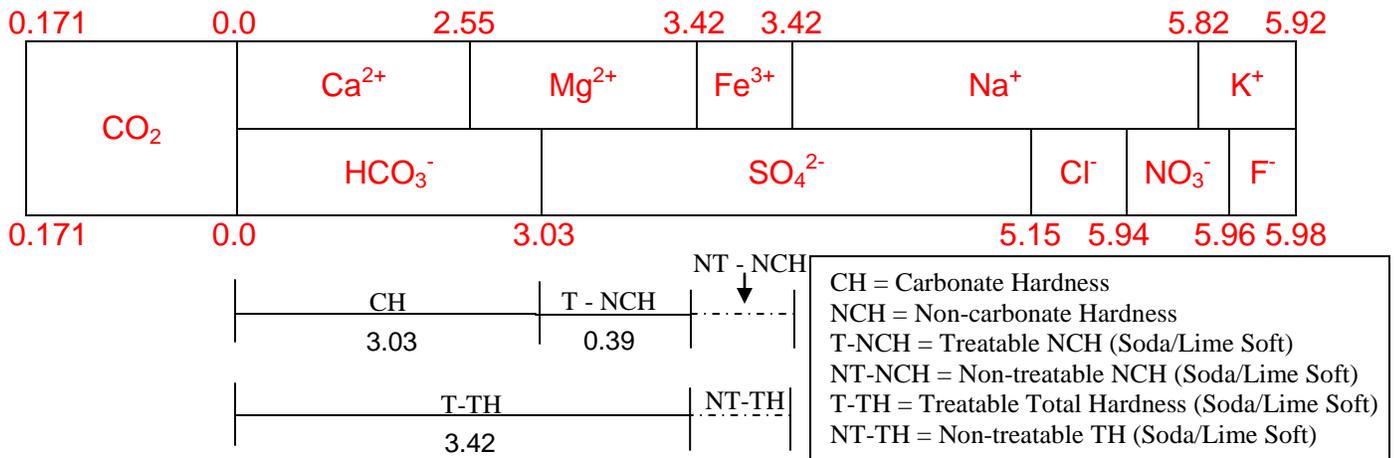
$$[\text{CO}_2] = \mathbf{8.57E-5 \text{ mol/L}};$$

therefore the concentration of CO₂ is **8.57E-5 mol/L** x 44 g/mol x 1000 mg/g = **3.77 mg/L**

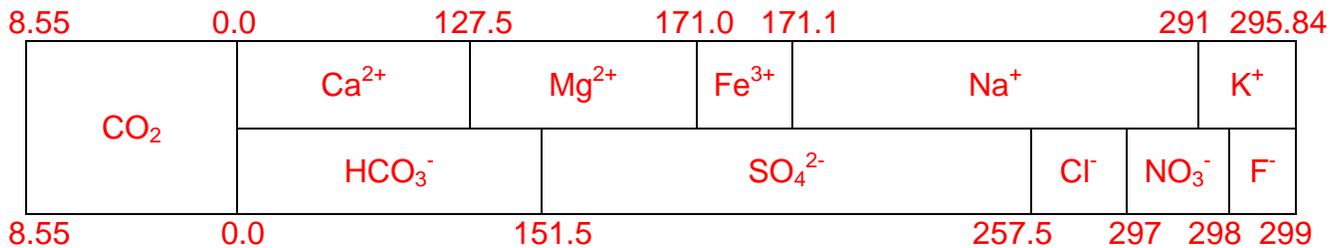
The concentration as milliequivalent/L is 3.77 mg/L / ((44 mg/meq)/2) = 0.171 meq/L

2) Draw a "Milliequivalent Bar Graph."

Milliequivalent Bar Chart (meq/L)



Calcium Carbonate (CaCO₃) Bar Chart (mg/L as CaCO₃)



Check Cation/Anion → +/- 5%:

$$\left(\frac{5.98 - 5.92}{5.92} \right) * 100 = 1.01\% \rightarrow \text{The system checks within specified boundaries.}$$

T-TH = 171.0 mg/L as CaCO₃ and TH = 171.1 mg/L as CaCO₃

CH = 151.5 mg/L as CaCO₃

T-NCH = 19.5 mg/L as CaCO₃ and NCH = 20.0 19.5 mg/L as CaCO₃

TDS – Total dissolved solids – two important considerations when calculating TDS

- 1) TDS is not reported as any particular chemical; therefore you simply add the weight of each compound.
- 2) If a TDS test is performed by evaporating the water in a crucible, it is important to know the HCO₃⁻ (bicarbonate) will be converted to carbonate and precipitate out as CaCO₃ or MgCO₃ (Only one CO₃⁺² to each Ca⁺² or Mg⁺²...not two...in other words, an equivalent amount of alkalinity will associate with Ca⁺² or Mg⁺²). The HCO₃⁻ that remains in the water will convert to H₂O vapor and CO₂ gas. (remember, with a charge of one there would be 2 HCO₃⁻ associated with each Ca⁺² or Mg⁺²) So the weight of CO₃⁺² would be 184.83 (30/61) = **90.90 mg/L**

TDS before Treatment = 55.20 mg/L + 51.00 mg/L + 0.04 mg/L + 10.68 mg/L + 3.70 mg/L + 90.90 mg/L + 28.12 mg/L + 0.4 mg/L + 1.30 mg/L + 102.0 mg/L = 343.34 mg/L

3) Report the Total Hardness (TH), Carbonate Hardness (CH), and Non-Carbonate Hardness (NCH) as mg/L as CaCO₃.

0.171	0.0	2.55	3.42	3.42		5.82	5.92
CO ₂	Ca ²⁺	Mg ²⁺	Fe ³⁺	Na ⁺			K ⁺
	HCO ₃ ⁻		SO ₄ ²⁻		Cl ⁻	NO ₃ ⁻	F ⁻
0.171	0.0	3.03			5.15	5.94	5.96 5.98

Carbonate Hardness Noncarbonate Hardness



CH = 151.5 mg/L as CaCO₃

Treatable NCH = 19.5 mg/L as CaCO₃ treatable by the Lime/Soda Softening process

Total NCH = 20.0 19.5 mg/L as CaCO₃

Total Hardness



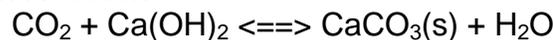
Treatable TH = 171.0 mg/L as CaCO₃ Ca²⁺ and Mg²⁺ - by the Lime/Soda Softening process

Total Hardness = 171.1 mg/L as CaCO₃

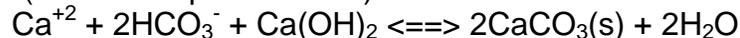
4) How much lime as **CaO** would be needed considering the theoretical approach to the *lime/soda ash softening process*? The only hardness that can be removed using the Lime/Soda Ash Softening process is Ca²⁺ and Mg²⁺.

5 Overall Reactions that are considered in Lime/Soda Softening:

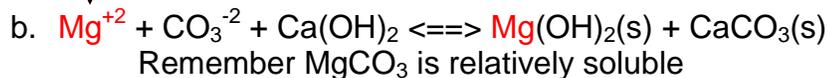
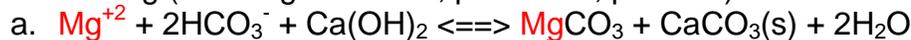
1) Neutralization Reaction



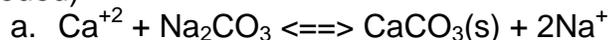
2) CH due to Ca (must raise pH to > 10.3)



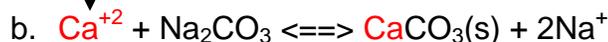
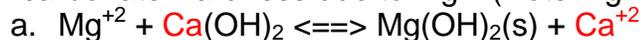
3) CH due to Mg (two stage reaction, pH > 10.3, pH > 11)



4) Noncarbonate Hardness due to Ca²⁺ (no further OH⁻ needed to adjust pH, CO₃⁻² needed)



5) Noncarbonate Hardness due to Mg²⁺ (Note Mg⁺² removed but not Ca⁺²)



Ca²⁺ and Mg²⁺ Ratio/Assessment Table – Milliequivalence						
Eq. #	Equivalent Ratios			Chemical/Sludge Assessment (MILLE)		
	Lime	Soda Ash	CaCO ₃ /MgOH ₂	Lime	Soda	CaCO ₃ /MgOH ₂
1	1:1	-	1:1 / -	0.171	-	0.171 / -
2	1:1	-	1:2 / -	2.55	-	2(2.55)/ -
3	1:2	-	1:2 / 1:1	2(0.48)	-	2(0.48) / 0.48
4	-	1:1	1:1 / -	-	-	-
5	1:1	1:1	1:1 / 1:1	0.39	0.39	0.39 / 0.39
Totals				4.071	0.39	6.621 / 0.87

Ca²⁺ and Mg²⁺ Ratio/Assessment Table – Calcium Carbonate						
Eq. #	Equivalent Ratios			Chemical/Sludge Assessment (CaCO ₃)		
	Lime	Soda Ash	CaCO ₃ /MgOH ₂	Lime	Soda	CaCO ₃ /MgOH ₂
1	1:1	-	1:1 / -	8.55	-	8.55 / -
2	1:1	-	1:2 / -	127.5	-	2(127.5) / -
3	1:2	-	1:2 / 1:1	2(24.0)	-	2(24.0)/ 24.0
4	-	1:1	1:1 / -	-	-	-
5	1:1	1:1	1:1 / 1:1	19.5	19.5	19.5 / 19.5
Totals				203.55	19.5	331.05 / 43.50

Therefore based on the assessment table and considering the appropriate equiv wts.:

EW of Lime, also call Quick Lime (CaO) = 56 mg/mmole / 2 meq/mmole = 28 mg/meq

EW of Slake Lime (Ca(OH)₂) = 74 mg/mmole / 2 meq/mmole = 37 mg/meq

EW of Soda Ash (Na₂CO₃) = 106 mg/mmole / 2 meq/mmole = 53 mg/meq

Calculating the amount of Quick Lime (CaO) needed for the LIME/SODA process

NOTE: In equations 1-5 slake lime is represented. It is important to note that an equivalent amount of quick lime could also be used.

Calculated using Quick Lime

Lime as CaO = (4.071 meq/L) x 28 mg/meq = **113.99 mg/L of Quick Lime NEEDED**

IF Slake Lime were used....

Calculated using Slake Lime

Lime as Ca(OH)₂ = (4.071 meq/L) x 37.0 mg/meq = **150.63 mg/L of Slake Lime**

- 5) How much Soda Ash (Na_2CO_3) would be needed to complete the lime/soda ash process to remove all of the hardness?

$$\text{Soda Ash } (\text{Na}_2\text{CO}_3) = 0.39 \text{ meq/L} \times 53 \text{ mg/meq} = \mathbf{20.67 \text{ mg/L of Soda Ash NEEDED}}$$

- 6) How much sludge would be produced?

$$\begin{aligned} \text{EW of CaCO}_3 &= 100 \text{ mg/mole} / 2 \text{ meq/mole} = 50 \text{ mg/meq} \\ \text{EW of MgOH}_2 &= 58 \text{ mg/mole} / 2 \text{ meq/mole} = 29 \text{ mg/meq} \end{aligned}$$

SLUDGE from EQUATION:

$$\begin{aligned} 1 &= \text{Neutralization} = \text{all CaCO}_3 \text{ sludge} = 0.171 \text{ meq/L} \times 50 \text{ mg/meq} = \mathbf{8.55 \text{ mg/L}} \\ 2 &= \text{CH due to Ca} = \text{all CaCO}_3 \text{ sludge} = 2(2.55 \text{ meq/L}) \times 50 \text{ mg/meq} = \mathbf{255.00 \text{ mg/L}} \\ 3 &= \text{CH due to Mg} = \text{part CaCO}_3 \text{ sludge and part MgOH}_2 \text{ sludge} \\ &\quad \text{CaCO}_3 \text{ sludge} = 2(0.48 \text{ meq/L}) \times 50 \text{ mg/meq} = \mathbf{48.00 \text{ mg/L}} \\ &\quad \text{MgOH}_2 \text{ sludge} = 0.48 \text{ meq/L} \times 29 \text{ mg/meq} = \mathbf{13.92 \text{ mg/L}} \\ 5 &= \text{Noncarbonate Hardness due to Mg}^{+2} = \text{part CaCO}_3 \text{ sludge and part MgOH}_2 \text{ sludge} \\ &\quad \text{CaCO}_3 \text{ sludge} = 0.39 \text{ meq/L} \times 50 \text{ mg/meq} = \mathbf{19.50 \text{ mg/L}} \\ &\quad \text{MgOH}_2 \text{ sludge} = 0.39 \text{ meq/L} \times 29 \text{ mg/meq} = \mathbf{11.31 \text{ mg/L}} \\ \hline &\quad \mathbf{\text{Total WEIGHT of SLUDGE} = 356.28 \text{ mg/L}} \end{aligned}$$

$$\mathbf{\text{Total WEIGHT of WET SLUDGE @ 12\% Solids} = 356.28 \text{ mg/L} / 0.12 = 2,968.75 \text{ mg/L}}$$

- 7) Total cost of chemicals and sludge disposal per month?

Cost of Quick Lime

$$113.99 \text{ mg/L} * 8.345 \frac{\# \cdot \text{L}}{\text{mg} \cdot \text{MGal}} * 20 \text{ MGal/day} * 30 \text{ day/Month} * 0.1 \text{ \$/\#} = \mathbf{\$57,074.79/\text{month}}$$

Cost of Soda Ash

$$20.67 \text{ mg/L} * 8.345 \frac{\# \cdot \text{L}}{\text{mg} \cdot \text{MGal}} * 20 \text{ MGal/day} * 30 \text{ day/Month} * 0.05 \text{ \$/\#} = \mathbf{\$5,174.73/\text{month}}$$

Cost for WET Sludge Disposal

$$\frac{356.28 \text{ mg/L} * 8.345 \frac{\# \cdot \text{L}}{\text{mg} \cdot \text{MGal}} * 20 \text{ MGal/day} * 30 \text{ day/Month} * 20 \text{ \$/ton}}{2000 \#/\text{ton} * 0.12} = \mathbf{\$148,657.7/\text{month}}$$

TOTAL COST = Cost of Quick Lime + Cost of Soda Ash + Cost for **Dry** Sludge Disposal

$$= \mathbf{\$57,074.79/\text{month} + \$5,174.73/\text{month} + \$17,838.93/\text{month} = \$80,087.10/\text{month}}$$

TOTAL COST = Cost of Quick Lime + Cost of Soda Ash + Cost for **WET** Sludge Disposal

$$= \mathbf{\$57,074.79/\text{month} + \$5,174.73/\text{month} + \$148,657.7/\text{month} = \$210,907.27/\text{month}}$$

Total Dissolved Solids (TDS) after treatment?

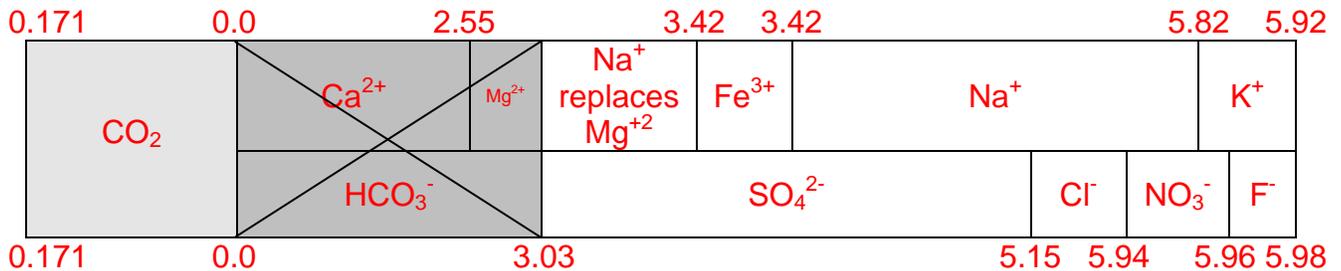
Initial Total Dissolved Solids (TDS)

As outlined in Part 2:

- 1) TDS is not reported as any particular chemical; therefore you simply add the mass/L of each compound.
- 2) If a TDS test is performed by evaporating the water in a crucible, it is important to know the HCO_3^- (bicarbonate) will be converted to carbonate and precipitate out as CaCO_3 or MgCO_3 (Only one CO_3^{+2} to each Ca^{+2} or Mg^{+2} ...not two...in other words, an equivalent amount of alkalinity will associate with Ca^{+2} or Mg^{+2}). The HCO_3^- that remains in the water will convert to H_2O vapor and CO_2 gas. (remember, with a charge of one there would be 2 HCO_3^- associated with each Ca^{+2} or Mg^{+2}) So the weight of CO_3^{+2} would be **184.83 (30/61) = 90.90 mg/L**

TDS before Treatment = 55.20 mg/L + 51.00 mg/L + 0.04 mg/L + 10.68 mg/L + 3.70 mg/L + **90.90 mg/L** + 28.12 mg/L + 0.4 mg/L + 1.30 mg/L + 102.0 mg/L = **343.34 mg/L**

Assessment of finished water TDS



We always disregard CO_2 when calculating TDS, it converts back to a gas. Ca^{2+} , Mg^{2+} and the bicarbonate have been removed from the water through the lime softening process, they became part the sludge that was hauled off. Also the Mg^{2+} NCH was replaced by Na^+ as shown in Equation 5.

Therefore:

Added Na^+ that replaces Mg^{2+} = $(3.42 \text{ meq/L} - 3.03 \text{ meq/L}) * 23 \text{ mg/meq} = \mathbf{8.97 \text{ mg/L}}$

Summing the cations and anions in the finished water:

$8.97 \text{ mg/L} + 55.20 \text{ mg/L} + 0.04 \text{ mg/L} + 3.70 \text{ mg/L} + 28.12 \text{ mg/L} + 0.4 \text{ mg/L} + 1.30 \text{ mg/L} + 102.0 \text{ mg/L} = \mathbf{199.73 \text{ mg/L of remaining TDS}}$ (plus whatever ions might be missing)