Lafayette College
Department of Civil and Environmental Engineering

CE 321: Environmental Engineering and Science **Fall 2012**

Homework #11
Due Friday: 12/4-6/12
SOLUTIONS – Handed out 2012

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 $CaCO_3$
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 CO_2 tested. You, as a well-trained environmental civil engineer, are able to calculate the approximate concentration of CO_2 knowing the pH. Be certain to define Total Hardness (TH), Carbonate Hardness (CH), and Non-Carbonate Hardness (NCH).

<u>Further Information</u>:
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 CO_2 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 $CaCO_3$.

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 (Na_2CO_3) 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 CO_2 present in the system

Alkalinity is given as $CaCO_3$. Most waterways have a pH range of 6 – 9, this one is at 7.9, therefore the predominate form of alkalinity would be bicarbonate (HCO_3^-). The following calculation is to convert the $CaCO_3$ to HCO_3^-. 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 CO_2 = to H_2CO_3. The reason has to do with equilibrium shifts in water. Since the weak acid, Carbonic Acid (H_2CO_3), 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 H_2CO_3 it will be present as bicarbonate (HCO_3^-). And based on research of how CO_2 speciates as it interacts with the water, researchers have found that the concentration of the intermediate specie, H_2CO_3, is about 0….therefore the forms of the weak acid present are CO_2 and HCO_3^-. 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 **CO_2 (aq)** and **HCO_3^-**

$$CO_2\,(gas) \leftrightarrow \mathbf{CO_2\,(aq)} + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + \mathbf{HCO_3^-}$$

We know that pK_{a1} for the equilibrium of H_2CO_3 to HCO_3^- is 6.35 (K_{a1} = 4.45E-7) and the equilibrium relationship is stated as: $K_{a1}=\frac{[HCO_3^-][H^+]}{[H_2CO_3]}$

Molar Concentration of $[HCO_3^-]$ = Conc/MW = 0.18483g/L / 61 g/mole = 3.03E-3 mole/L

Solving for CO_2 molar concentration

$[CO_2] = [H_2CO_3] \rightarrow K_{a1} = \frac{[HCO_3^-][H^+]}{[H_2CO_3]} \rightarrow$ 4.45E-7 mole/L = $\frac{[0.00303\,{}^{mole}/_{L}][1.26\text{E}-8\,{}^{mole}/_{L}]}{[CO2]}$

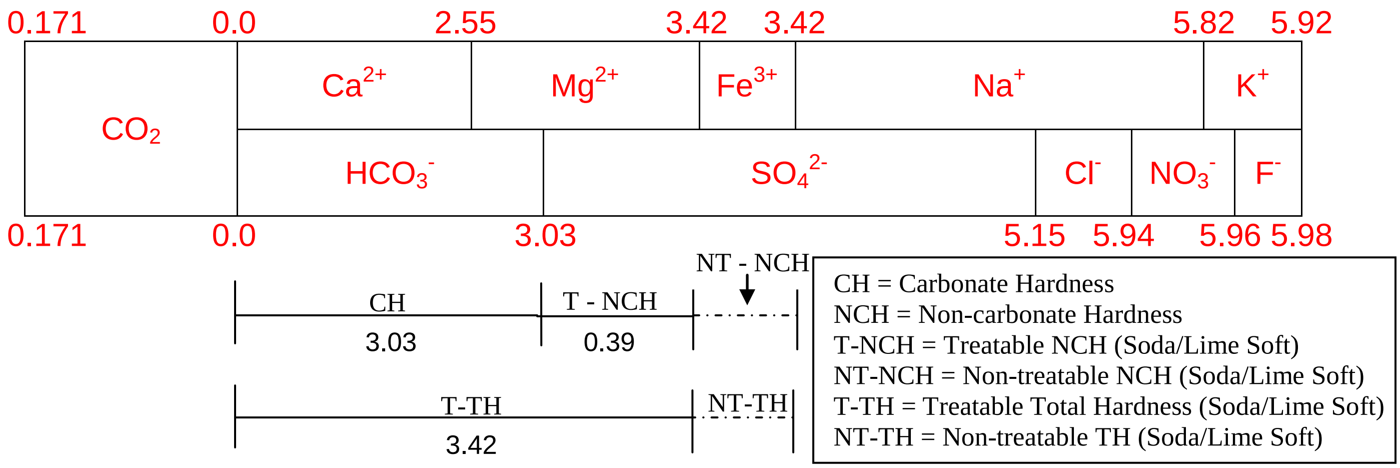
$[CO_2]$ = **8.57E-5 mol/L**;

therefore the concentration of CO_2 is **8.57E-5 mol/L** x 44 g/mol x 1000 mg/g = **3.77 mg/L**

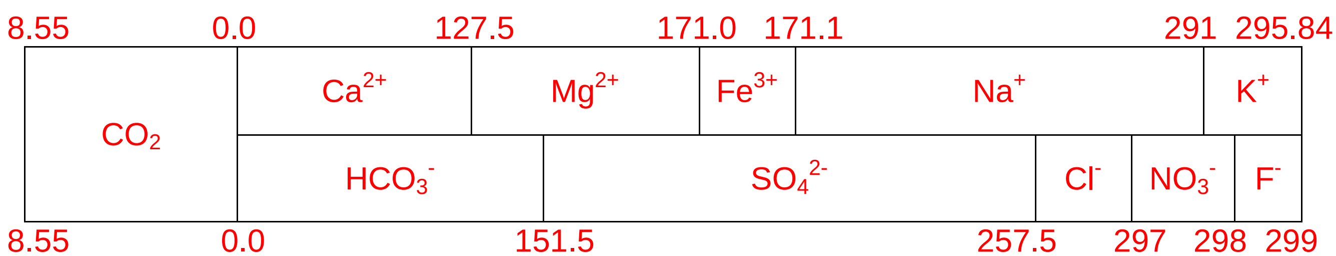
The concentration as milliequivalent/L is 3.77 mg/L / ((44 mg/meq)/2) = 0.171 meq/L

2) Draw a "Milliequivalent Bar Graph."

Milliequivalent Bar Chart (meq/L)



Calcium Carbonate ($CaCO_3$) Bar Chart (mg/L as $CaCO_3$)



Check Cation/Anion ➔ +/- 5%:

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

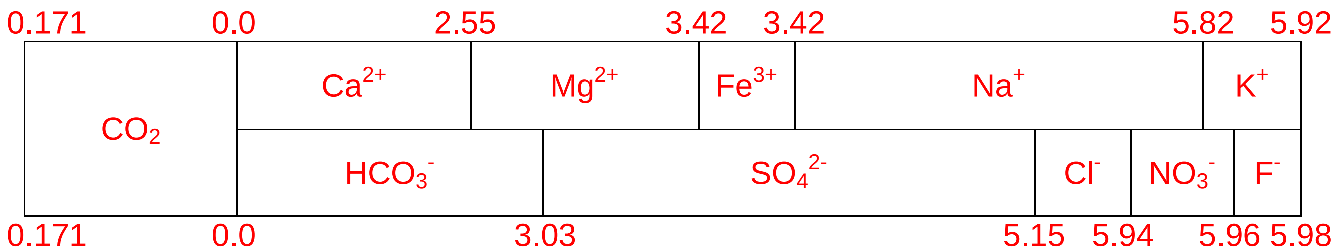
T-TH = 171.0 mg/L as $CaCO_3$ and TH = 171.1 mg/L as $CaCO_3$
CH = 151.5 mg/L as $CaCO_3$
T-NCH = 19.5 mg/L as $CaCO_3$ and NCH = 20.0 19.5 mg/L as $CaCO_3$

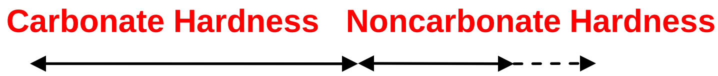
TDS – Total dissolved solids – two important considerations when calculating TDS

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 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

3) Report the Total Hardness (TH), Carbonate Hardness (CH), and Non-Carbonate Hardness (NCH) as mg/L as $CaCO_3$.





CH = 151.5 mg/L as $CaCO_3$

Treatable NCH = 19.5 mg/L as $CaCO_3$ treatable by the Lime/Soda Softening process

Total NCH = 20.0 19.5 mg/L as $CaCO_3$

Treatable TH = 171.0 mg/L as $CaCO_3$ Ca^{2+} and Mg^{2+} - by the Lime/Soda Softening process

Total Hardness = 171.1 mg/L as $CaCO_3$

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 Ca^{2+} and Mg^{2+}.

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

1) Neutralization Reaction

$$CO_2 + Ca(OH)_2 \Longleftrightarrow CaCO_3(s) + H_2O$$

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

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

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

a. $Mg^{+2} + 2HCO_3^- + Ca(OH)_2 \Longleftrightarrow MgCO_3 + CaCO_3(s) + 2H_2O$

b. $Mg^{+2} + CO_3^{-2} + Ca(OH)_2 \Longleftrightarrow Mg(OH)_2(s) + CaCO_3(s)$

Remember $MgCO_3$ is relatively soluble

4) Noncarbonate Hardness due to Ca^{+2} (no further OH^- needed to adjust pH, CO_3^{-2} needed)

a. $Ca^{+2} + Na_2CO_3 \Longleftrightarrow CaCO_3(s) + 2Na^+$

5) Noncarbonate Hardness due to Mg^{+2} (Note Mg^{+2} removed but not Ca^{+2})

a. $Mg^{+2} + Ca(OH)_2 \Longleftrightarrow Mg(OH)_2(s) + Ca^{+2}$

b. $Ca^{+2} + Na_2CO_3 \Longleftrightarrow CaCO_3(s) + 2Na^+$

Ca^{2+} and Mg^{2+} Ratio/Assessment Table – Milliequivalence						
	Equivalent Ratios			Chemical/Sludge Assessment (MillE)		
Eq. #	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

Ca^{2+} and Mg^{2+} Ratio/Assessment Table – Calcium Carbonate						
	Equivalent Ratios			Chemical/Sludge Assessment ($CaCO_3$)		
Eq. #	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 (Na_2CO_3) = 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?

Soda Ash (Na_2CO_3) = 0.39 meq/L x 53 mg/meq = **20.67 mg/L of Soda Ash NEEDED**

6) How much sludge would be produced?

EW of $CaCO_3$ = 100 mg/mmole / 2 meq/mmole = 50 mg/meq
EW of $MgOH_2$ = 58 mg/mmole / 2 meq/mmole = 29 mg/meq

SLUDGE from EQUATION:

1= Neutralization = all $CaCO_3$ sludge = 0.171 meq/L x 50 mg/meq = **8.55 mg/L**
2 = CH due to Ca = all $CaCO_3$ sludge = 2(2.55 meq/L) x 50 mg/meq = **255.00 mg/L**
3 = CH due to Mg = part $CaCO_3$ sludge and part $MgOH_2$ sludge
$CaCO_3$ sludge = 2(0.48 meq/L) x 50 mg/meq = **48.00 mg/L**
$MgOH_2$ sludge = 0.48 meq/L x 29 mg/meq = **13.92 mg/L**
5 = Noncarbonate Hardness due to Mg^{+2} = part $CaCO_3$ sludge and part $MgOH_2$ sludge
$CaCO_3$ sludge = 0.39 meq/L x 50 mg/meq = **19.50 mg/L**
$MgOH_2$ sludge = 0.39 meq/L x 29 mg/meq = **11.31 mg/L**

Total WEIGHT of SLUDGE = 356.28 mg/L

Total WEIGHT of WET SLUDGE @ 12% Solids = 356.28 mg/L/0.12 = 2,968.75 mg/L

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

Cost of Quick Lime

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

Cost of Soda Ash

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

Cost for WET Sludge Disposal

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

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

= $57,074.79/month + $5,174.73/month + $17,838.93/month = $80,087.10/month

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

= $57,074.79/month + $5,174.73/month + $148,657.7/month = $210,907.27/month

Total Dissolved Solids (TDS) after treatment?

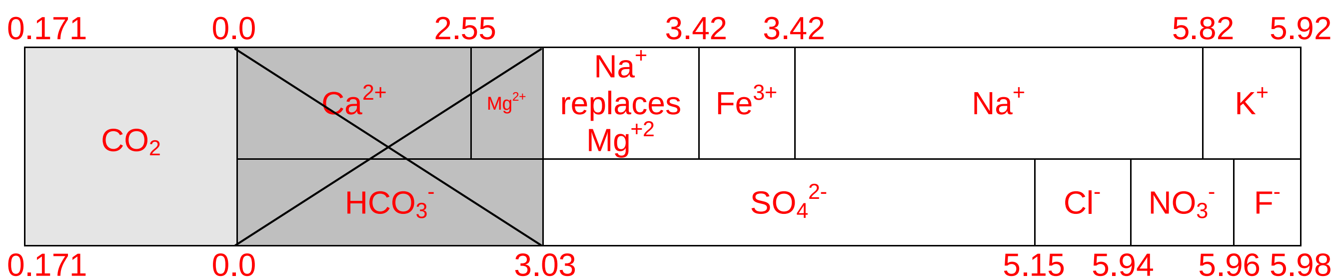
Initial Total Dissolved Solids (TDS)

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, is converts bag 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 replace by Na+ as shown in Equation 5**.**

Therefore:
Added Na^+ that replaces Mg^{2+} = (3.42 meq/L – 3.03 meq/L) * 23 mg/meq = **8.97 mg/L**
Summing the cations and anions in the finished water**:**

8.97 mg/L + 55.20 mg/L + 0.04 mg/L + 3.70 mg/L + 28.12 mg/L + 0.4 mg/L + 1.30 mg/L + 102.0 mg/L = **199.73 mg/L of remaining TDS** (plus whatever ions might be missing)