# CE 418 Homework III

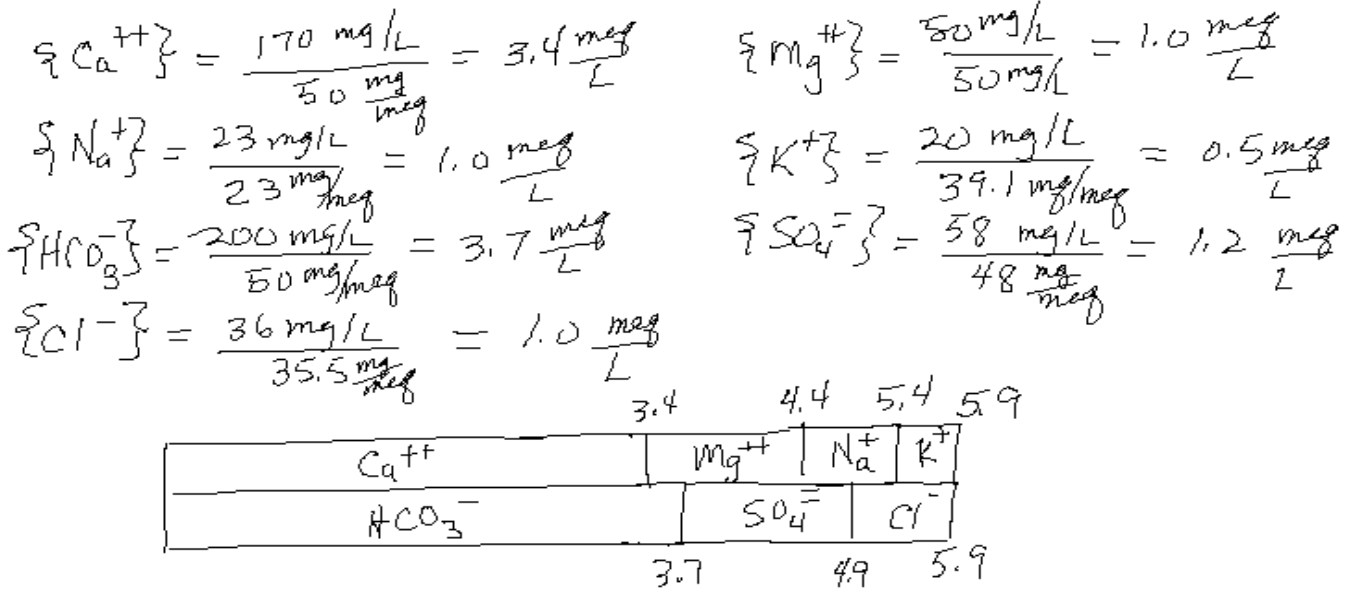Spring 2019                    Due April 5                    B.A. DeVantier

## Problem 1

Class Text Problem 11.5. Draw a milliequivalent-per-liter bar graph for the following water analysis.

calcium hardness = ~~185~~ mg/L          alkalinity = ~~200~~ mg/L

magnesium hardness = 50 mg /L          sulfate ion = 58 mg/L

sodium ion = 23 mg/L                          chloride ion = 36 mg/L

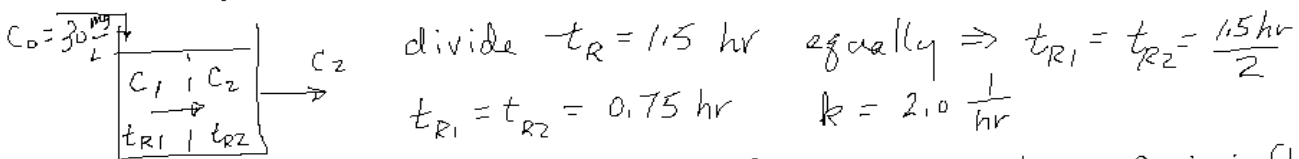potassium ion = 20 mg/L          pH = 7.7

*Except make **calcium hardness = 170 mg/L** and **alkalinity = 185 mg/L**. Note that all hardness and alkalinity concentrations are **as CaCO₃** , and all alkalinity can be assumed to exist as bicarbonate, because pH is in the natural water range of 6.5-9.5.*

$$\{Ca^{++}\} = \frac{170\ mg/L}{50\ \frac{mg}{meq}} = 3.4\ \frac{meq}{L} \qquad \{Mg^{++}\} = \frac{50\ mg/L}{50\ mg/L} = 1.0\ \frac{meq}{L}$$

$$\{Na^{+}\} = \frac{23\ mg/L}{23\ \frac{mg}{meq}} = 1.0\ \frac{meq}{L} \qquad \{K^{+}\} = \frac{20\ mg/L}{39.1\ mg/meq} = 0.5\ \frac{meq}{L}$$

$$\{HCO_3^{-}\} = \frac{200\ mg/L}{50\ mg/meq} = 3.7\ \frac{meq}{L} \qquad \{SO_4^{=}\} = \frac{58\ mg/L}{48\ \frac{mg}{meq}} = 1.2\ \frac{meq}{L}$$

$$\{Cl^{-}\} = \frac{36\ mg/L}{35.5\ \frac{mg}{meq}} = 1.0\ \frac{meq}{L}$$



## Problem 2

Class Text Problem 11.12. A reaction that proceeds by first order irreversible kinetics is an oxidizing chemical A in a wastewater treatment basin with a mean residence time of 1.5 hr. The reaction rate constant is 2.0 hr⁻¹. The basin is unbaffled and may be characterized as two completely mixed tanks in series. If the steady-state influent concentration is 30 mg/l, find the effluent concentration. If baffles are placed in the basin so that it may be characterized as four completely mixed tanks in series and the mean residence time remains constant, find the effluent concentration.

Treating tank as 2 complete mix eactors (CMRs) in series

$C_0 = 30\frac{mg}{L}$

divide $t_R = 1.5$ hr equally $\Rightarrow t_{R1} = t_{R2} = \frac{1.5\ hr}{2}$

$t_{R1} = t_{R2} = 0.75$ hr          $k = 2.0\ \frac{1}{hr}$

For a single CMR $C = C_0/(1+k\,t_R)$ where $C_0$ is influent
C is effluent

For 2 CMRs in series effluent of 1st is influent for second

For First: $C_1 = \frac{C_0}{(1+k\,t_R)} = \frac{30\ mg/L}{(1+[2.0\frac{1}{hr}][0.75\,hr])} = 12.0\ mg/L$

For second: $C_2 = \dfrac{(12.0\ mg/L)}{(1+[2.0\ hr][0.75\ hr])} = \underline{\underline{4.8\ mg/L}}$

If 4 CMRs in series $\quad C_4 = C_0\left(\dfrac{C_1}{C_0}\right)\left(\dfrac{C_2}{C_1}\right)\left(\dfrac{C_3}{C_2}\right)\left(\dfrac{C_4}{C_3}\right)$

$t_{Ri} = 0.375\ hr \quad C_4 = (30\ mg/L)\left[\dfrac{1}{1+(2.0\ 1/hr)(0.375\ hr)}\right]^4 = \underline{\underline{3.199\ mg/L}}$

## Problem 3

Class Text Problem 11.17. Define the terms *coagulation* and *flocculation* in reference to destabilization of colloidal suspensions. When these terms are used by an environmental engineer in reference to water treatment processes, what are their meanings.

**Coagulation is the reduction of electrical repulsive forces of colloidal particles by adding coagulant chemicals. Flocculation is agglomeration by joining of the colloidal particles once the repulsive forces have been reduced. In a water treatment plant, the coagulation occurs in a mixing tank and the agglomeration process is accelerated by churning of the water to increase the rate of particle collision. Agglomerated masses then are sent to settling units and/or filtration. Flocculation units are volumes in which gentle mixing allows particle growth in chemically destabilized colloidal suspensions.**

## Problem 4

For the water of **Problem 1**, a) calculate the lime and soda ash dose necessary for excess lime (1 meq/L) and soda ash treatment, b) calculate the $CO_2$ dose to neutralize the excess and convert 75% of the alkalinity in the finished water to bicarbonate, c) draw the finished water bar chart.

(a) Raw water

|  | 3.4 | 4.4 | 5.4 | 5.9 |
|---|---|---|---|---|
| $Ca^{++}$ | $Mg^{++}$ | $Na^+$ | $K^+$ | |
| $HCO_3^-$ | $SO_4^=$ | $Cl^-$ | | |
|  | 3.7 | 4.9 | 5.9 | |

Dose Chart:

| Component | Lime | Soda |
|---|---|---|
| $Ca(HCO_3)_2$ | 3.4 | 0 |
| $Mg(HCO_3)_2$ | 2(0.3) | 0 |
| $Mg\,SO_4$ | 0.7 | 0.7 |
| Excess lime  *(can be anything from 1.0 to 1.5)* | 1.0 | 0 |
|  | 5.7 | 0.7 |

So doses: $CaO \rightarrow 5.7\ \dfrac{meq}{L} \qquad Na_2CO_3 \rightarrow 0.7\ \dfrac{meq}{L}$

(b) after dose, the bar chart would be

| 1.0 | 0 | 0.6 0.8 | | 2.5 3.0 | |
|---|---|---|---|---|---|
| $Ca^{++}$ | $Ca^{++}$ | $Mg$ | $Na^+$ | $K^+$ | |
| $OH^-$ | $OH$ | $CO_3^=$ | $SO_4^=$ | $Cl^-$ | |
| 1.0 | 0 | 0.2 0.8 | 2.0 | 3.0 | |

note: $\{Ca^{++}\} = \{CO_3^=\} = 0.6 \qquad \{Mg^{++}\} = \{OH^-\} = 0.2 \quad$ practical precip. limits

all others stay the same except $\{Na^+\} = 1.0 + 0.7 = 1.7$
            ↑ original    ↑ Soda dose

$CO_2$ for excess → 1.0     (could be up to 1.5)

$CO_2$ for 3/4 $\{alk\} = \{OH^-\} + \{CO_3^=\} = 0.8$   see (a)

→ 3/4(0.8) = 0.6 meq/L

Note rxns: $H_2CO_3 + OH^- → H_2O + HCO_3^-$          for $CO_2$ as $H_2CO_3$

$H_2CO_3 + CO_3^= → 2 HCO_3^-$

$OH^-$ converted first, then   0.6 − 0.2 = 0.4 meq/L

remaining is 0.2 $CO_3^=$ not converted

dose $CO_2$ → 1.0 + 0.6 = 1.6 meq/L

Text adds addition 0.2 meq/L (so OK if you wish)

For finished water, excess precipitates

$\{Ca^{++}\} = 0.6$ meq/L   $\{Mg^{++}\} = 0.2$ meq/L   at limits still

3/4 (0.8 $\frac{mg}{L}$) dose produces $\{CO_3^=\} = 0.2$, $\{HCO_3^-\} = 0.6$

all else remains as after doses above



## Problem 5
Rework **Problem 4** for selective calcium removal. Discuss the trade-off involved with the reduced chemicals used compared to the recommended maximum magnesium hardness (Class Text p. 412) for a finished water.

Using raw water chart from previous problem

Dose chart:

| Component | Lime | Soda |
|---|---|---|
| $Ca(HCO_3)_2$ | 3.4 | 0 |
| $Mg(HCO_3)_2$ | 0 | 0 |
| $MgCl_2$ | 0 | 0 |
| excess | 0 | 0 |
| | 3.4 | |

only needed for Mg removal →

allow Mg to remain

$\{CaO\} = 3.4$ meq/L       (mass conc's not requested but ok if calculated — same for previous problem)

## Problem 6

Class Text Problem 11.42 The results of a chlorine demand test on a raw water at 20°C are given in the following table.

| Sample | Chlorine Dose (mg/L) | Residual Chlorine after 10 min Contact (mg/L) |
|---|---|---|
| 1 | 0.2 | 0.19 |
| 2 | 0.4 | 0.37 |
| 3 | 0.6 | 0.51 |
| 4 | 0.8 | 0.50 |
| 5 | 1.0 | 0.20 |
| 6 | 1.2 | 0.40 |
| 7 | 1.4 | 0.60 |
| 8 | 1.6 | 0.80 |

(a) Sketch the chlorine demand curve

**(a) From spreadsheet below, the plot is generated.**

| | Cl Dose | Residual |
|---|---|---|
| 0 | 0 | 0 |
| 1 | 0.2 | 0.19 |
| 2 | 0.4 | 0.37 |
| 3 | 0.6 | 0.51 |
| 4 | 0.8 | 0.5 |
| 5 | 1 | 0.2 |
| 6 | 1.2 | 0.4 |
| 7 | 1.4 | 0.6 |
| 8 | 1.6 | 0.8 |
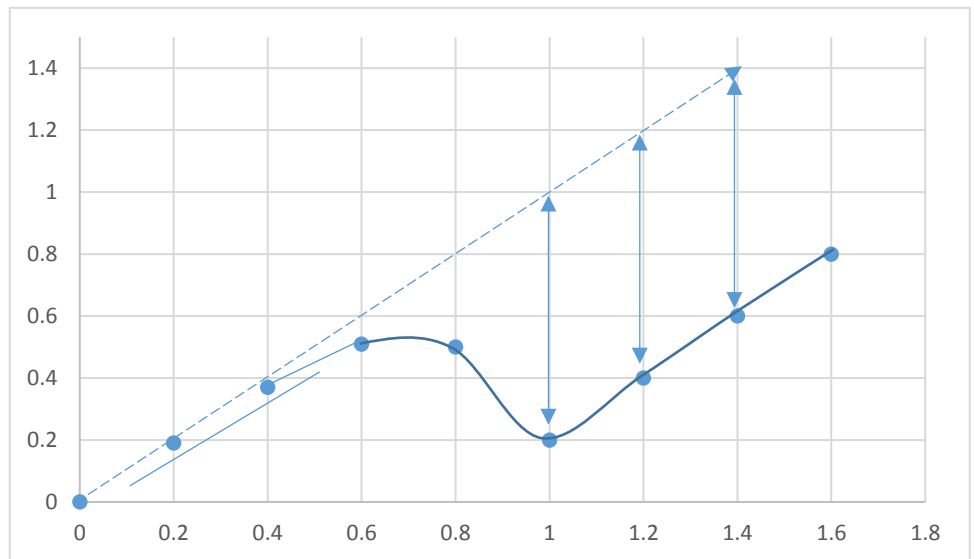


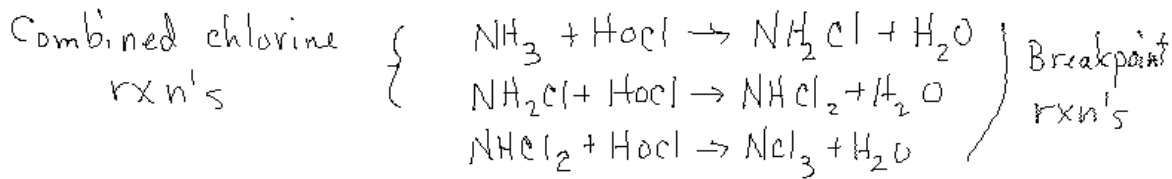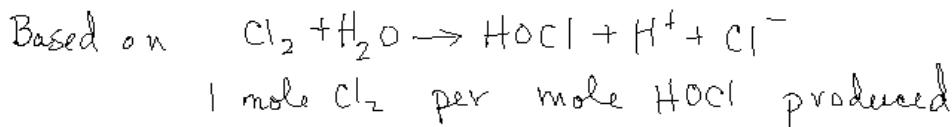(b) What is the chlorine breakpoint dose?
(b) The dose is the independent axis, so the dose at minimum free and combined dose is 1.0 mg/L
(c) What is the chlorine demand at a chlorine dosage of 1.20 mg/L?
(c) The demand at breakpoint is applied (dashed line) minus remaining chlorine (solid line) $= 1.2 - 0.4 = $ **0.8 mg/L.**

## Problem 7

Class Text Problem 11.43 The practice of combined residual chlorination involves feeding both chlorine and anhydrous ammonia. Calculate the stoichiometric ratio of chlorine feed to ammonia feed for combined chloramination. Additionally calculate the theoretical stoichiometric ratio of $Cl_2$ to $NH_3$ to reach breakpoint in wastewater chlorination. Note that you should give the mass not molar stoichiometric ratio in lb/lb. Assume that for combined chlorination in water treatment, the chlorine dose should be approximately half-way between the doses necessary to convert all ammonia to monochloramine and dichloramine forms.

Based on $Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$

1 mole $Cl_2$ per mole $HOCl$ produced

Combined chlorine {$\quad NH_3 + HOCl \rightarrow NH_2Cl + H_2O$ } Breakpoint
rxn's $\quad\quad\quad\quad\quad\quad$ ( $\quad NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O$ ) rxn's
$\quad\quad\quad\quad\quad\quad\quad\quad\quad NHCl_2 + HOCl \rightarrow NCl_3 + H_2O$

Using 1 to 2 moles $HOCl$ (or $Cl_2$) $\Rightarrow$ 1.5 mole $Cl_2$

mass ratio $= \left(1.5 \dfrac{mole\ Cl_2}{mole\ NH_3}\right)\left(\dfrac{71\ g\ Cl_2}{mole\ Cl_2}\right)\left(\dfrac{1\ mole\ NH_3}{17\ g\ NH_3}\right)$ $\dfrac{mole\ Cl_2}{mole\ NH_3}$

$\quad\quad = 6.26 \dfrac{g\ Cl_2}{g\ NH_3}$

Breakpoint uses $3 \dfrac{mole\ Cl_2}{mole\ NH_3}$

so mass ratio $= 2(6.26) = 12.5 \dfrac{g\ Cl_2}{g\ NH_3}$

**Problem 8**

Class Text Problem 11.49. From Table 11.9, what is the C·t value for 99.9% (3-log) inactivation of *Giardia* cysts at a free chlorine residual of 1.0 mg/L, temperature of 10 °C, and pH 7.0? How does a water temperature increase to 20°C affect the C·t value? How does a pH increase to 8.0 affect the C·t value? Also, calculate the empirical temperature correction factors ($\theta$) that the temperature change implies, and compare the pH effect to the empirical EPA equation for 4-log giardia C·t.

From Table 11.9 $\quad$ for $\quad c = 1.0\ mg/L$

$\quad\quad c \cdot t = 112 \left(\dfrac{mg}{L}\right) \cdot min \quad @\ 10°C \quad pH = 7$

$\quad\quad c \cdot t = 56 \left(\dfrac{mg}{L}\right) \cdot min \quad @\ 20°C \quad pH = 7$

$\quad\quad c \cdot t = 162 \left(\dfrac{mg}{L}\right) \cdot min \quad @\ 10°C \quad pH = 8$

increasing T by 10°C decreases c·t by a factor of $\underline{2}$ $\left(\dfrac{112}{56}\right)$

increasing pH from 7 to 8 increase c·t by a factor of $\underline{1.45}$ $\left(\dfrac{162}{112}\right)$

From class derivation $\dfrac{(c \cdot t)_{T_2}}{(c \cdot t)_{T_1}} = \theta^{(T_1 - T_2)} \quad \Rightarrow \dfrac{112}{56} = \theta^{(20-10)}$

or $\dfrac{56}{112} = \theta^{(10-20)}$ $\quad$ solving either yields $\quad \underline{\theta = 1.072}$

4-log empirical eq $\Rightarrow$ $c \cdot t_{99.99} = 0.985\ C^{0.176}\ pH^{2.75}\ T^{-0.147}$

$\dfrac{(c \cdot t)_{pH_1}}{(c \cdot t)_{pH_2}} = \left(\dfrac{7}{8}\right)^n = \dfrac{112}{162}$ $\quad \Rightarrow \underline{n = 2.76}$ $\quad$ (near empir. eq.)

**Problem 9**

Class Text Problem 11.50. A surface water treatment plant at a winter resort city has been designed to process cold, low turbidity water by direct filtration based on the pilot-plant study described in Problem 11.23. The filtered water has a turbidity of less than 0.1 NTU, temperature of 10 °C, and a pH of 7.4 during the period of highest water consumption in the winter. Tracer analyses of the clear-well reservoir are illustrated in Figure 11.28. At the critical hourly flow of 3.0 MGD, $t_{10} = 90$ min. To comply with the EPA surface water disinfection regulation, what free chlorine residual must be maintained in filtered water at the outlet of the clear well? What would be the required dose of chlorine dioxide if it were used instead of chlorine.

Table 11.8 for direct filtration gives 2-log credit of the 3-log req'd & 1-log credit of the 4-log req'd (Giardia) (Virus)

Since dose is what we want to solve for, we must use Table 11.9 iteratively for Giardia

Starting w/ largest dose (1.2 mg/L) @ pH 7 $c \cdot t = 114 \left(\frac{mg}{L}\right) \cdot min$

@ pH 8 $c \cdot t = 166 \left(\frac{mg}{L}\right) \cdot min$ interpolating

$c \cdot t = \frac{0.4}{1}(166-114)+114 = 122 \left(\frac{mg}{L}\right) \cdot min$

This value is for 3-log kill, but only $3-2 = 1$-log is req'd

so $(c \cdot t)_{req} = \frac{1}{3}\left(122 \frac{mg}{L \cdot min}\right) = 40.7 \frac{mg}{L \cdot min}$

$C = \frac{(c \cdot t)_{req}}{t_{10}} = \frac{40.7 \ mg \cdot min/L}{90 \ min} = 0.45 \ mg/L$

@ 0.4 mg/L $(c \cdot t)_{99.9} = 104 \frac{mg \cdot min}{L}$ pH=7, $(c \cdot t)_{99.9} = 149 \frac{mg \cdot min}{L}$ pH=8

@ 0.6 mg/L $(c \cdot t)_{99.9} = 107 \frac{mg \cdot min}{L}$ pH=7, $(c \cdot t)_{99.9} = 153 \frac{mg \cdot min}{L}$ pH=8

@ pH 7.4, 0.4 mg/L $(c \cdot t)_{99.9} = 0.4(149-104)+104 = 122$

@ pH = 7.4, 0.6 mg/L $(c \cdot t)_{99.9} = 0.4(153-107)+107 = 125$

@ pH 7.4, 0.45 $\frac{mg}{L}$ $(c \cdot t)_{99.9} = \frac{0.45-0.4}{0.6-0.4}(125-122)+122 = 123 \frac{mg \cdot min}{L}$

Checking Virus $(c \cdot t)_{99.99} = 6 \frac{mg \cdot min}{L}$ $4-1 = 3$ req'd

so $(c \cdot t)_{req} = \frac{3}{4}\left(6 \frac{mg \cdot min}{L}\right) = 4.5 \ll 123$ ∴ Virus met too

The iterative interpolated solution for chlorine could be more accurately solved using the EPA empir. eg.

for Giardia $(C \cdot t)_{99.99} = 0.985 \, c^{0.176} \, pH^{2.75} \, T^{-0.147}$

so $(C \cdot t)_{req} = \dfrac{0.985}{4} \, c^{0.176} (7.4)^{2.75} (10)^{-0.147}$

Using Solver on $C = \dfrac{0.985 \, c^{0.176} (7.4)^{2.75} (10)^{-0.147} \, \frac{mg \cdot min}{L}}{90 \, min}$

$C = 0.41 \, \dfrac{mg}{L}$

<span style="color:red">For chlorine dioxide</span>

Noting that above Virus $C \cdot t$ is from Table 11.10, $ClO_2$ is also from Table 11.10, Giardia $(C \cdot t)_{99.9} = 23 \, \frac{mg \cdot min}{L}$ & Virus $(C \cdot t)_{99.99} = 25 \, \frac{mg \cdot min}{L}$

For Giardia $(C \cdot t)_{req} = \dfrac{23}{3} = 7.67$ $\qquad C = \dfrac{7.67}{90} = 0.085 \, \dfrac{mg}{L}$

For Virus $(C \cdot t)_{req} = 25.1 \left(\dfrac{3}{4}\right) = 18.8$ $\qquad C = \dfrac{18.8}{90} = 0.21 \, \dfrac{mg}{L}$

The higher dose for Virus must be used ↗