**CEE 483 Winter 2009 HW#5 Solutions**

1. (a) The flow rate through each fiber is $v_x A_x$, where $v_x$ is the given crossflow velocity of 1.0 m/s and $A_x$ is the cross-sectional area of the fiber. This flow will pass through 10,000 fibers, so the crossflow is:

$$Q_{cf,in} = N_{fibers} v_{x,in} A_x$$

$$= \left(10,000 \text{ fibers}\right)\left(1.0\frac{\text{m}}{\text{s}}\right)\left(\frac{\pi\left(9.0\text{x}10^{-4}\text{m}\right)^2}{4}\right) = 6.36\text{x}10^{-3}\,\frac{\text{m}^3}{\text{s}}$$

(b) The permeate flow rate is the product of the given flux and the membrane surface area, so:

$$Q_p = N_{fibers} J A_m = N_{fibers} J\left(\pi d_f L_f\right)$$

$$= \left(10,000 \text{ fibers}\right)\left(75\frac{\text{L}}{\text{m}^2\text{-h}}\right)\left(\pi\left(9.0\text{x}10^{-4}\text{m}\right)\left(1.2 \text{ m}\right)\right)\left(\frac{1 \text{ h}}{3600 \text{ s}}\right)\left(\frac{1 \text{ m}^3}{1000 \text{ L}}\right)$$

$$= 7.07\text{x}10^{-4}\,\frac{\text{m}^3}{\text{s}}$$

(c) The crossflow flow rate at the end of the module is less than that at the beginning by the amount that has permeated, so the velocity at the outlet of the module can be calculated as follows:

$$Q_{cf,out} = Q_{cf,in} - Q_p = \left(6.36\text{x}10^{-3} - \right)\frac{\text{m}^3}{\text{s}} = 5.65\text{x}10^{-3}\,\frac{\text{m}^3}{\text{s}}$$

$$v_{x,out} = \frac{Q_{cf,out}}{N_{fibers} A_x} = \frac{5.65\text{x}10^{-3}\text{m}^3/\text{s}}{\left(10,000 \text{ fibers}\right)\left(\frac{\pi\left(9.0\text{x}10^{-4}\text{m}\right)^2}{4}\right)} = 0.89\frac{\text{m}}{\text{s}}$$

(d) The velocity of the permeating fluid is the flux, so:

$$\frac{v_{cf,in}}{J} = \frac{1.0 \text{ m/s}}{\left(75\frac{\text{L}}{\text{m}^2\text{-h}}\right)\left(\frac{1 \text{ h}}{3600 \text{ s}}\right)\left(\frac{1 \text{ m}^3}{1000 \text{ L}}\right)} = 48,000$$

(e) $\dfrac{Q_p}{Q_{cf,in}} = \dfrac{7.07\text{x}10^{-4}\text{m}^3/\text{s}}{6.36\text{x}10^{-3}\text{m}^3/\text{s}} = 0.11$

2. (a) The specific flux is expected to be inversely proportional to the viscosity, other things being equal, so the specific flux at 20$^\circ$C is expected to be:

$$\left(\frac{J}{\text{TMP}}\right)_{20^\circ\text{C}} = \frac{\mu_{20^\circ\text{C}}}{\mu_{23^\circ\text{C}}}\left(\frac{J}{\text{TMP}}\right)_{23^\circ\text{C}} = \frac{9.08\text{x}10^{-4}\ \text{N-s/m}^2}{1.0\text{x}10^{-3}\ \text{N-s/m}^2}\left(\frac{650\ \text{LMH}}{0.69\ \text{atm}}\right) = 855\frac{\text{LMH}}{\text{atm}}$$

(b) The resistance of the clean membrane, based on the performance at 23$^\circ$C, is:

$$\begin{aligned}\mathcal{R} &= \frac{\text{TMP}}{\mu J}\\ &= \frac{0.69\ \text{atm}}{\left(9.08\text{x}10^{-4}\ \text{N-s/m}^2\right)\left(650\ \text{LMH}\right)}\left(\frac{100{,}000\ \text{N/m}^2}{\text{atm}}\right)\left(\frac{1000\ \text{L}}{\text{m}^3}\right)\left(\frac{3600\ \text{s}}{1\ \text{h}}\right)\\ &= 4.2\text{x}10^{11}\text{m}^{-1}\end{aligned}$$

(c) The resistance of the before and after backwashing is calculated as follows:

$$\begin{aligned}\mathcal{R}_{\text{before BW}} &= \frac{\text{TMP}}{\mu J}\\ &= \frac{1.0\ \text{atm}}{\left(1.0\text{x}10^{-3}\ \text{N-s/m}^2\right)\left(95\ \text{LMH}\right)}\left(\frac{100{,}000\ \text{N/m}^2}{\text{atm}}\right)\left(\frac{1000\ \text{L}}{\text{m}^3}\right)\left(\frac{3600\ \text{s}}{1\ \text{h}}\right)\\ &= 3.8\text{x}10^{12}\,\text{m}^{-1}\end{aligned}$$

$$\begin{aligned}\mathcal{R}_{\text{after BW}} &= \frac{\text{TMP}}{\mu J}\\ &= \frac{0.45\ \text{atm}}{\left(1.0\text{x}10^{-3}\ \text{N-s/m}^2\right)\left(120\ \text{LMH}\right)}\left(\frac{100{,}000\ \text{N/m}^2}{\text{atm}}\right)\left(\frac{1000\ \text{L}}{\text{m}^3}\right)\left(\frac{3600\ \text{s}}{1\ \text{h}}\right)\\ &= 1.4\text{x}10^{12}\,\text{m}^{-1}\end{aligned}$$

Assuming that resistances are additive, the difference between the resistance before and after backwashing is attributable to reversible fouling; this difference is $2.4\text{x}10^{12}\ \text{m}^{-1}$. Similarly, the difference in resistance between the clean membrane and after backwashing is attributable to irreversible fouling; this difference is $1.0\text{x}10^{12}\ \text{m}^{-1}$.

3. The required area based on summer flow can be calculated as follows:

$$A_m = \frac{Q_p}{J} = \frac{190{,}000\ \text{m}^3/\text{d}}{80\ \text{L/m}^2\text{-h}}\left(\frac{1\ \text{d}}{24\ \text{h}}\right)\left(\frac{1000\ \text{L}}{\text{m}^3}\right) = 99{,}000\ \text{m}^2$$

Assuming the same TMP is applied in winter as in summer, the flux and the total flow rate will equal the corresponding values in the summer, multiplied by the ratio of the viscosities. Thus, the flow rate in the winter will be:

$$Q_{p,winter} = Q_{p,summer}\frac{\mu_{summer}}{\mu_{winter}} = \left(190,000\ \mathrm{m^3/d}\right)\frac{1.08\mathrm{x}10^{-3}\ \mathrm{N\text{-}s/m^2}}{1.57\mathrm{x}10^{-3}\ \mathrm{N\text{-}s/m^2}} = 131,000\frac{\mathrm{m^3}}{\mathrm{d}}$$

Since the required flow during the winter is 136,000 $\mathrm{m^3/d}$, the size of the plant will be governed by the winter flow requirement.

4. (a) At the given pH, the $HCO_3^-$ concentration in mol/L can be approximated as the alkalinity in equiv/L, *i.e.*, $(HCO_3^-) = 1.10 \times 10^{-3}$ mol/L. We can then compute the $H_2CO_3$ and $CO_3^{2-}$ concentrations from the $K_a$ values, as follows:

$$\left(H_2CO_3\right) = \frac{\left(HCO_3^-\right)\left(H^+\right)}{K_{a1}} = \frac{\left(1.10\mathrm{x}10^{-3}\right)\left(10^{-7.4}\right)}{10^{-6.3}} = 8.74\mathrm{x}10^{-5}$$

$$\left(CO_3^{2-}\right) = \frac{\left(HCO_3^-\right)K_{a2}}{\left(H^+\right)} = \frac{\left(1.10\mathrm{x}10^{-3}\right)\left(10^{-10.3}\right)}{10^{-7.4}} = 1.38\mathrm{x}10^{-6}$$

The initial concentration of $Ca^{2+}$ is 115 mg/L, or, in mol/L:

$$\left(Ca^{2+}\right) = \frac{85\ \mathrm{mg/L}}{40,000\ \mathrm{mg/L}} = 2.125\mathrm{x}10^{-3}\ \frac{\mathrm{mol}}{\mathrm{L}}$$

The product $(Ca^{2+})(CO_3^{2-})$ is therefore:

$$\left(Ca^{2+}\right)\left(CO_3^{2-}\right) = \left(2.125\mathrm{x}10^{-3}\right)\left(1.38\mathrm{x}10^{-6}\right) = 2.93\mathrm{x}10^{-9} = 10^{-8.53}$$

Since this product is less than $K_{s0}$, the solid is undersaturated.

(b) The dosage of lime required to convert all the carbonate species to $CO_3^{2-}$ is:

$$\text{Lime Dosage} = \frac{1}{2}\left[\left(HCO_3^-\right) + 2\left(CO_3^{2-}\right)\right]$$

$$= \frac{1}{2}\left[\left(1.10\mathrm{x}10^{-3}\right) + 2\left(8.74\mathrm{x}10^{-5}\right)\right] = 6.37\mathrm{x}10^{-4}\ \mathrm{mol/L}$$

The question was somewhat unclear. If one also considers the lime required to neutralize the $H^+$ initially in the solution and to provide for the increase in $OH^-$, then one must choose a value for the final pH. If that is done, and the pH is assumed to be 10.8, the following additional amount of lime is required:

$$\begin{pmatrix}\text{Additional mol/L}\\ \text{of } OH^- \text{ required}\end{pmatrix} = \Delta\left(OH^-\right) - \Delta\left(H^+\right) = \left(10^{-3.2} - 10^{-7.4}\right) - \left(10^{-7.4} - 10^{-10.8}\right) = 10^{-3.2}$$

$$\begin{pmatrix}\text{Additional mol/L}\\ \text{of lime required}\end{pmatrix} = 10^{-3.2}/2 = 10^{-3.5} = 3.1\text{x}10^{-4}$$

(c) If essentially all the carbonate species were converted to $CO_3^{2-}$, the concentration of $CO_3^{2-}$ would equal the sum of the original concentrations of $H_2CO_3$, $HCO_3^-$, and $CO_3^{2-}$, or $1.19 \times 10^{-3}$ mol/L. The concentration of $Ca^{2+}$ in solution at that time would be the original concentration ($2.125 \times 10^{-3}$) plus the amount added as lime ($6.37 \times 10^{-4}$), for a total of $2.78 \times 10^{-3}$.

Then, when $x$ mol/L of $CaCO_3(s)$ precipitated, the new concentrations of $Ca^{2+}$ and $CO_3^{2-}$ would be (assuming that, even after the precipitation, the approximation $(CO_3^{2-}) = TOTCO_3$ applied):

$$\left(\text{Ca}^{2+}\right) = 2.78\text{x}10^{-3} - x \qquad \left(\text{CO}_3^{2-}\right) = 1.19\text{x}10^{-3} - x$$

Once equilibrium is reached, the solubility product expression must be satisfied, so:

$$\left(\text{Ca}^{2+}\right)\left(\text{CO}_3^{2-}\right) = \left(2.78\text{x}10^{-3} - x\right)\left(1.19\text{x}10^{-3} - x\right) = 10^{-8.3}$$

Solving the above expression, we find that $x = 1.19 \times 10^{-3}$, *i.e.*, almost all the carbonate precipitates, leaving $1.59 \times 10^{-3}$ mol/L $Ca^{2+}$ in solution. The value of $x$ is the concentration of solid that forms, in mol/L, when the solution reaches equilibrium. Since the molecular weight of $CaCO_3(s)$ is 100, the concentration of the solid in mg/L is:

$$1.19\text{x}10^{-3}\,\frac{\text{mol CaCO}_3(s)}{\text{L}}\left(100{,}000\,\frac{\text{mg}}{\text{mol}}\right) = 119\,\frac{\text{mg CaCO}_3(s)}{\text{L}}$$

5. (a) The concentrations of $Cu^{2+}$ and $Pb^{2+}$ in the downstream water can be found using the equilibrium constants (solubility products) for the two solids. To carry out those calculations, we need to compute the concentrations of $OH^-$ and $CO_3^{2-}$ in solution. We can carry out these calculations based on other equilibrium constants, as follows. First, we note that, at pH 6.7, the alkalinity can be equated with the $HCO_3^-$ concentration. Substituting known values into the equilibrium constant expressions, we find:

$$\left(\text{OH}^-\right) = \frac{K_w}{\left(\text{H}^+\right)} = \frac{10^{-14.0}}{10^{-6.7}} = 10^{-7.3}$$

$$\left(\text{CO}_3^{2-}\right) = \frac{\left(\text{HCO}_3^-\right)K_{a2}}{\left(\text{H}^+\right)} = \frac{\left(5.0\text{x}10^{-4}\right)\left(10^{-10.3}\right)}{10^{-6.7}} = 1.26\text{x}10^{-7}$$

Then, we can substitute these values into the solubility product expressions to compute the concentrations of the metals expected to be in solution:

For $PbCO_3$(s): $$K_{s0} = \frac{\left(\mathrm{Pb}^{2+}\right)\left(\mathrm{CO_3}^{2-}\right)}{\left(\mathrm{PbCO_3}(s)\right)} = \left(\mathrm{Pb}^{2+}\right)\left(\mathrm{CO_3}^{2-}\right)$$

$$\left(\mathrm{Pb}^{2+}\right) = \frac{K_{s0}}{\left(\mathrm{CO_3}^{2-}\right)} = \frac{10^{-13.13}}{1.26\mathrm{x}10^{-7}} = 5.90\mathrm{x}10^{-7}$$

For $Cu_2(OH)_2CO_3(s)$: $$K_{s0} = \frac{\left(\mathrm{Cu}^{2+}\right)^2\left(\mathrm{OH}^{-}\right)^2\left(\mathrm{CO_3}^{2-}\right)}{\left(\mathrm{Cu_2(OH)_2CO_3}(s)\right)} = \left(\mathrm{Cu}^{2+}\right)^2\left(\mathrm{OH}^{-}\right)^2\left(\mathrm{CO_3}^{2-}\right)$$

$$\left(\mathrm{Cu}^{2+}\right) = \sqrt{\frac{K_{s0}}{\left(\mathrm{OH}^{-}\right)^2\left(\mathrm{CO_3}^{2-}\right)}} = \sqrt{\frac{10^{-33.2}}{\left(10^{-7.3}\right)^2\left(1.26\mathrm{x}10^{-7}\right)}} = 1.41\mathrm{x}10^{-6}$$

(b) The action levels for Pb and Cu are 15 μg/L and 1.3 mg/L, respectively. The concentrations computed in part *a* can be converted to mass per volume units using the atomic weights of Pb (207) and Cu (63.5):

$$\left(\mathrm{Pb}^{2+}\right) = 5.90\mathrm{x}10^{-7}\,\frac{\mathrm{mol}}{\mathrm{L}}\left(207\mathrm{x}10^{6}\,\frac{\mu\mathrm{g}}{\mathrm{mol}}\right) = 122\,\frac{\mu\mathrm{g}}{\mathrm{L}}$$

$$\left(\mathrm{Cu}^{2+}\right) = 1.41\mathrm{x}10^{-6}\,\frac{\mathrm{mol}}{\mathrm{L}}\left(63{,}500\,\frac{\mathrm{mg}}{\mathrm{mol}}\right) = 8.98\mathrm{x}10^{-2}\,\frac{\mathrm{mg}}{\mathrm{L}}$$

The action level for Pb is greatly exceeded, but that for Cu is not. (Note: In truth, $Cu^{2+}$ participates in another equilibrium reaction that generates a species $CuOH^{+}$. At pH 6.8, that species is much more concentrated than $Cu^{2+}$. As a result, if all the copper in solution were considered, the action level for Cu would be exceeded as well.)

A $Pb^{2+}$ concentration of 15 $\mu$g/L corresponds to 15 $\mu$g/L / 207 x $10^6$ $\mu$g/mol, or 7.25 x $10^{-8}$ mol/L. To reduce the equilibrium concentration of $Pb^{2+}$ to this value, the $CO_3^{2-}$ concentration would have to be:

$$\left(\mathrm{CO_3}^{2-}\right) = \frac{K_{s0}}{\left(\mathrm{Pb}^{2+}\right)} = \frac{10^{-13.13}}{7.25\mathrm{x}10^{-8}} = 1.02\mathrm{x}10^{-6}$$

This value of ($CO_3^{2-}$) represents almost an order of magnitude increase in the $CO_3^{2-}$ concentration, and can be achieved by increasing the solution pH, so that some $HCO_3^{-}$ and/or $H_2CO_3$ is converted to $CO_3^{2-}$. When the pH changes, the concentrations of $HCO_3^{-}$ and $H_2CO_3$ will also change, but the total concentration of all carbonate species will remain the same. Therefore, we can write:

$$TOT\text{CO}_{3,\text{final}} = TOT\text{CO}_{3,\text{init}} = \left(\text{H}_2\text{CO}_3\right)_{\text{init}} + \left(\text{HCO}_3^{\;-}\right)_{\text{init}} + \left(\text{CO}_3^{\;2-}\right)_{\text{init}}$$

We found $\left(\text{HCO}_3^{\;-}\right)_{\text{init}}$ and $\left(\text{CO}_3^{\;2-}\right)_{\text{init}}$ in part *a*, so we need to determine $\left(\text{H}_2\text{CO}_3\right)_{\text{init}}$, which we can do as follows:

$$\left(\text{H}_2\text{CO}_3\right) = \frac{\left(\text{HCO}_3^{\;-}\right)\left(\text{H}^+\right)}{K_{a1}} = \frac{\left(5.0\text{x}10^{-4}\right)\left(10^{-6.7}\right)}{10^{-6.3}} = 1.99\text{x}10^{-4}$$

Thus:

$$TOT\text{CO}_{3,\text{final}} = 1.99\text{x}10^{-4} + 5.0\text{x}10^{-4} + 1.26\text{x}10^{-7} = 6.99\text{x}10^{-4}$$

We know what the final value of $\left(\text{CO}_3^{\;2-}\right)$ must be in order to reduce the $\text{Pb}^{2+}$ concentration to the action level. Using that value, we can compute the concentrations of the other carbonate species and the pH as follows:

$$TOT\text{CO}_{3,\text{final}} = 6.99\text{x}10^{-4} = \frac{\left(\text{H}^+\right)^2}{K_{a1}K_{a2}}\left(\text{CO}_3^{\;2-}\right) + \frac{\left(\text{H}^+\right)}{K_{a2}}\left(\text{CO}_3^{\;2-}\right) + \left(\text{CO}_3^{\;2-}\right)$$

$$6.99\text{x}10^{-4} = \frac{\left(\text{H}^+\right)^2}{10^{-6.3}10^{-10.3}}\left(1.26\text{x}10^{-7}\right) + \frac{\left(\text{H}^+\right)}{10^{-10.3}}\left(1.26\text{x}10^{-7}\right) + \left(1.26\text{x}10^{-7}\right)$$

Solving for $\left(\text{H}^+\right)$, we find:

$$\left(\text{H}^+\right) = 3.22\text{x}10^{-8} = 10^{-7.49}$$

The required pH to avoid exceeding the action level is thus 7.49.