

ENV 4417: WATER QUALITY & TREATMENT

Fall 2015
Problem set #2
Due Thursday, Sept. 17

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On the first homework assignment, you examined the quality of Evian water. Consider a water with the following composition, which is quite close to that of Evian water:

Calcium, Ca^{2+}	80.
Magnesium, Mg^{2+}	26.
Sodium, Na^+	6.5
Bicarbonate, HCO_3^-	360.
Chloride, Cl^-	8.9
Sulfate, SO_4^{2-}	12.6
pH	7.2

1. (10 pts) Draw a meq/L bar graph for this water. See, for instance, pages 376–378 and Figure 11.1 in your text book. It is safe to ignore the concentrations of H^+ and OH^- here.
2. (5 pts) Express the hardness and the alkalinity in units of mg/L as CaCO_3 . How much of the hardness is carbonate hardness, and how much is non-carbonate hardness?

This water is pretty hard, as you found in problem (2). Let's suppose we wanted to soften it using lime-soda softening, and in particular, we want to use excess-lime treatment (one of the choices described in your text). According to your text (p 409), "a two-stage system is preferred for excess-lime treatment.... Lime is applied in first-stage mixing...to precipitate both calcium and magnesium. Then [in the second stage] carbon dioxide is added to neutralize the excess lime, and soda ash is added to reduce noncarbonate hardness."

3. (10 pts) Using the theoretical stoichiometries as given in the text, estimate/calculate how much $\text{Ca}(\text{OH})_2$ you would need to add in the first stage to remove all the Ca^{2+} and Mg^{2+} . Report your answer in mg/L of $\text{Ca}(\text{OH})_2$. For the purposes of this problem, do not add any "excess" lime (even though you would probably would in practice) – just estimate how much lime you need based on the stoichiometric removal of all Ca^{2+} and Mg^{2+} . Hint: you have to divide the problem up into three pieces – $\text{Ca}(\text{OH})_2$ for removal of Ca^{2+} , $\text{Ca}(\text{OH})_2$ for removal of Mg^{2+} associated with carbonate hardness, and $\text{Ca}(\text{OH})_2$ for removal of Mg^{2+} associated with non-carbonate hardness.

4. (10 pts) Draw the meq/L bar graph that would theoretically result from adding the lime in the first-stage softener. Hints:
- The concentrations of some of the ions are not changed by the lime addition.
 - You added enough $\text{Ca}(\text{OH})_2$ to remove all the original Ca^{2+} and all the original Mg^{2+} ...
 - ...but some of the $\text{Ca}(\text{OH})_2$ was added to deal with non-carbonate hardness, as shown in equation 11.61 of your text. So the concentration of Ca^{2+} is not zero. There is Ca^{2+} from the lime that was added to remove the non-carbonate Mg^{2+} .

Your book notes that, in reality, we do not get complete removal of Ca^{2+} and Mg^{2+} during this softening process, because CaCO_3 is somewhat soluble in water. Therefore, the stoichiometries that we used are only *approximations* to what really happens. What really happens when you add the lime is that it raises the pH. This shifts HCO_3^- to CO_3^{2-} so CaCO_3 precipitates because $[\text{Ca}^{2+}][\text{CO}_3^{2-}]$ exceeds the solubility product constant (K_{sp}). Also, $\text{Mg}(\text{OH})_2$ precipitates because at high pH, there are lots of OH^- ions in solution, so the K_{sp} for $\text{Mg}(\text{OH})_2$ is exceeded. Let's look at the chemistry in some more detail to see how well our approximate stoichiometries work. To do that, we will need a few pieces of information:

- Your text book gives a K_{sp} value of 4.6×10^{-9} for CaCO_3 (p 379). Let's assume this value is correct.
- Assume a K_{sp} value of 1.0×10^{-11} for $\text{Mg}(\text{OH})_2$. I looked for values for this K_{sp} and I found values that range from 0.56×10^{-11} to 1.8×10^{-11} . Therefore we will use 1.0×10^{-11} as an estimate.
- Based on the $\text{Ca}(\text{OH})_2$ addition that you calculated in problem (3), assume that the pH of the water rises to 10.44 or 10.45 in the first-stage softener. (You can calculate this, but it is not easy – well beyond what we will do in ENV 4417. If you want to learn the details, take ENV 6666.)
- For the acid/base equilibrium of HCO_3^- and CO_3^{2-} , assume a K_A of 4.69×10^{-11} (p 379).

5. (30 pts) Assuming that adding the lime raises the pH to 10.445 in the first-stage softener, estimate/calculate the concentrations of the following ions in the water: H^+ , Na^+ , Mg^{2+} , Ca^{2+} , OH^- , Cl^- , SO_4^{2-} , HCO_3^- , CO_3^{2-} . Report your answers in both mol/L and meq/L. Here are some hints on how to find these:

- Calculate $[\text{H}^+]$ and $[\text{OH}^-]$ from the assumed pH value.
- Think about how $[\text{Na}^+]$, $[\text{Cl}^-]$, and $[\text{SO}_4^{2-}]$ are affected by the lime addition.
- Check if any Mg^{2+} precipitates as $\text{Mg}(\text{OH})_2$. If so, then use the K_{sp} to estimate $[\text{Mg}^{2+}]$.

That leaves $[\text{Ca}^{2+}]$, $[\text{CO}_3^{2-}]$, and $[\text{HCO}_3^-]$. These are a bit trickier. To get these values, you need to introduce one additional unknown into the system: the amount of CaCO_3 precipitated. For simplicity, let's call that p , with units of mol/L. We now have four unknowns (three concentrations plus p), so we need four equations. These are:

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- K_{sp} for CaCO_3
- Acid/base equilibrium between HCO_3^- and CO_3^{2-}
- $[\text{Ca}^{2+}] = \{\text{initial } [\text{Ca}^{2+}]\} + \{[\text{Ca}^{2+}] \text{ added in lime}\} - p$
- $[\text{HCO}_3^-] + [\text{CO}_3^{2-}] = \{\text{initial } [\text{HCO}_3^-]\} - p$

You can solve these four equations and thereby get everything you need. Solving the equations is not completely straightforward, though, because the equations are non-linear. I recommend guessing a value of p , using that to calculate the three unknown concentrations, and checking if everything agrees. Then update your guess at p until all the equations are satisfied.

By following this procedure, you can estimate the concentrations of all 9 ions of interest.

6. (10 pts) Draw the meq/L bar graph for the concentrations you found in problem (5). Compare the bar graphs from problem (5) to that from problem (4). Do they look pretty similar, or pretty different? What are the major similarities and/or differences? Based on that, do you think the theoretical stoichiometries from equations 11.58–11.60 do a good job? It is certainly much easier to use equations 11.58–11.60 than it is to do all the calculations from problem 5, so if the theoretical stoichiometries are “good enough”, we would rather use those. Do you think the approximation is good enough? Or do you think we need to go through all the complicated chemistry calculations?
7. (5 pts) Based on your results from problem 5, what fraction of the original hardness has been removed in the first-stage softener? Is lime addition an effective method for removing hardness?

In the second-stage softener, we add soda ash, along with CO_2 for recarbonation. The soda ash is required to remove the non-carbonate hardness. I had originally intended for us to work through the chemistry of that second-stage softener, too – but I think that would make this assignment too long and complicated. Let’s keep things simple(r) for the remainder of the assignment.

8. (5 pts) Estimate/calculate how much soda ash would be required to remove the non-carbonate hardness. Use equations 11.61 and 11.62 in your text. Report your answer as mg/L Na_2CO_3 . We will assume that these stoichiometries are OK and we will not investigate the water chemistry in detail for the second stage.

9. (10 pts) Draw the bar graph for the water after both stages of softening. Use the simplified stoichiometries from 11.58 through 11.62. These predict complete removal of all Ca^{2+} and Mg^{2+} . As we know from the text and/or from problem (5), we don't actually get complete removal of these ions – but for the purposes of this problem, let's just stick with the simplified (theoretical) stoichiometries and assume that they are removed 100%.

10. (5 pts) Estimate/calculate the required amounts of lime and soda ash in units of pounds (mass) required per million gallons of water treated. For a plant that treats 10 million gallons per day, what is the chemical usage in units of tons per year?

And we didn't even get into the sludge handling. What do you do with all that CaCO_3 and $\text{Mg}(\text{OH})_2$ that you precipitate?!? But that is left for another assignment.