

## CE 474/574 - Unit Operations in Environmental Engineering

### Design Assignment 5. [For 5 pts credit with possible 1 pt extra credit] Hardness Removal for the Drain, OR Public Water Supply

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A stumbling block has occurred in Drain. The city council is balking at the price of the flocculators, clarifiers and filters to meet LT-1 for a surface water supply. The council has insisted that Sal Monella provide them with any feasible alternative. After consulting with a regulatory specialist and hydrologists, Monella has learned that deep groundwater does *not* need to be filtered to meet the new standards (it merely must be chlorinated). Geological surveys indicate there is a fairly productive aquifer about 200 feet below Drain, but it is in a limestone formation and has significant hardness. The U.S.G.S. indicates the water from this formation will have the following composition:

Constituent	Concentration
pH	7.3
Total alkalinity	150 mg/L as CaCO <sub>3</sub>
Total hardness	165 mg/L as CaCO <sub>3</sub>
Calcium hardness	150 mg/L as CaCO <sub>3</sub>

Because this water is so hard, Mr. Monella wants you to design a hardness removal system that would bring the total hardness down to 75 mg/L as CaCO<sub>3</sub>. Obviously you want to keep this system as simple and cheap as possible, so do only what is necessary to achieve this goal. For now, *don't* worry about designing the clarifier for the system; you can assume your prior design of a clarifier is pretty close to what would be needed here. (The net savings of using groundwater will come from not needing a flocculator or a filter gallery). Do NOT worry about the recarbonation step unless you want extra credit (see information below).

Here are a few tips to guide you with respect to the chemistry.

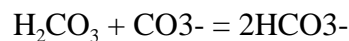
- The table above gives you everything you need to know about the composition of the water to follow the basic design principles we reviewed in class.
- You can get the breakdown of bicarbonate and carbonate alkalinity from a simple consideration of carbonate chemistry, as we discussed in class and as outlined in the supplemental synopsis (on the web page).
- Likewise, you can find the concentration of H<sub>2</sub>CO<sub>3</sub>\* (= [CO<sub>2</sub>]) as it is denoted in the text example of lime requirement) from a simple calculation and the data given above. NOTE: This is deep groundwater and the carbonic acid is NOT in equilibrium with the atmosphere. Therefore, do NOT assume it is just 10<sup>-5</sup> mol/L. Calculate it.
- Remember that carbonic acid is diprotic, hence you multiply the concentration by 2 to get equivalents per liter.

- Don't add any chemicals you don't need.
- Calculate the final composition of the water, including the pH (without recarbonating the water). Remember that the bicarbonate remaining is the amount you started with minus the amount of carbonate hardness you removed. Also, when calculating the pH, remember to switch  $[\text{CO}_3^{2-}]$  into mol/L units from eq/L.

**BONUS CALCULATION FOR 1 POINT OPTIONAL EXTRA CREDIT:**

For the final recarbonation step, let's try something cheap and easy. When you are all done with the treatment, find the final alkalinity and pH of the water. If the pH is greater than 9 (as it likely will be) you can recarbonate the water to some extent (and lower the pH) by just aerating the water so that it is in equilibrium with the atmospheric  $\text{CO}_2$ . You can then find the pH that results if you keep in mind the following points:

- Exchange of  $\text{CO}_2$  does NOT alter the alkalinity. Therefore, the alkalinity is the same before and after you aerate.
- $[\text{H}_2\text{CO}_3^*] = 10^{-5}$  mol/L at equilibrium with the atmosphere.
- If we get the pH down to significantly less than pH 10.3, we know that bicarbonate will be the dominant species; we can neglect carbonate and just use the ratio of bicarbonate to  $\text{H}_2\text{CO}_3^*$  to solve for pH. But...
- Adding  $\text{CO}_2$  converts  $\text{CO}_3^{2-}$  to  $\text{HCO}_3^-$  by the reaction



So, you not only convert each mole of carbonate to bicarbonate, you add a second mole of bicarbonate in the process (assuming you are working in moles and not equivalents). Therefore:

- The final  $[\text{HCO}_3^-]$  is going to be the pre-aeration bicarbonate concentration plus twice the pre-aeration carbonate concentration (when all are expressed in mol/L units and not eq/L).

You should find that the pH ends up pretty close to neutral, so this seems like the perfect way to go. In practice, however, it takes way too long to aerate the water to achieve this. Pure  $\text{CO}_2$  is so soluble in water that it is much faster to just squirt in some pure carbon dioxide. The (low) cost of the pure carbon dioxide offsets the mechanical energy cost of aeration, even though the  $\text{CO}_2$  itself is free in the aeration system.