LAB X3: HARDNESS REMOVAL

Learning Objectives

- Discuss treatment options for hardness removal.
- Describe water softening mechanism using chemical precipitation.
- Calculate the amount of chemicals needed to remove a given amount of hardness.
- Analyze experimental results on hardness removal using chemical addition, flocculation and settling:

References

American Public Health Association (APHA). (1995). *Standard methods for the examination of water and wastewater* (19th ed.). Washington, DC: APHA, pp. 2-35 - 2-38, 3-56 - 3-57, 3-72 -3-74.

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Davis, M.L., & Masten, S.J. (2004). *Principles of environmental engineering and science*. New York, NY: McGraw-Hill, pp. 337-347.

Nazaroff, W.W., & Alvarez-Cohen, L. (2001). *Environmental engineering science*. New York: Wiley, pp. 338-346.

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Background

Hardness, mainly due to Ca^{2+} and Mg^{2+} ions, is a term that characterizes the degree to which water causes scum to form on a bathroom tub, does not lather well, leaves scale on water heaters, pipes, etc. The interaction of calcium or magnesium ions with soap can be represented by:

$Ca^{2+} + (Soap)^{-} \leftrightarrow Ca(Soap)_2(s)$ **Equation 1**

Where $Ca(Soap)_2(s)$ is an undesirable precipitate that forms, preventing some soap from reacting as desired with dirt on clothing or dishes. Though not a health hazard, people dislike the characteristics listed above that are associated with hard water (>120 mg/L as $CaCO_3$). Some water treatment plants treat water to have hardness in the range of 60 to 120 mg/L as $CaCO_3$.

The removal of hardness is referred to as "softening" and one treatment option for removing hardness is "lime soda softening". In this process chemicals are added to the hard water to cause $CaCO_3(s)$ and $Mg(OH)_2(s)$ to precipitate out. There are several ways this could be done, but due to cost-effectiveness, the chemicals typically used are lime (CaO) or hydrated lime ($Ca(OH)_2$) and soda/soda ash (Na_2CO_3). The reactions induced are:

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

$Mg^{2+} + 2HCO_3^{-} + 2Ca(OH)_2 \leftrightarrow Mg(OH)_2(s) + 2CaCO_3(s) + 2H_2O$ **Equation 3**

Lime soda softening cannot remove 100% of hardness. In fact, **practical limits** of lime soda softening (i.e., the lowest final levels of hardness typically obtained) are 30 mg/L and 10 mg/L as $CaCO_3$ for Ca and Mg respectively.

Another treatment option for hard water is "ion-exchange softening." During this process, the hard water is passed through a column containing a resin, a solid whose surface area has synthetic polymers or zeolite sites which have ion-exchange properties. In a reversible reaction, the hardness ions are exchanged with ions in the resin. For example:

$Ca^{2+} + 2NaR \leftrightarrow CaR_2 + 2Na^+$ **Equation 4**

Here R represents the active sites of the resin. According to Equation 4, two sodium ions are released per calcium ion exchanged (magnesium and other hardness cations are exchanged the same way). The resulting increase in sodium concentration is a minor drawback of the ion-exchange process for cooking and drinking water, since some people try to limit sodium intake. The ion-exchange resin can remove up to 100% of hardness; however, its capacity to remove hardness decreases as the resin sites become loaded with hardness cations. Thus the ion-exchange material must be regenerated periodically by flushing a high concentration of sodium through the system to remove the calcium. The flush process is another drawback of the ion-exchange process, since it is a source of very salty waste water which is problematic to dispose of properly.

Lime Soda Softening Reagent Requirements

Table 1 summarizes the chemical precipitation reactions pertaining to the lime softening process.

Table 1: Reactions in the Lime-Soda Softening Process. Note that some limitations apply to this methodology, including that pH of water to be treated is assumed to be 8 or less. From Nazaroff and Alvarez-Cohen (2001).

(1) Addition of calcium hydroxide to precipitate $CaCO_3(s)$

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

(2) Addition of calcium hydroxide to precipitate $Mg(OH)_2(s)$

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

(3) Addition of calcium hydroxide to eliminate carbonic acid (needed to raise the pH)

$$H_2CO_3^* + Ca(OH)_2 \rightarrow CaCO_3(s) + 2H_2O$$

(4) Addition of calcium hydroxide to raise the pH to 11 (needed to precipitate $Mg(OH)_2$)

$$pH = 11 \Rightarrow [OH^-] = 10^{-3}\,M = 1.0\ meq/L,\ \text{unreacted;}$$

as rule of thumb, add 1.25 meq/L to raise pH if Mg^{2+} removal is required

(5) Addition of sodium carbonate to precipitate Ca^{2+} if alkalinity of raw water is insufficient

$$Ca^{2+} + Na_2CO_3 \rightarrow CaCO_3(s) + 2Na^+$$

Several parameters of the hard water to be treated must be known in order to calculate the reagent requirements for lime soda softening. They are:

- Total Alkalinity (ALK_{Total}) of solution. This is determined via titration (see Lab X1 *ALKALINITY AND THE CARBONATE SYSTEM* in this workbook).
- Total hardness (TH) of solution (determined from a titration as in Water Hardness Lab)
  - TH = (Ca^{2+} hardness) + (Mg^{2+} hardness)

- As an indication of the relative amount of carbonate available in the water, TH is subdivided into carbonate hardness (CH) and non-carbonate hardness (NCH), i.e.:
  - TH = CH + NCH
  - CH (carbonate hardness) is the amount of hardness for which carbonate species are available to balance the Ca^{2+} and Mg^{2+} present;
  - NCH (non-carbonate hardness) is any remaining hardness that is balanced by non-carbonate anions (such as Cl^{-}) if there is insufficient carbonate
    - Since most alkalinity in natural waters is due to the carbonate system (H_2CO_3, HCO_3^{-}, CO_3^{2-}), use an approximation: NCH = TH – ALK_{Total}
    - but if TH < ALK_{Total}, then NCH = 0 and TH = CH (i.e., NCH cannot be negative)

Carbonic acid (H_2CO_3*) content of solution must be estimated.

- If pH of the solution is below 8 (one of the assumptions of this method), then the major form of alkalinity is HCO_3^{-} and the following approximation may be made based on the equilibrium relationship between HCO_3^{-} and H_2CO_3*:

$$(H_2CO_3^*) = \frac{(2)(10^{-pH})}{4.47\text{E-}7} ALK_{Total} \quad \text{where concentrations are all in mg/L as } CaCO_3$$

It is also necessary to determine whether Mg should be targeted for removal from the solution.

- Magnesium removal requires the pH to be raised above 11 and is more expensive to perform than calcium removal. Hence, target Mg for removal only if its reduction is required to meet water quality standards. In practice, Mg is generally targeted for removal only if the magnesium concentration exceeds 40 mg/L as $CaCO_3$.
  - Is Mg ≥ 40 mg/L as $CaCO_3$? If yes, target Mg for removal.

Table 2: Reagent Requirements for Lime-Soda Softening with all concentrations expressed as mg/L as $CaCO_3$. Adapted from Nazaroff and Alvarez-Cohen (2001).

Condition	Required $Ca(OH)_2$ (mg/L as $CaCO_3$)	Required Na_2CO_3 (mg/L as $CaCO_3$)
ALK_{Total} ≥ TH	TH + Mg^{2+} + H_2CO_3* + 62.5[a]	None
ALK_{Total} < TH	ALK_{Total} + Mg^{2+} + H_2CO_3* + 62.5[a]	NCH

[a]: If Mg^{2+} removal is not required, then the target pH is not as high and the 62.5 should be omitted.

Equipment	Reagents
Buret, Pipets	$Ca(OH)_2$, Na_2CO_3
150 mL beaker	Standard EDTA solution, 0.0100 M
1L or 2L "jar test" jar	pH indicator paper
Filter paper, funnel	Buffer solution
Stir bar, magnetic stirrer	EBT indicator
Rapid Mix reactors	1M NaOH
Stop watch	HNB or Murexide indicator

Procedure

Use soda-lime softening to treat a water sample, then analyze the softened water. Record parameters for unsoftened water provided by TA in Table 3.

1. Based on water quality data provided by the TAs for the water to be softened (Table 3), use the equations in Table 2 to calculate:
    a. the amount of $Ca(OH)_2$ needed in mg/L as $CaCO_3$, and
    b. the amount of Na_2CO_3 needed in mg/L as $CaCO_3$

Table 3: Parameters of untreated water provided by TA.

pH	ALK_{Total} (mg/L as $CaCO_3$)	TH (mg/L as $CaCO_3$)	Calcium Hardness (mg/L as $CaCO_3$)	Magnesium Hardness (mg/L as $CaCO_3$)
6.97	192	317	258	59

2. You will be given the concentration of the stock solutions of $Ca(OH)_2$ and Na_2CO_3. Compute the volume of each stock solution needed to treat 1 L of water to be softened.
3. 1 L of water to be softened was placed in a "jar" for the Rapid Mix Reactor.
4. Add the appropriate volume of water softening chemicals (You will assume that the results given in Table 4 correspond to the amount you calculated in Step 2)
5. Rapid mix at 80 RPM for 1 minute.
6. Flocculate for 30 minutes at 30 RPM.
7. Retrieve your jar; allow particles to settle for 20 minutes with the jar at your lab station.
8. Filter solution. Measure the pH of the filtered product (pH paper is sufficiently accurate).
9. Measure the total hardness and calcium concentration of the softened water using the methods used in the Water Hardness lab. Table 4 provided to organize data for this lab.

Table 4: Table of data for hardness and other parameters of softened water. A set of table cells is provided for the approximate titration determination recommended for calcium hardness titration. Only the final, accurate titration is important to the final results.

pH	Starting position (mL)	Ending position (mL)	Volume of 0.0100 M EDTA for total hardness titration (mL)	Starting position (mL)	Ending position (mL)	Volume of 0.0100 M EDTA for Calcium hardness titration (mL)
10	0.0	3.8	3.8	-	-	
13				0.0	2.60	2.60

Data Analysis

Calculate total hardness, calcium hardness, and magnesium hardness of the softened water. The following questions ask you to compare the softened water parameters to the unsoftened water.

Questions

1. What amount of $Ca(OH)_2$ is needed in mg/L as $CaCO_3$, and what amount of Na_2CO_3 is needed in mg/L as $CaCO_3$ to meet the requirements in Table 2 given the information provided in Table 3?

2. Based on this experiment what is one additional step needed to make this water suitable for human consumption?

3. What was the percentage removal of total hardness, calcium and magnesium during this process?

4. How close did the treatment process come to the practical limits of reduction of hardness to about 30 mg/L and 10 mg/L as $CaCO_3$ for Ca and Mg respectively?

5. Assume that your untreated water sample is representative of the hardness of all potable water distributed by the City of Tampa. The Tippin Water Treatment Facility processes about 59 million gallons of water per day, per FAQ on www.tampagov.net/dept_Water website. Based on your calculations in Procedure steps 1.a. and 1.b., how many metric tons (1 tonne = 1000 kg) of $Ca(OH)_2(s)$ and of $Na_2CO_3(s)$ would be required per day to soften all the water for the city coming out of the Tippin plant?

6. Summarize the water softening treatment method used by a firm where you live. Use Tampa if you don't have any. Include name of company, website, and description of process.