CHEMICAL PRECIPITATION: WATER SOFTENING

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ABSTRACT

Hard water can cause many problems including scaling and excessive soap consumption. In the United States, hard water is mostly found in the mid western and western states. It ranges between 120-250 mg/L as $CaCO_3$ or beyond 250 mg/L as $CaCO_3$ for very hard waters. The acceptable water hardness range is between 60-120 mg/L as $CaCO_3$. A water softening experiment was conducted in replicate to observe the changes in parameters such as total hardness, calcium hardness, magnesium hardness, alkalinity and pH with varying dosages of lime. A lime dosage range of 30-180% of the stoichiometric amount was chosen for the experiments. The sample used was groundwater from an East Lansing well which had a total hardness of 332 mg/L as $CaCO_3$. Results indicated that an increase in lime dosage upto 90% caused a decrease in total hardness, alkalinity, magnesium hardness and calcium hardness concentrations. However, for a lime dosage beyond 120%, the total hardness, alkalinity, and calcium hardness concentrations increased while magnesium hardness concentration decreased to lower values. The pH continually increased for a lime dosage between 30% and 180%.

INTRODUCTION

Hard water is the most common water quality problem reported by consumers throughout the United States. More than 60 percent of the Earth's water is ground water and hard water is found in more than 85% of the country. The water travels through rocks and soil picking up minerals including calcium and magnesium, ions which produce hard water. (Water Review, Consumer report, 1990).

Hard water interferes with almost every cleaning task from laundering and dishwashing to bathing and personal grooming (IANR, Water Quality 1996). Clothes laundered in hard water may look dingy and feel harsh and scratchy. Dealing with hard water problems in the home can be a nuisance. In addition, hard water affects the amount of soap and detergent necessary for cleaning. Soap used in hard water combines with the minerals to form a sticky soap curd. Some synthetic detergents are less effective in hard water because the active ingredient is partially inactivated by hardness, even though it stays dissolved. Bathing with soap in hard water leaves a film of sticky soap curd on the skin. The film may prevent removal of dirt and bacteria. Soap curd interferes with the return of skin to its normal, slightly acid condition, and may lead to irritation. Soap curd on hair may make it dull, lifeless and difficult to manage.

Hard water also contributes to inefficient and costly operation of water treatment equipment. Heated hard water forms a scale of calcium and magnesium minerals that can contribute to the inefficient operation or failure of water treatment equipment . Pipes can become clogged with scale which reduces water flow and ultimately results in pipe replacement.

Hard water is not a health hazard. In fact, the National Research Council (National Academy of Sciences) states that drinking hard water generally contributes to the total calcium and magnesium needs in humans.

Water utilities struggling with source water that contains high amounts of calcium and/or magnesium often turn to lime softening to remove hardness. Raising treatment pH above 9.6 converts soluble calcium bicarbonate hardness to insoluble calcium carbonate. An increase in pH beyond 10.6 converts soluble magnesium bicarbonate to insoluble magnesium hydroxide. Aggressive magnesium removal often requires a treatment pH of 11 or higher, a process known as excess lime softening (Jones, C; et.al. 2005).

Chemistry of Hardness Removal Process

During precipitation softening, calcium is removed form water in the form of $CaCO_3$ precipitate and magnesium is removed as $Mg(OH)_2$ precipitate (Frederick W. Pontius). The carbonic acid concentration present and the pH play an important role in the precipitation of these two solids. Carbonate hardness can be removed by the addition of hydroxide ions and raising the pH by which the bicarbonate ions are converted to carbonate form having a pH above 10. Due to the increase in carbonate concentration, precipitates of calcium carbonate is formed. The remaining calcium, i.e. non carbonate hardness, cannot be removed by simple adjustment of pH. Therefore, soda ash (sodium carbonate) must be externally added to precipitate this remaining calcium. Magnesium is removed due to the precipitation of magnesium hydroxide. In the lime soda ash process, lime is added to raise the pH while sodium carbonate is added to provide a source of carbonate ion.

$$H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2H_2O \qquad (1)$$

Eq.(1) is the neutralization reaction between CO_2 carbonic acid and lime. This equation does not result any net change in water hardness. This also suggest that for each mg/L of carbonic acid expressed as $CaCO_3$ present, 1mg/L of lime expressed as $CaCO_3$ will be required for neutralization by knowing the stoichiometric ratios.

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

Eq.(2) presents the removal of calcium carbonate hardness. It also shows that for each molecule of calcium bicarbonate present, two carbonate ions can be formed by increasing the pH. This also suggest that for each mg/L of calcium bicarbonate present, 1mg/L of lime expressed as $CaCO_3$ will be required for its removal by knowing the stoichiometric ratios between them.

$$Ca^{2+} + \begin{bmatrix} SO_4^{2-} \\ 2Cl^- \end{bmatrix} + Na_2CO_3 \rightarrow CaCO_3 + 2Na^+ + \begin{bmatrix} SO_4^{2-} \\ 2Cl^- \end{bmatrix} \qquad (3)$$

Eq.(3) reflects the removal of calcium noncarbonated hardness. The stoichiometric coefficient suggest that for each mg/L of calcium noncarbonate hardness present, 1mg/L of sodium carbonate expressed as $CaCO_3$ will be required for its removal.

$$Mg^{2+} + 2HCO_3 + 2Ca(OH)_2 \rightarrow 2CaCO_3 + Mg(OH)_2(s) + 2H_2O \tag{4}$$

Eq. (4) is similar to eq.(2). If the magnesium bicarbonate and lime are expressed as $CaCO_3$, then the stoichiometric ratios suggest that for each mg/L of magnesium bicarbonate hardness present, 2 mg/L of lime expressed as $CaCO_3$ will be needed for its removal.

$$Mg^{2+} + \begin{bmatrix} SO_4^{2-} \\ 2Cl^- \end{bmatrix} + Ca(OH)_3 \rightarrow Mg(OH)_2(s) + Ca^+ + \begin{bmatrix} SO_4^{2-} \\ 2Cl^- \end{bmatrix} \tag{5}$$

Eq. (5) represents the removal of magnesium noncarbonate hardness. If the magnesium noncarbonate hardness and lime are expressed as $CaCO_3$, stoichiometric ratios suggest that for each mg/L of magnesium noncarbonate hardness present, 1 mg/L of lime expressed as $CaCO_3$ will be needed for its removal. Here no net change in the hardness level resulted as for each magnesium ion removed calcium ion is added.

Thus to complete the hardness removal process, sodium carbonate required to be added to precipitate the calcium as presented in the equation below.

$$Ca^{2+} + \begin{bmatrix} SO_4^{2-} \\ 2Cl^- \end{bmatrix} + Na_2CO_3 \rightarrow CaCO_3(s) + 2Na^+ + \begin{bmatrix} SO_4^{2-} \\ 2Cl^- \end{bmatrix} \tag{6}$$

OBJECTIVE

The objective of the water softening experiment was to determine the effects of varying lime dosages on parameters such as total hardness, calcium hardness, magnesium hardness, alkalinity and pH.

METHODS and MATERIALS

Very hard ground water was obtained from a well located in East Lansing provided by Joseph Nguyen. Initial sample characteristics such as pH, alkalinity, and total hardness are provided in Appendix 2. A lime, $Ca(OH)_2$, stock solution of 10mg/mL was prepared for dosing the sample with 30, 60, 90, 120, 150 and 180 percent of the stoichiometric amount of lime. The jar test was executed with the conventional apparatus with six 2-liter beakers (Appendix-2) mixing the groundwater with the various amounts of lime for 20 min at 30 rpm. The samples were then filtered through 0.45µm filter and then titrated for total hardness, calcium hardness, and alkalinity. In addition pH and magnesium hardness were noted down. This experiment was done in replicate to compare results and determine the degree of experimental error. Detailed protocols for this experiment, including titrations and calculations, are available in the appendix.

RESULTS and DISSCUSSION

Run 1: Water Softening

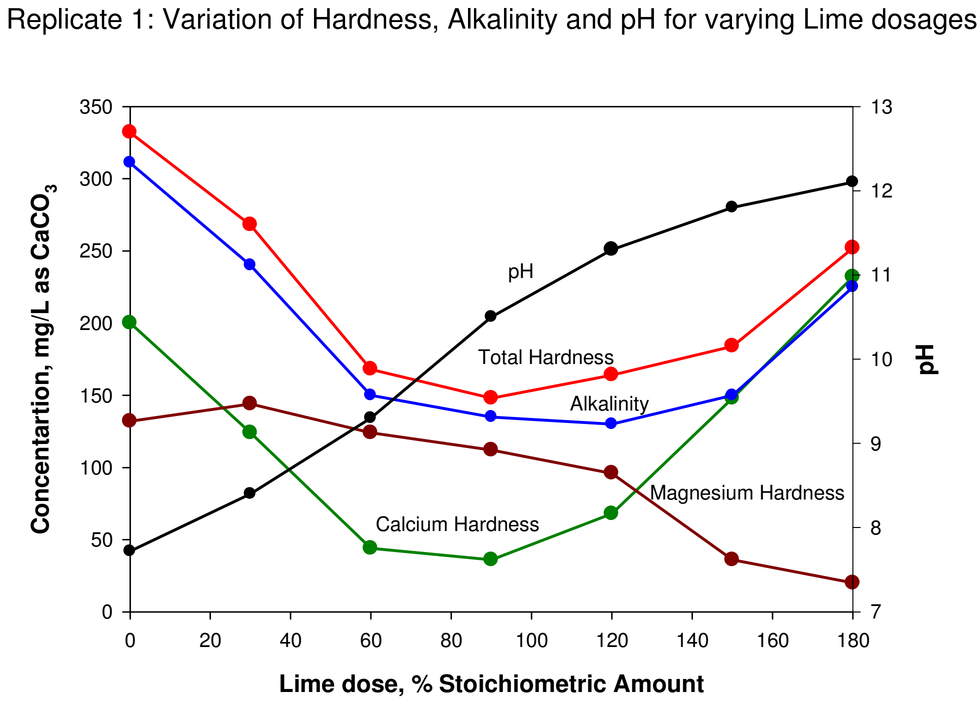

Figure 1: Variation of Hardness, Alkalinity and pH for varying Lime dosages (Run1)

Replicate runs for the water softening experiment evaluated parameters such as alkalinity, hardness and pH in response to varying lime dosages from 30% to 180% of the stoichiometric amount. In Run 1, the total hardness reached a minimum value of approximately 160 mg/L as $CaCO_3$ for a lime dosage of 90% (fig.1). The calcium hardness first decreased in concentration to a minimum of 35mg/L as $CaCO_3$ for a lime dosage of 90% and then after that continued to increase in concentration with an increase of lime dosage. This increase in calcium hardness was observed due to the addition of excess lime and the absence of alkalinity caused by carbonates. The plateau between 60% and 90% of lime is due to the presence of extra alkalinity. Any excess lime added in this region converts bicarbonates to carbonates and those carbonates combine with the free calcium ions to form precipitates.

Magnesium hardness concentration decreased with the increasing dosage of lime. Alkalinity decreased to a minimum at approximately 90% of lime and increased thereafter. This is due to the addition of lime and the precipitation of species, which consumes alkalinity that causes the initial decrease. At lime dosages higher than 120%, alkalinity increases due to an addition of excess lime. For every addition of lime, free

OH^- ions are released, therefore an increase in OH^- ions is responsible for an increase in pH.

Run 2: Water Softening

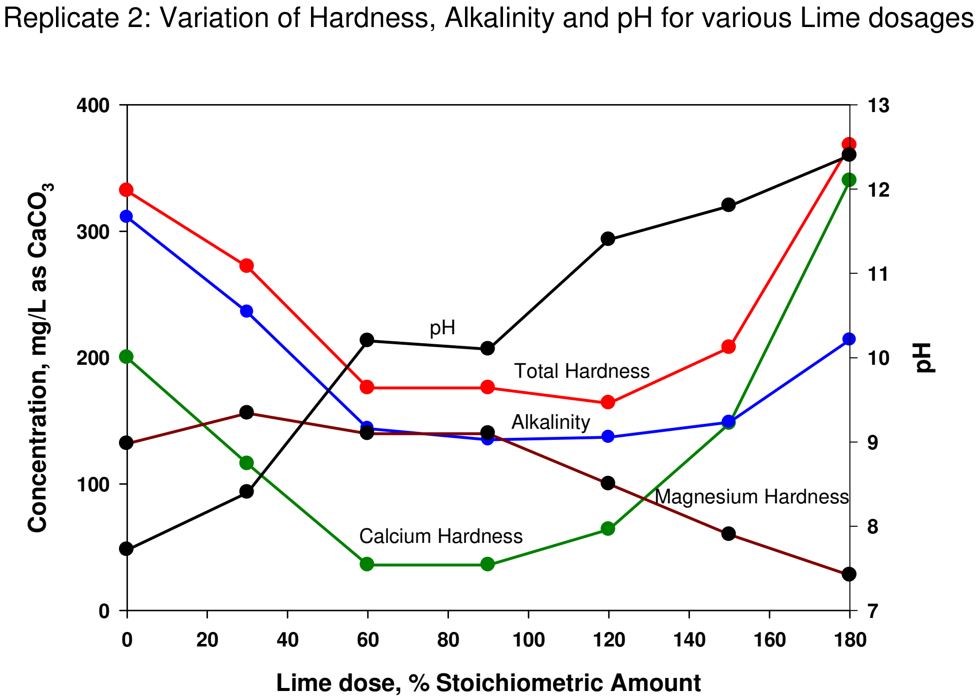

Figure 2: Variation of Hardness, Alkalinity and pH for varying Lime dosages (Run2)

In Run 2, the total hardness reaches a minimum value of approximately 160 mg/L as $CaCO_3$ for a lime dosage of 120% (fig.2). The calcium hardness concentration first decreases to a minimum of 35 mg/L as $CaCO_3$ for a lime dosage of 60% and then starts to increase above a lime dosage of 90%. This result was due to the addition of excess lime and the absence of alkalinity caused by carbonates. The plateau between 60% and 90% of lime was because of the presence of extra alkalinity. Any excess lime added in this region converts bicarbonates to carbonates and combine with the free calcium ions to form precipitates.

Magnesium hardness decreases with an increase in lime dosage and reaches a concentration of 30mg/L as $CaCO_3$, for a lime dosage of 180%. This concentration indicates an approximate solubility limit of magnesium ions. In addition alkalinity decreased to a minimum around 90% of lime but increases thereafter. The trends observed in Run1 and Run2 were in good correlation with each other.

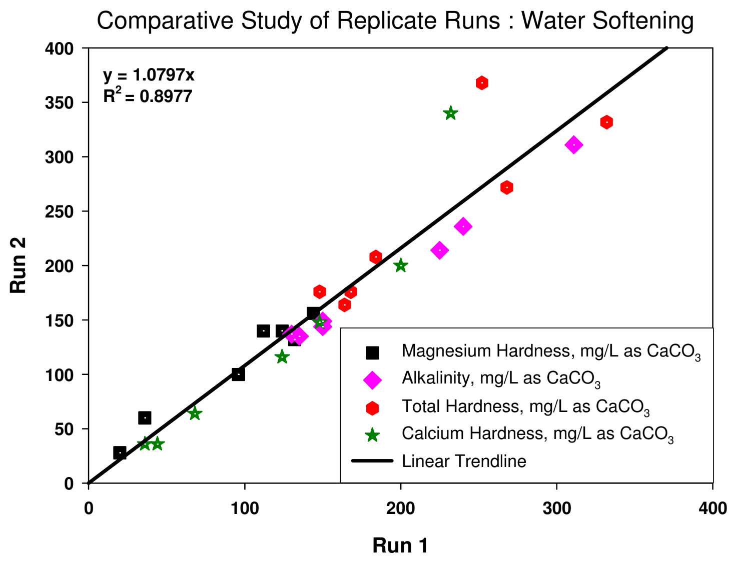

Figure 3: Comparison of Replicate Runs

This plot is a comparative study of the data obtained from run 1 and run2. The data from each run have an R^2 correlation of 0.90 for the parameters of this study. Hence, the experiment is reproducible and the trends observed for each parameter in response to varying lime dosages are in agreement with the expected trends.

CONCLUSIONS

This experiment yielded the following conclusions:

- Calcium hardness concentrations decreased with an increase in lime dosage but concentrations increased at dosages higher than 90%.
- Magnesium hardness decrease with an increase in lime dosage, especially when calcium hardness was increased (dosage higher than 90%)
- Alkalinity decreased to a minimum value of approximately 135 mg/L as $CaCO_3$ at a lime dosage of 90% and increased thereafter due to the addition of excess lime.
- pH increased with an increase in lime dosage due to the generation of free OH^- ions.
- The replicate runs conducted were in correlation with each other, thereby demonstrating reproducibility.

REFERENCES

1. IANR, Water Resources management, Water Quality, 1996.
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3. Syed Hashsham. Chemical Precipitation: Water Softening. Lab Report, 1993
4. Water Quality and Treatment: A Handbook of Community Water Supplies. American Water Works Association. Fourth edition, 1990
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6. Water Treatment Principles and Design. MWH. Second edition, 2005

APPENDIX 1 – RAW DATA

Table1: Run 1

Lime dose (%)	Ca hardness (Titrant Volume)	Total hardness (Titrant Volume)	Alkalinity (Titrant volume)	Ca Hardness	Total Hardness	Alkalinity	Mg Hardness	pH
0	5	8.3	31.1	200	332	311	132	7.7
30	3.1	6.7	24	124	268	240	144	8.4
60	1.1	4.2	15	44	168	150	124	9.3
90	0.9	3.7	13.5	36	148	135	112	11
120	1.7	4.1	13	68	164	130	96	11
150	3.7	4.6	15	148	184	150	36	12
180	5.8	6.3	22.5	232	252	225	20	12

Table2: Run 2

Lime dose (%)	Ca hardness (Titrant Volume)	Total hardness (Titrant Volume)	Alkalinity (Titrant volume)	Ca Hardness	Total Hardness	Alkalinity	Mg Hardness	pH
0	5	8.3	31.1	200	332	311	132	7.7
30	2.9	6.8	23.6	116	272	236	156	8.4
60	0.9	4.4	14.4	36	176	144	140	10
90	0.9	4.4	13.5	36	176	135	140	10
120	1.6	4.1	13.7	64	164	137	100	11
150	3.7	5.2	14.9	148	208	149	60	12
180	8.5	9.2	21.4	340	368	214	28	12

APPENDIX 2 – Sample Calculation to Determine the Lime Dosage

Sample: Ground water

pH= 7.72

Ca^{2+} = 200 mg/L

Mg^{2+} = 132 mg/L

Temperature= 20 ^{0}C

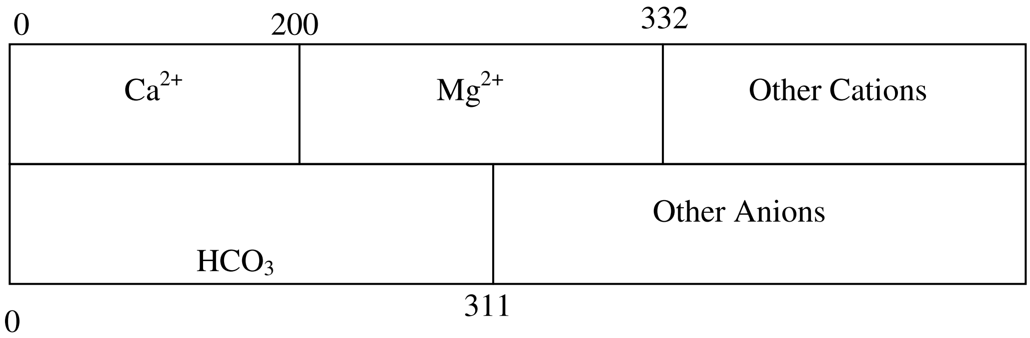
Alkalinity= 311 mg/L

Total Hardness= 332 mg/L

Carbonate Hardness= Alkalinity = 311 mg/L $CaCO_3$

Non Carbonate hardness = Total hardness- Alkalinity = 21 mg/L $CaCO_3$

From the above values we know that it is an excess lime soda –ash process



Step1: Assume pH=7, so all alkalinity is in the bicarbonate form

a) $[HCO_3]=311 \times (\frac{61}{50}) \times (\frac{1}{1000}) \times (\frac{1}{61}) = 6.22 \text{ x } 10^{-3}$ mol/L

b) $K_1=10^{14.8435- 3404.71 /293 – 0.032786 (293)}$

$K_1 = 4.26 \text{ x } 10^{-7}$

$K_2= 10^{6.498- 2909.39/293-0.02379(293)}$

$K_2 = 3.97 \text{ x } 10^{-11}$

c) $$\alpha_1 = \frac{1}{1\times10^{-7}/K_1 + 1 + K_2/1\times10^{-7}}$$

$$= \frac{1}{1\times10^{-7}/4.26\times10^{-7} + 1 + 3.97\times10^{-11}/1\times10^{-7}}$$

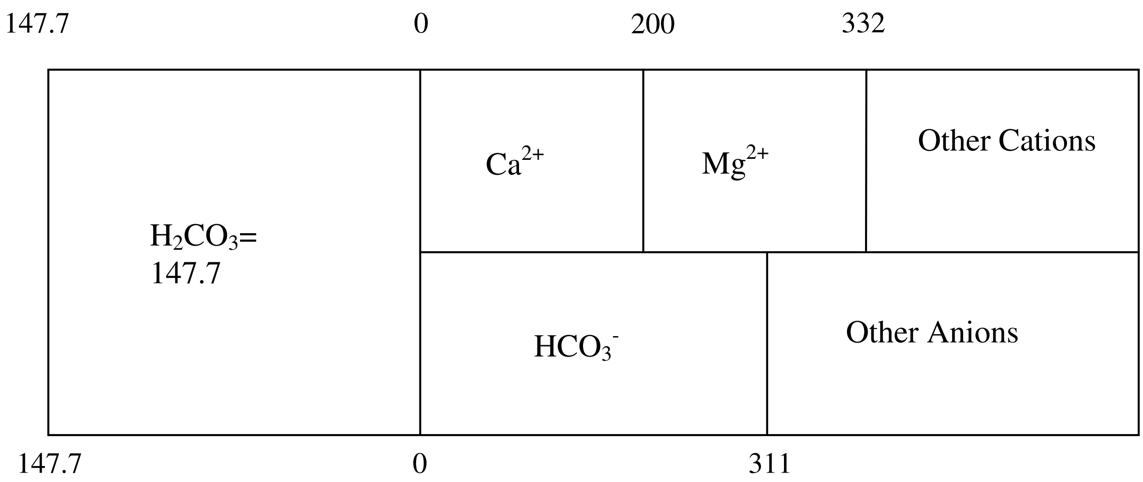
= 0.81

d) $C_T = \frac{6.22\times10-3}{0.81} = 7.679\times10^{-3}$ mol/L

e) $[HCO_3^*]$= 7.679 x 10^{-3}-6.22 x 10^{-3} = 1.477 x 10^{-3} mol/L

$[HCO_3^*]$= 1.477 x 10^{-3} mol/L x 62 g/mol = 0.0915 g/L= 91.5 mg/L

$[HCO_3^*]$= 147.7 mg/L $CaCO_3$



Step2:

Total Hardness= 332 mg/L

Ca^{2+} Carbonate Hardness = 200 mg/L

Ca^{2+} Non Carbonate Hardness = 0 mg/L

Mg^{2+} Carbonate Hardness = 311-200 = 111 mg/L

Mg^{2+} Non Carbonate Hardness= 332-311= 21 mg/L

Step3:

Lime Dosage:

147.7 + 200 +2(111) +21= 590.7 mg/L as $CaCO_3$

590.7 X (37/50) = 437.118 mg/L as $Ca(OH)_2$

Soda Ash dose:

=0+21=21 mg/L as $CaCO_3$

Soda ash dose $= 21\times\frac{53}{50} =$ 22.26 mg/L as Na_2CO_3

APPENDIX 3 - Water Softening and alkalinity Protocol

Water Softening Protocol

TRIAL RUN:

1. Prepare a Lime stock of 10 mg/mL
2. Prepare 0.1 M EDTA stock
3. Using ground water samples measure Total hardness, Calcium hardness, Magnesium hardness, Alkalinity, pH and Temperature
   a. Total hardness, Calcium hardness and Alkalinity protocols attached at the end of this document.
4. Determine the appropriate water softening process:
   a. i.e. East Lansing well water= excess lime soda-ash
5. Calculate and add lime dosage for 100% stoichiometric amount to a liter of ground water
   a. Use AWWA equations for dosage calculation
2. Conduct flocculation for 20 min at 30 RPM
3. Filter the entire sample through 0.45 uL filter (smooth side of filter facing down in the funnel)
4. Collect supernatant and measure Alkalinity, Calcium and Total hardness and pH
5. Calculate Magnesium hardness

RUN 1 & 2:

1. Calculate and add lime dosage for 30, 60, 90, 120, 150, and 180% of the stoichiometric amount to a liter of ground water.
   a. Use AWWA equations for dosage calculation
2. Conduct flocculation for 20 min at 30 RPM
3. Filter the entire sample through 0.45 uL filter (smooth side down in the funnel)
4. Collect supernatant and measure Alkalinity, Calcium and Total hardness and pH
5. Calculate Magnesium hardness
6. Repeat experiment to determine degree of experimental error

ALKALINITY PROTOCOL:

1. Use pH 7.0 buffer and adjust the pH meter to 7.0. Use pH 4.0 buffer and adjust the pH meter to 4.0.
2. Titrate 100 mL of sample with 0.02 N H_2SO_4 to obtain pH 4.5 by vigorously stirring towards the end of the titration step. This is done in order to break the surface and to obtain rapid equilibrium between CO_2 in solution and CO_2 in the atmosphere.
3. Total Alkalinity is measured as $CaCO_3$ in mg/L= (ml of titrant) X 10

To prepare 0.02N H_2SO_4, Use the following formula:

$N_f*V_f=N_i*V_i$

Where:

Nf: Final normality desired

Vf: Final total volume

Ni: Initial normality

Vi: Initial volume

TOTAL HARDNESS:

1. Take 25mL of sample and add 25 mL of DI water
2. Add 1 mL of hardness buffer and measure pH
   - Ideal pH for reaction is above 10
3. Add a scoop of Erichrome Black T indicator
   - The solution will turn pink
4. Titrate 0.1M EDTA until a permanent blue color appears
   - This is when Ca^{++} and Mg^{++} ions complex w/ EDTA
5. Total Hardness= Volume of titrant*1*(1000/vol. of sample)

Ca^{++} HARDNESS:

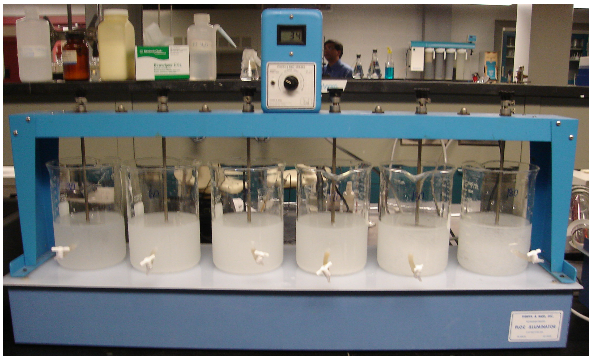
1. Take 25mL of sample and add 25mL of DI water
2. Add 2mL 8N NaOH solution and measure pH
    - pH ideally above 10, usually 12 or 13
3. Add a scoop of Erichrome Blue Black R indicator
    - The solution will turn pink
4. Titrate 0.01 N EDTA until a permanent blue color appears
5. Calcium Hardness=Volume of titrant*1*(1000/vol. of sample)

Total Hardness= Ca^{++} Hardness + Mg^{++} Hardness

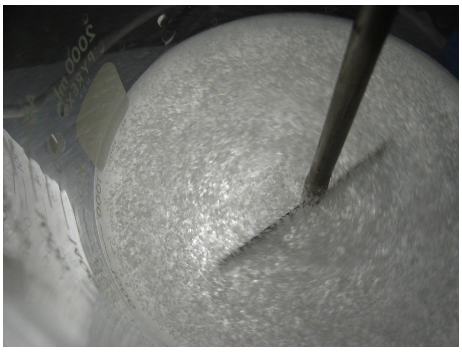
Carbonate Hardness=Alkalinity

Non-carbonate Hardness=Total Hardness – Alkalinity

APPENDIX 4 - Pictures



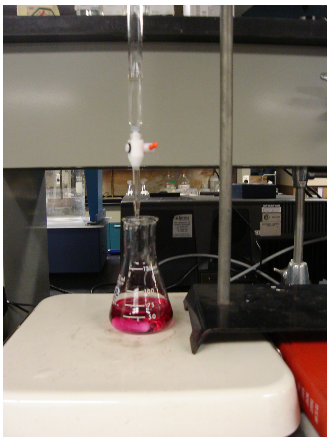
Setup & Samples with Lime Dosage



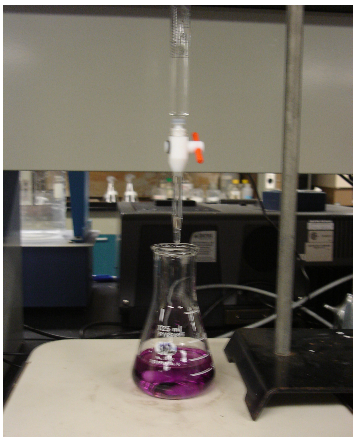
Floc. Formation

Filtration Setup

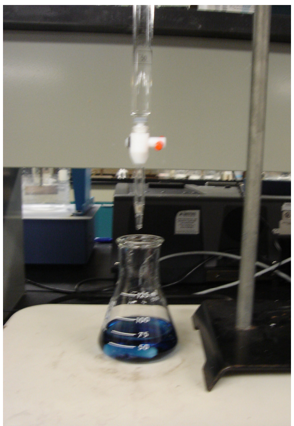
Samples After Filtration



Before Titration



Mid-Titration



End of Titration