ENE 806, Project Report 3

CHEMICAL PRECIPITATION: WATER SOFTENING

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ABSTRACT

The groundwater with high level initial hardness was softened with various lime dosage varying from 30 % to 180% of the stoechiometric amount. Both the initial and final parameters such as total hardness, calcium hardness, total alkalinity, pH were measured and compared to get the idea of removal efficiency with different lime dosage. The results showed that with 120 % lime dosage, the treated water has lowest total alkalinity, magnesium hardness and total hardness compared to the other lime dosages. The total hardness removal could achieve 60 %, while the alkalinity could get the 72 % removal. However, the optimum lime dosage for removing calcium hardness was found to be 90% of the stoichiometric lime dosage.

SUMMARY

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1. INTRODUCTION

The hardness of water is due to the presence of polyvalent metallic ions, principally Ca^{2+} and Mg^{2+} (Crittenden and Montgomery Watson Harza (Firm) 2005). There are many negative aspects resulting from hard water both for domestic and industrial usage. For example, in lather production, if the water is hard, it requires considerable amounts of soap before a lather can be produced. In the ordinary life, hard water produces scale in hot water pipes, heater, boilers, and other units where the temperature of the water is increased appreciably. The chemical equation for this process is showing below:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H2O.$$

Where the $CaCO_3$ is the main component for the scale when hard water is heated (Reynolds and Richards 1996).

Hardness of waters varies considerably from place to place. In general, groundwaters are harder than surface waters. Hardness can be expected in regions where large amounts of limestone are found, since water with carbon dioxide will dissolve limestone, releasing the calcium ion. Hardness is measured in terms of milli-equivalents per liter or equivalent CaCO3, and the degree of hardness was listed in many books, see Table 1 (according to table 4.6, (Reynolds and Richards 1996)).

Hardness, mg/l As $CaCO_3$	Degree of hardness
1-75	Soft
75-150	Moderately hard
150-300	Hard
300 and more	Very hard

Table 1: Degree of hardness as a function of the hardness dosage

Knowing the hardness of water is important in evaluating its use as a domestic or industrial water supply. The hardness must be known in determining the amount of chemicals required for lime-soda softening and in the design of ion exchange softening units.

On the other hand, public acceptance of hardness varies from community to community, consumer sensitivity being related to the degree to which the consumer is accustomed. Because of this variation in consumer acceptance, finished water hardness produced by different utility softening plants will range from 50 mg/L to 150 mg/L as CaCO3. Based on the table 1, the hardness range of finished water covers the scale from soft water to hard water (Letterman and American Water Works Association. 1999).

In this report, we studied the effect of different lime dosage on the efficiency of hardness removal and the consequent changes in total alkalinity and pH as well. This study gives us an idea of how to achieve the required hardness degree for final water.

2. MATERIAL AND METHODS

2.1. Calcium hardness

For determining the calcium hardness, we added 2 to 3 drops of 8 N Sodium hydroxide solution to achieve pH around 11 to 13. Eriochrome Blue black R was chosen for the color indicator. EDTA standard of 0.01 M was used to titrate the mixture from red to blue end-point, then the calcium hardness was calculate as

$$mg\ CaCO_3/L = A * B * 1000 / ml\ sample,$$

Where A= volume of titrant for sample (mL)

and B= mass of $CaCO_3$ (mg) equivalent to 1.00 mL EDTA titrant at the calcium indicator end point.

2.2. Total hardness

As for total hardness, the buffer solution was prepared in this way: 1) dissolve 16.9 g ammonium chloride (NH_4Cl) in 143 mL ammonium hydroxide; and 2) add 1.25 g magnesium salt of EDTA and dilute to 250 mL with distilled water. The indicator used for total hardness is Eriochrome Black T. The EDTA standard is still at the concentration of 0.01 M. Then the total hardness was calculated as

$$mg\ CaCO_3/L = A * B *1000 / ml\ sample,$$

Where A= mL titrate

and B=1, mg CaCO3 equivalent to 1.00 mL EDTA titrant at the calcium indicator end point. (standard books)

2.3. Alkalinity

For alkalinity, we titrated 100 mL of sample with 0.02 N H_2SO_4 to pH 4.5 and stirred the water during the titration. The total alkalinity as $CaCO_3$ was getting by multiplying the volume (as ml) used of titrant by ten. The equation is:

$$\text{Total alkalinity as mg } CaCO_3/L = \text{mL of titrant} * 10.$$

2.4. pH measurement

The pH values of all the samples have been measured with a pH meter (SA 720, Orion, Thermo Scientific, Waltham, MA) before and after softening.

2.5. Water softening

Eight beakers with one liter each of ground water have been treated in a common jar test apparatus (Phipps&bird Stirrer, Richmond, VA) with different concentrations of lime ranging from 0% to 180% (0%, 30%, 60%, 90%, 100%, 120%, 150% and 180%) of the theoretical dose that is required to remove all the hardness. The lime treating time is 20 min at the stirring speed of 30 rpm. At the end of the softening reaction, the water of each sample has been filtered with a 0.45 µm filter. The supernatants were collected and measured for all the parameters described above.

3. RESULTS

We tested the initial status of the groundwater. Those values have been reported in the following table.

Alkalinity, mg/L as $CaCO_3$	305
Total hardness, mg/L as $CaCO_3$	288
Hardness due to Ca^{2+}, mg/L as $CaCO_3$	204
Hardness due to Mg^{2+}, mg/L as $CaCO_3$	84
pH	7.94
Temperature, °C	24

Table 2: Initial status of groundwater

The source water has high calcium (204 mg/L as $CaCO_3$), high magnesium carbonate hardness (84 mg/L as $CaCO_3$) and since the total hardness is less than the carbonate and bicarbonate alkalinity, then the total hardness is equivalent to the carbonate hardness and the noncarbonated hardness is zero. Based on these characterizations, the type of treatment process necessary for softening this water is the excess lime process.

3.1. Calculation explanations

3.1.1. Estimate the carbonic acid concentration.

Determination of the bicarbonate concentration in moles per liter (alkalinity is assumed to be in the bicarbonate form since the pH is 7.94).

$$[HCO_3^-] = 305\left[\frac{61}{50}\right]\left[\frac{1}{1000}\right]\left[\frac{1}{61}\right] = 6.1\times10^{-3} mol/L$$

Computation of the dissociation constants for carbonic acid at 20°C

$$K_1 = 10^{14.8435-3404.71/293-0.032786\times293} = 4.14\times10^{-7}$$

$$K_2 = 10^{6.498-2909.39/293-0.02379\times 293} = 3.96\times 10^{-11}$$

Computation of α_1

$$\alpha_1 = \frac{1}{1.0\times 10^{-7.94}/4.14\times 10^{-7} + 1 + 3.96\times 10^{-11}/1.0\times 10^{-7.94}} = 0.97$$

Determine the total carbonic species concentration,

$$C_T = \frac{6.1\times 10^{-3}\, mol/L}{0.97} = 6.29\times 10^{-3}\, mol/L$$

Computation of the carbonic acid concentration,

$$\left[H_2CO_3^*\right] = C_T - [HCO_3^-] = 6.29\times 10^{-3} - 6.1\times 10^{-3} = 0.19\times 10^{-3}\, mol/L$$

Or $\left[H_2CO_3^*\right] = 19 mg/L$ as $CaCO_3$.

Draw a bar diagram of the untreated groundwater

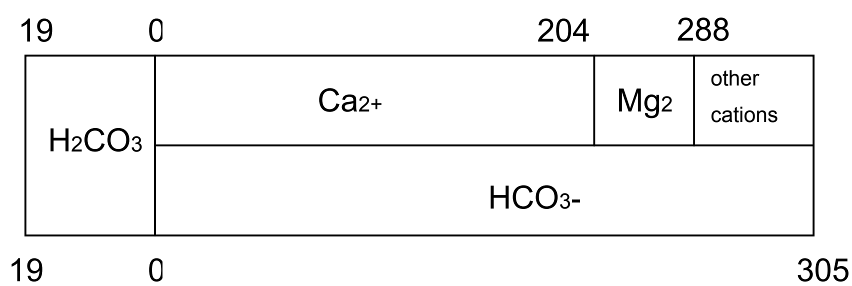

Figure 1: hardness diagram of the ground water used in this experiment

3.1.2. Establishment of the hardness distribution (based on the measured concentration of alkalinity, calcium, and magnesium hardness).

Total hardness = 288 mg/L

Calcium carbonate hardness = 204 mg/L

Magnesium carbonate hardness=84 mg/L

3.1.3. Estimation of the lime dose requirements by application of the relationship for the excess lime process:

Lime dose for excess lime process = carbonic acid concentration + total alkalinity + magnesium hardness + 60 mg/L excess lime

= 19 + 305 + 84 + 60

= 468 mg/L as CaCO3

Or Lime dose = 346.32 mg/L as $Ca(OH)_2$.

3.1.4. Estimation of the finished water hardness

Usually, with the lime dose estimated from step 3.1.3, the final hardness of the water is all the Mg^{2+} in the untreated water plus the practical limit of $CaCO_3$ removal. So it will be between 110-130 mg/L as $CaCO_3$.

3.2. Data analysis

Calcium and magnesium were removed by the lime softening process, in which the unwanted ions are precipitated by adding slaked lime. This reagent produced a voluminous precipitate of calcium carbonate and magnesium hydroxide, which acts by sweep coagulation, thus enmeshing the suspended particles as the precipitate is formed (Letterman and American Water Works Association. 1999). The alkalinity, pH, total hardness and hardness due to calcium were measured (see Table 2).

The lime dose has been calculated to be in 100% stoechiometric proportion with the amount of total hardness initially present in the ground water. This lime dose has been calculated to be 346.32 mg/L as $Ca(OH)_2$.

Then, lime has been added in the different samples at different proportion ranging between 0 and 180%. The results for the pH, hardness and alkalinity have been measured after filtration of the softened water in the above described conditions. Those results have been plotted on the following graph.

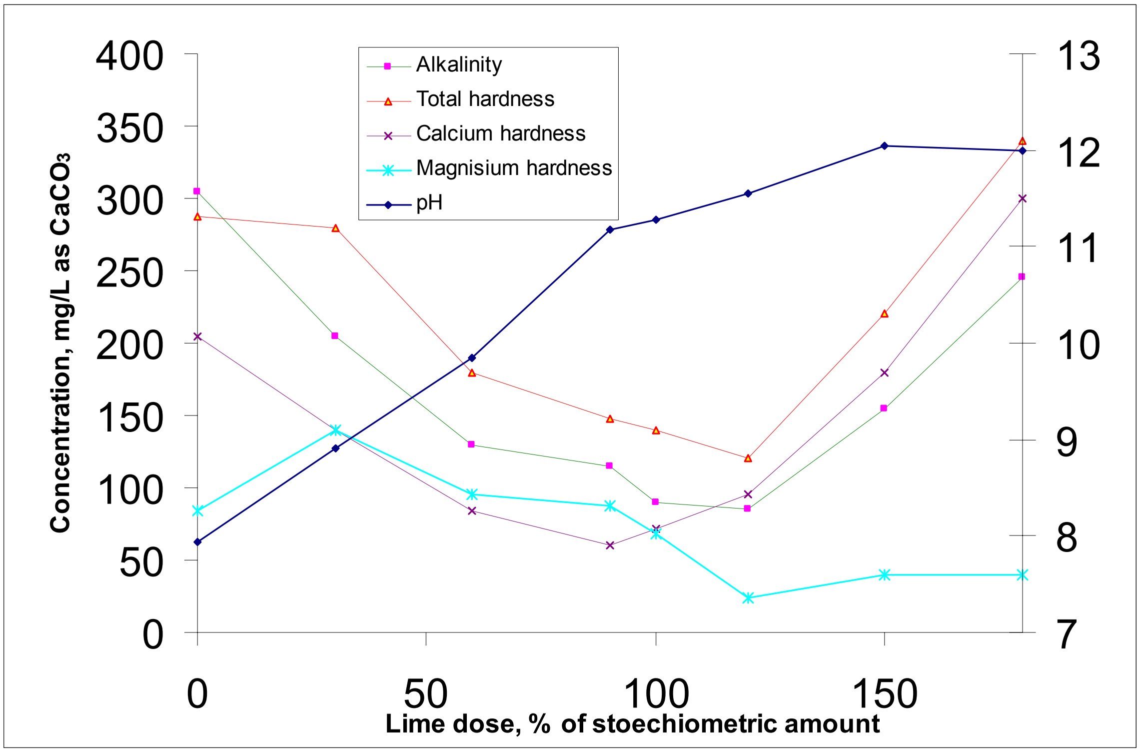

Figure 2: Evolution of hardness, alkalinity and pH as a function of the lime dosage

We can see on this graph that, as expected, the pH is increasing with the increase in lime dose. This corroborates with the fact that lime is a basic component whose dose increases the solution pH.

Total hardness stays stable between 0% and 20% of lime addition and begins to decrease significantly with the increase of lime dose. This total hardness decreasing trend is observed for lime dosages ranging from 20% to 120%. With 120% lime dosage, the minimum total hardness we achieved is 41% of the initial value. When the dosage exceeded 120%, the total hardness becomes strongly increasing with the increase in lime dosage to reach a maximum that is higher than the initial total hardness. These observations confirms the previous trend observed from the other groups (Hashsham

1993), that is 120% dosage of lime seems to be the most efficient dosage to remove total hardness, although the source of groundwater is different.

The hardness due to calcium tends to follow the same trend as the total hardness, however, we observed two main differences. Firstly, calcium hardness decreases spontaneously with the lime dose even at the first point of 20% lime dosage. Secondly, the best lime dosage to remove calcium hardness was found to be close to 90%. The minimum calcium hardness was found to be 30% of the initial value with 90% lime dosage. In the other word, beyond this value, the calcium hardness is increasing again to reach a maximum that is also higher than the initial Ca^{2+} hardness in water. The explanation we gave here for the best removal rate with 90% lime dosage is that the ideal pH to precipitate calcium carbonate hardness is determined to be about 9.5 (Reynolds and Richards 1996), which is corresponding to the observation from our experiments.

The hardness due to magnesium was achieved with 120% lime dosage. The best removal rate is 28% of the initial magnesium hardness. It fits for the fact that the ideal pH to precipitate magnesium hydroxide requires a pH higher than that required for calcium hardness removal (Reynolds and Richards 1996).

As for the alkalinity, it is initially decreasing to a minimum value of 85 mg/L (as $CaCO_3$) for a lime dosage of 120%. This observation is consistent with the fact that alkalinity (due to OH^- function) is supposed to be consumed by the lime and the precipitating species. Beyond the lime dosage of 120%, the alkalinity is rising with the lime dosage and reaches a maximum concentration of 245 mg/L for a lime dosage of 180%. This observation corroborates the fact that after reaching the ideal lime dosage, the lime will provides free OH^- ions which are responsible for the increasing alkalinity.

The equations that could be used to explain the main chemical reactions during the softening processes are presented as follows:

The lime reacts with carbonate hardness:

$$Ca(OH)_2 + Ca(HCO_3)_2 \rightarrow 2CaCO_3 (\downarrow) + 2H_2O$$

And $$Ca(OH)_2 + Mg(HCO_3)_2 \rightarrow MgCO_3 + CaCO_3 (\downarrow) + 2H_2O$$

The product magnesium carbonate is soluble, but more lime will remove it by the reaction $Ca(OH)_2 + MgCO_3 \rightarrow CaCO_3 (\downarrow) + Mg(OH)_2 (\downarrow)$

Part of the excess lime can be stabilized by carbon dioxide.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 (\downarrow) + H_2O$$

4. CONCLUSIONS

In this experiment we have successfully analysed the effect of lime dosage on ground water softening in an "excess lime process" conditions. When the pH was constantly increasing with the lime dosage, the alkalinity, the total hardness and the hardness due to magnesium were found to be more efficiently removed with a lime dosage of 120%.

The experiment also helped us to learn the fact that it is not possible to remove all of the hardness from the water because of the slight solubility of calcium carbonate and magnesium hydroxide and also, the presence of some of the precipitate as very fine, nonsettling flocs. Once stabilization has been accomplished, the fine precipitate dissolves back into solution. Just like what was estimated by step 3.1.4, the practical softening by lime-soda process can reduce the hardness to about 110 to 130 mg/L as calcium carbonate.

5. REFERENCES

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