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ANC Fall 2010 Reflection Report 1

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ANC Control Reflection Report

Primary Author: Larry Lin

Secondary Author(s): Roy Guarecuco, Drew Hart

Primary Editor: Drew Hart

Secondary Editor(s): Larry Lin, Roy Guarecuco

AguaClara Reflection Report

Cornell University

School of Civil & Environmental Engineering

Ithaca, NY 14853-3501

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Abstract

Flocculation in AguaClara plants operates optimally within a pH range between 6.5 and 7.5, but due to the low alkalinity in many Honduran water sources, the acidity of the alum solution used as a coagulant at the beginning of the plant sequence generally lowers the pH well out of that range. The main objective of the Acid Neutralizing Capacity Control team is to investigate the possibility of designing a lime feeder system to deliver saturated calcium hydroxide solution to be mixed with the plant flow in order to provide alkalinity to offset the acidity of the alum solution. We believe that the failure of the lime feeder in maintaining saturated effluent for the expected length of time which has been consistently observed is largely due to the nucleation of calcium carbonate crystals on the surface of the solid calcium hydroxide in the reactor. This coating of the lime particle inhibits dissolution. In the past two weeks, we have ordered, cleaned, and assembled supplies in the new lab space to prepare for our experiments. During this semester, we will attempt to remove carbonate ions from the influent water with an effluent recycle system, determine the Honduran lime composition with respect to carbonate impurities, and maximize lime feeder efficiency by experimenting with changes in upflow reactor velocity, initial mass of lime added, and the physical form of the original lime.

Introduction

AguaClara plants use flocculation to grow particles before sedimentation. The optimal pH range for alum flocculation is between 6.5 and 7.5. Outside of this range undesirable aluminum hydroxide complexes form instead of $\text{Al}(\text{OH})_3$, the precipitate which acts as the coagulant necessary for flocculation. Low alkalinity source waters in Honduras do not provide sufficient buffering capacity to maintain the pH in the optimal range after the addition of alum, whose Al^{+3} ion effectively acts as an acid. Therefore, the ANC Control team is investigating the possibility of producing a base to counter changes in pH. Soluble compounds such as sodium carbonate can be dissolved in a stock solution and used with a dose controller, but are relatively expensive. Slaked lime (calcium hydroxide) is an inexpensive and readily available compound in Honduras. Because calcium hydroxide is relatively insoluble, a stock solution of sufficient quantity is impractical. Thus, the ANC Control team is investigating the possibility of using a lime reactor system, in which a reservoir of lime particles are dissolved, to constantly deliver effluent saturated with calcium hydroxide to the plant flow. Past teams have run experiments with a lime feeder apparatus in the lab and measured effluent pH in order to see how long the effluent remains saturated. In all cases, the effluent pH drops, indicating a calcium hydroxide concentration below saturation, well before the projected time calculated from the amount of lime added. The anticipated run time is calculated as the amount of time saturated effluent can be produced at the chosen flow rate before all of the solid lime added to the reactor at the beginning of the run has dissolved. We assume that the saturation concentration corresponds to the K_{sp} value found in the literature ($5 \times 10^{-6} \text{ mol}^3/\text{L}^3$) and that all effluent would remain saturated until the solid lime has been depleted, which is impossible but provides a theoretical upper bound on run time.

Although experimental runs during the summer of 2010 with distilled water and Honduran lime have produced better results than those seen in earlier semesters, the majority of the lime used is never dissolved. An average efficiency of 16% was calculated for the 2.5 cm tube settler, and an average efficiency of 19% was calculated for the 5 cm tube settler, which has a lower capture velocity due to the factor of four reduction in the upflow velocity in the tube settler resulting from the increase in cross-sectional area. These efficiencies are significantly lower than the minimum of 25% necessary to make calcium hydroxide theoretically viable as a base compared to sodium carbonate. Because sodium carbonate dosing would effectively be 100% efficient because all solid chemical purchased would be dissolved in the stock solution, the rough 25% efficiency criterion is based on the fact that sodium carbonate is approximately four times as expensive per equivalent of acid neutralizing capacity than calcium hydroxide.

It is believed that the unintended precipitation of calcium carbonate is hindering lime dissolution. Because of the high calcium concentration in the saturated calcium hydroxide solution, the supersaturation index (Equation 1) for the relatively insoluble CaCO_3 is approximately 35, whereas a value of only 1.6 is necessary to have favorable heterogeneous nucleation.

$$S = \frac{g_{\text{Ca}^{+2}} [\text{Ca}^{+2}] g_{\text{CO}_3^{2-}} [\text{CO}_3^{2-}]}{K_{sp}} \quad (1)$$

There was insufficient time for a large set of samples to be analyzed, but during two sample runs with the Total Organic Carbon analyzer solid sampler, the fraction of calcium carbonate in the solid lime was found to be 0.0232 and 0.0311. In order to finish the analysis of the carbonate content of the lime the team only needs to collect more data with the instrument.

One proposed solution to the calcium carbonate nucleation problem is to install a recycle line which carries about 20% of the saturated calcium hydroxide effluent back to a pre-treatment reactor in which calcium carbonate will precipitate on seed particles. If successful, this will reduce the concentration of carbonates in the influent enough to extend the run time of the lime feeder.

Literature Review

Heterogeneous nucleation and growth of calcium carbonate on calcite and quartz

Lioliou et al. (2007).

This study examined the heterogeneous nucleation and growth of calcium carbonate crystals in supersaturated solutions. Experiments were done with supersaturated calcium carbonate solutions both with and without seed particles to serve as precipitation nuclei. In the latter case, there is an induction time which is inversely proportional to supersaturation of the solution which was measured in the study. A surface energy for calcite of 64 mJ/m^2 was calculated from a fit of the induction time-supersaturation data based on a polynuclear growth model. When calcite (CaCO_3) crystals were used as the seed particles, nucleation occurred in supersaturated solutions without any induction time. When quartz was used, the induction time was reduced relative to the absence of seed particles. The symbol Ω is used for the supersaturation index (Equation 1). For unstable supersaturation solutions ($\Omega > 1.66$), rates of precipitation showed a high-order dependence on supersaturation.

This study suggests that calcium carbonate is likely nucleating on the surfaces within our reactor because the supersaturation with respect to calcium carbonate is very high due to the presence of more soluble calcium carbonate. The nucleation probably contributes to inefficiency of the lime feeder by coating the calcium hydroxide particles with calcite crystals, thereby inhibiting dissolution. In addition, the study suggests that calcium carbonate precipitation will be much more likely if we have calcite crystals as seed particles and as high a supersaturation index as possible. It was also proposed last semester that calcium hydroxide may have surface properties similar enough to calcium carbonate that it would provide a comparable nucleation site.

Particle size distribution dynamics during precipitative softening declining solution composition

Nason et al. (2008).

The new pre-treatment reactor the ANC team is experimenting with is designed to increase calcium carbonate (CaCO_3) precipitation. Calcium carbonate inhibits the lime dissolution rate in the main reactor, causing coagulation in the lime feeder and preventing a continuous supply of lime-saturated effluent from leaving the lime feeder towards the rest of the AguaClara plant. The research by Nason et al. (2008) indicates that the rate of flocculation in precipitative coagulation removal processes (such as AguaClara's use of alum) largely depends on the initial saturation ratio. The calcium ion distribution in the lime-feeder effluent will affect the precipitation and flocculation of new solids in the particle-removal process that uses adsorption to remove large particles that consist of accumulated organic matter, carbonate, and calcium ions.

Effect of water chemistry on calcium carbonate deposition on metal and polymer surfaces

Wu et al. (2010).

Wu et al. (year) documents an experiment involving the precipitation of calcium carbonate within tubes of polypropylene and copper. It was discovered that in a given amount of time, there was more calcium carbonate deposition on the polypropylene. The hypothesized factors were differences in surface roughness, the inhibition effect of copper ions released by the copper surfaces, and differences in surface chemistry and interfacial energy. Different water chemistries were also tested. Solutions with low supersaturation resulted in lower accumulation, as well as high supersaturation solutions with high a pH. This result indicates utilizing a higher pH inhibits the precipitation of calcium carbonate.

Detailed Task List

1. Set up new lab space

Complete by: Tuesday, 9/28

The team has started by cleaning the lime feeders and all tubing and connections with an acidic solution to remove the calcium carbonate coating which formed during summer (2010) experiments. Clean apparatus make it easier to observe what is happening inside the reactor and eliminates the possible effect of dissolution of deposited carbonate at the beginning of experiments. The presence of carbonate deposits would confound the team's analysis of carbonate activity in the reactor. The cleaning has been finished with the lime-removing solvent ordered from McMaster-Carr.

The team will now set up the lime feeder apparatus, as it was previously set up in HO 150, in HO B60, including: (i) the lime feeder with all necessary tubing, (ii) the electrically isolated pH measurement system, (iii) peristaltic pumps, and (iv) a distilled water source. The team will set up a system to replace the direct distilled water supply available in the previous lab with a large reservoir filled by carrying buckets of distilled water down from the source upstairs.

The ANC team will need to obtain two clear tubes similar to the 1-inch glass tubes from the lab in HO150 to use as the pre-treatment reactor in the effluent recycle system. We have obtained two pieces of schedule 80 1-inch clear PVC and ordered parts to fit push-to-connect adapters on the ends. We will also need two peristaltic pumps which can be operated manually and at least one pH probe with a stamp box to connect it to the data acquisition box. For now, the team will set up assuming that we will only use the lime feeder with the 2-inch diameter tube settler, so that we use less distilled water and equipment.

2. Experiment with effluent recycle system

Control run: Tuesday, 9/28

Recycle System run: Thursday, 9/30

The team will begin with a control run to reproduce the failure seen in past semesters. We will continue to use a flow rate of 30 mL/s and add 100g of lime to allow comparison with previous experiments. The team will then set up the effluent recycle system detailed in the summer team's final report and run an experiment with identical parameters to the control. The pre-treatment reactor, pictured in *Figure 1* below, will be "seeded" with solid calcium hydroxide to provide nucleation sites for

precipitating calcium carbonate, and it will serve to remove calcium carbonate from the influent water before it reaches the lime feeder. If successful, we believe this will extend the useful life of the lime feed system by slowing the buildup of calcium carbonate on the lime surface.

The team will use the TOC analyzer's solid sampler to determine the carbonate content of the raw lime (Task #3) and the leftover solids in the feeder after the experiments are complete. If done accurately, this will give us an estimate of the amount of carbonate that comes in with the influent, so that we will have another parameter by which to measure the success of the pre-treatment reactor, in addition to the measuring of time at saturation and reactor efficiency. One difficulty will be in removing the solids from the reactor after the experiment. The team will attempt to drain the reactor from the bottom while flushing from the top with distilled water, capturing all water and solids in a container. We will then likely need to use a drying oven to isolate the solids.

3. Finish lime composition analysis

Collect Data: Tuesday, 10/5

The team will collect data from the TC analyzer and analyze the data using the calibration curve created during the summer. The Total Carbon analysis will be done on the Honduran Lime. The team will determine the amount of carbonate that is in the lime both before and after running the first experiment with the new effluent recycle system. If the recycle system works efficiently, the amount of carbonate in the lime should differ only slightly before and after the experiment. If the difference in carbonate before and after the experiment is substantial, then we will know the effluent recycle system is not working efficiently. Knowing the raw lime composition will also allow us to include that source of carbonate in our lime feeder model.

4. Measure pH of saturated solution over several time points

During the summer, the team approximated the time that the lime feeder effluent remained saturated by plotting the effluent pH over time and then observing when the pH began to drop, indicating the effluent was no longer saturated. Although the values measured by the pH probe are useful for this purpose, the values themselves are inaccurate because we are measuring a pH outside of the calibrated range. Actual measurements vary significantly from run to run. In order to more accurately measure the effluent pH and check for consistency between runs, the team will need to take effluent samples and first test for acid neutralizing capacity and total carbonates, from which pH can be calculated. The acid neutralizing capacity is measured by titrating the sample with a strong acid and making a Gran plot, while the total carbonates can be found using the TOC machine liquid sampler. It may be possible, once we have an accurate value for the pH of saturated lime feeder effluent, to then calibrate the pH probes to be accurate in that range.

5. Determine best parameters for a successful run

Before a lime feeder design can be implemented, the team will need to determine what parameter values (up-flow velocity, initial lime amount added, and method of lime addition) produce the lime feeder's best performance. The team will first experiment with the parameters that maximize the efficiency of the new effluent recycle system if it is successful.

6. Effluent Recycle System with higher carbonate contents

If the team determines the new effluent recycle system is working efficiently, then new experiments will be done using tap water, which has much higher carbonate content than distilled water. We will want to run the system under a variety of conditions to test its versatility. It is possible that under high-alkalinity conditions, there is insufficient residence time in the pre-treatment reactor to cut down the carbonate concentration enough before the water reaches the lime feeder, so that premature failure still occurs. We will need to determine at what raw water carbonate concentration the alkalinity is sufficiently high that a lime feeder would not be necessary. Under these condition, the performance of the lime feeder is not important.

Experimental Design

Experimental runs will be done using the proposed effluent recycle system designed to remove carbonates from the source water before it reaches the lime feeder (Figure 1).

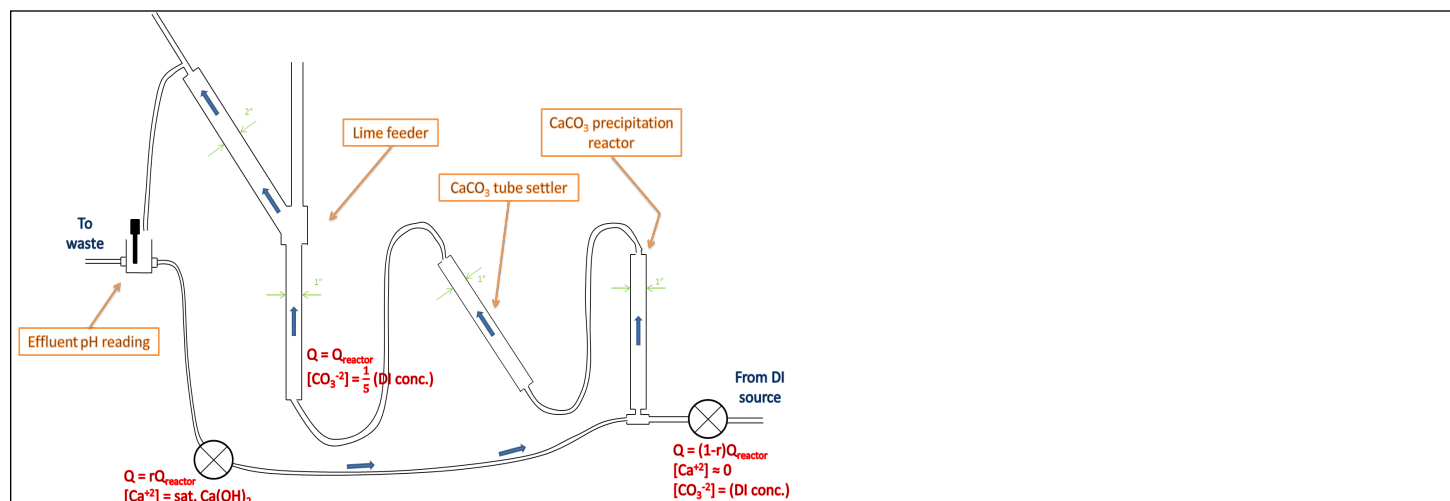


Figure 1. The effluent recycle system will carry a fraction, r , of the effluent flow back to a pre-treatment reactor which serves to remove carbonates from the influent before it reaches the lime feeder.

Water first flows into the system from the far right of the diagram and passes up the vertical precipitation reactor that contains calcium carbonate and recycled calcium hydroxide from the lime feeder effluent to aid in precipitation before the influent goes into the tube settler. A fluidized bed of solid precipitates in the first reactor is expected to decrease the carbonate concentration in the effluent by a factor of 5, assuming a calcium hydroxide recycle rate of 22%. This recycle rate is needed to maintain a supersaturation index of 1.6 for the one-fifth reduction in carbonate concentration in the effluent. Recycling the effluent is expected to delay the time it takes for calcium carbonate to build up on the surface of the lime and enhance the lime dissolution rate. By reducing the carbonate concentration in the lime feeder influent to one-fifth of its initial concentration, the team believes the lime feeder will be able to deliver saturated effluent for twenty-four hours because of the reduced build-up of insoluble solids on the lime feeder surfaces. The longer the effluent stays basic enough to add sufficient alkalinity for further chemical dosing, the more efficiently the lime feeder is working. The goal for a viable lime feeder is to determine an initial amount of lime as well as appropriate flow rates, to allow a plant manager to only add lime to the main reactor once every twenty-four hours. For the first experiments, the team will utilize 100 g of lime and a flow rate of 30 mL/s.

The team will measure the effluent pH in two different ways. A comparison should be done between the data pH data collected with the pH meters and the pH calculated by using acid neutralizing capacity and total carbonate tests. An acid neutralizing test will be done by titrating the effluent sample with a strong acid and analyzing a Gran plot. The Total Organic Carbon analyzer will be used to determine the number of carbonates in the samples. The team will collect this data at several time points during the experimental run, and compare calculated pH values with effluent pH values recorded using the pH probes.

The team will also perform a Total Carbon analysis on samples of the Honduran lime used in the lime feeder, and this analysis will determine the amount of carbonate that is in the lime both before it is placed in the reactor, and at the end, when the pH probes indicate that the effluent is no longer saturated. Effluent samples from several time points in between will also be analyzed to determine when the effluent begins to show decreasing alkalinity. If the effluent recycle system works efficiently, there will be only a small difference in the carbonate concentrations measured at the beginning and end of the experimental run.

Future Work

The team will begin with a control run to reproduce the failure seen in past semesters. Then the team will set up the effluent recycle system detailed in the summer team's final report and run an experiment with identical parameters to the control. The pre-treatment reactor, which will be "seeded" with solid calcium hydroxide to provide nucleation sites for precipitating calcium carbonate, and will serve to remove calcium carbonate from the influent water before it reaches the lime feeder.

We will also use the TOC analyzer's solid sampler to determine the carbonate content of the raw lime and the leftover solids in the feeder after the experiments are complete. If done accurately, this will give us an estimate of the amount of carbonate which comes in with the influent, so that we will have another parameter by which to measure the success of the pre-treatment reactor.

Team Roles and Expectations

Team expectations:

- Meetings planned by the team are not optional and should be focused, since we have limited time to work together. If someone cannot make a planned meeting, they should let the rest of the team know as early as possible.
- Experimentation should be done carefully and precisely, since data collected from poorly run experiments are much less useful. The team should take its time and make sure experiments are done well.
- For writing assignments, the team should plan ahead and make sure all of the respective parts are sent to the compiler with plenty of time for them to edit the parts before the due date (at least twelve hours).

ANC Team Roles

- Data compiling: After an experiment the Microsoft Excel data sheets created by Process Controller need to be organized and prepared for analysis by creating graphs and doing appropriate calculations.
- Setting up and running experiments: This includes cleaning of the apparatus, collecting the distilled water, lime, and all other necessary materials, and starting the experiments by adding lime to the reactor and initiating data collection. It also includes calibrating pH probes and collecting effluent samples for later TOC and ANC tests. This will require the most time and will be shared by the entire team.
- Writing: Biweekly reflection reports will be split up among the team members, and we expect to rotate which parts we write each time. One editor will ultimately compile the report and look over the whole thing, checking for correctness, style, and eliminating excessive repetition.

Team Availability

Some part of the team will meet Monday afternoons after 2:30pm, Tuesdays from 11am until after class, and Thursday often beginning at 11am. It will also be necessary for one or more people to come in at other times to start and stop experiments and check on progress.

Team leader: Drew Hart

Bibliography

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