

EXPERIMENTS IN BATCH MODE AND RESULTING DESIGN ELEMENTS FOR STRUVITE CRYSTALLIZER

Experiments in batch mode were conducted on locally obtained lagoon effluent to observe its behavior as it relates to several aspects of struvite precipitation. The observations enabled better-informed formulation of the basic design elements of a struvite crystallizer for removing phosphorus from that liquid. The experiments included (1) nutrient removal tests; (2) nutrient partitioning tests; (3) Mg supplementation tests; (4) pH enhancement tests; and (5) rate tests. Each of the five groups of tests are reported on below, followed by a summary of the crystallizer design elements. Methods of analysis for OP, TP, TAN, and Mg are summarized in the “Analysis of Liquid Samples” subsection of “Experiments with Laboratory-Scale Continuous Crystallizer.”

Experiments

Nutrient Removal Tests

These tests were performed to check whether literature review information on struvite solubility had been interpreted properly for lagoon waste. Applying the equilibrium solubility product and conditional solubility product data from the review to analyses of typical lagoon effluent, the effluent should be near saturation and therefore an increase in concentration of the product of the three ions (Mg, ammonium, or phosphate) should tend to precipitate struvite. The precipitation, unless caused by an increase in total OP, should reduce dissolved OP and dissolved TP. To test this, effluent from one anaerobic lagoon near Rocky Mount, North Carolina and effluent from a covered, ambient temperature in-ground digester near Clayton, North Carolina, were treated by adding magnesium bicarbonate solution to increase the Mg ion concentration and adding ammonia to increase the pH. The Rocky Mount lagoon effluent had a pH of 7.8 and contained 62.2 ppm TP, 55.8 ppm OP, 552 ppm TAN, and 30.1 ppm Mg. The Clayton digester effluent had a pH of 7.6 and contained 46.8 ppm TP, 45.4 ppm OP, 1,087 ppm TAN, and 18.5 ppm Mg.

The treatments consisted of the six combinations of two levels of ammonia addition (0 and

200 ppm) and three levels of Mg addition (0, 10.5 and 31.5 ppm). After the additions, the effluent was stirred for 20 minutes and then allowed to stand, covered, overnight. Then, samples of the untreated and treated liquids were centrifuged to remove suspended, i.e., non-dissolved material. The clear, brownish yellow centrifugate was poured off the grayish pink sediment and analyzed for TP and OP content and comparison against TP and OP content of centrifugate from untreated liquid from the lagoon and digester. The results for the Rocky Mount lagoon are depicted in Figure 4, and Figure 5 shows the results for the Clayton digester.

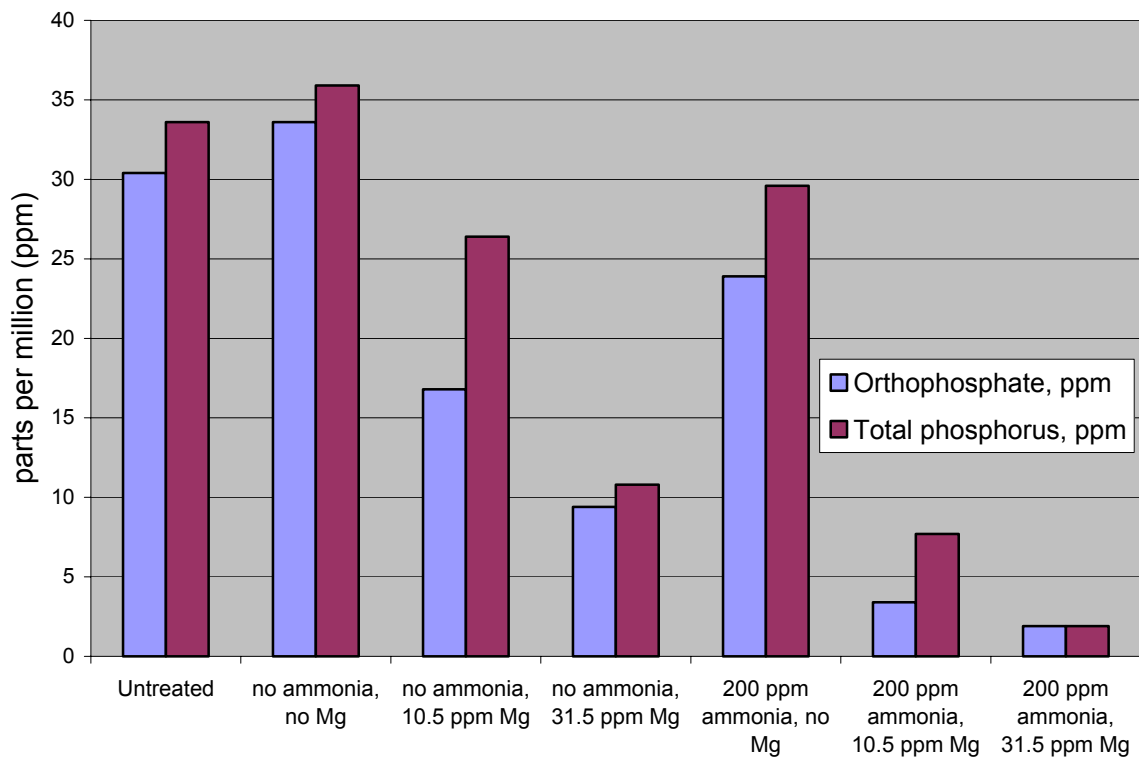


Figure 4: Dissolved OP and TP (ppm) in Untreated and Treated Effluent from Rocky Mount Lagoon

For effluent from both sources, increasing Mg content or ammonia (thus raising pH approximately 1.5 points), whether individually or jointly, reduced phosphorus content of the liquid. The greater the Mg addition, the greater was the reduction in phosphorus. The greatest reductions occurred with the

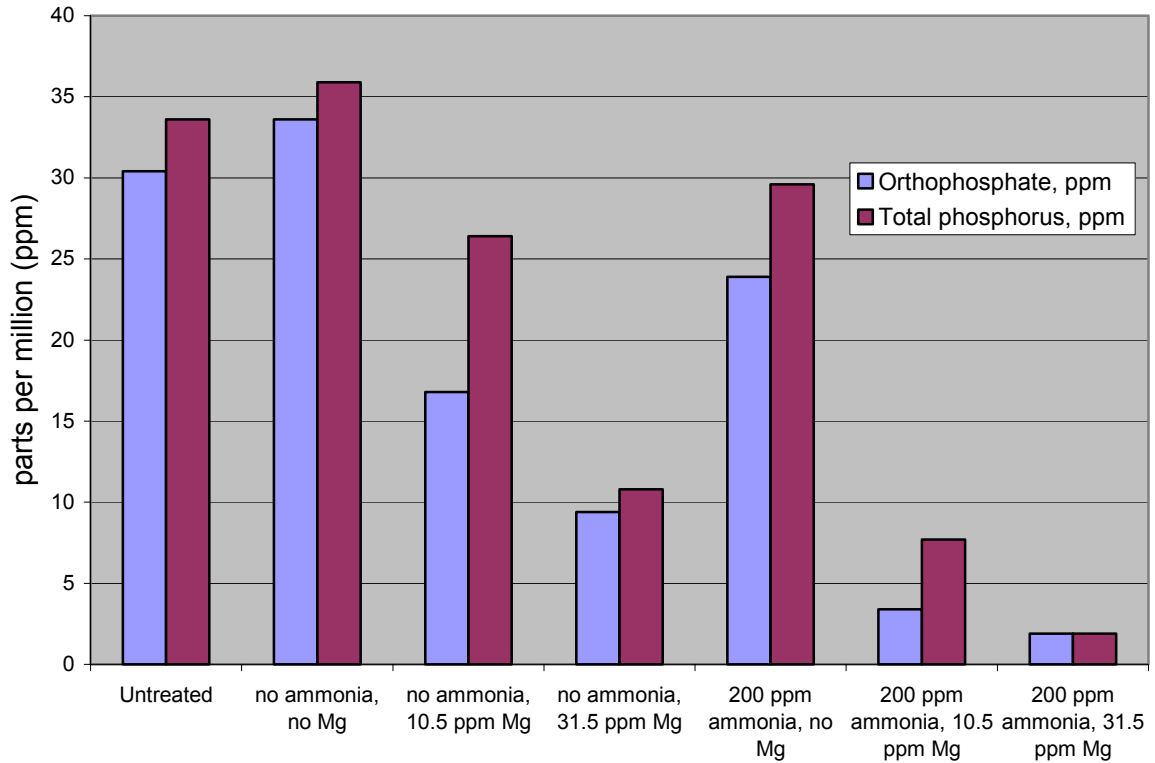


Figure 5: Dissolved OP and TP (ppm) in Untreated and Treated Effluent from Clayton Digester

highest level of Mg combined with ammonia addition. The trends held true regardless of whether the reduction was based on OP or TP. While these observations do not prove that struvite precipitated, they are consistent with expectations built upon the equilibrium solubility data from the literature.

Nutrient Partitioning Tests

These tests sought to determine how various species in lagoon effluent are partitioned between the liquid phase and the suspended solid phase. Of primary interest are phosphorus, Mg, and TAN. Amounts of these species in lagoon liquid have been reported, but no data could be located on how they are distributed between the two phases.

To be removed by struvite precipitation, phosphorus must exist as liquid-phase OP. Conceivably, conversion to this form from liquid-phase non-orthophosphate phosphorus or from

phosphorus in the suspended phase could occur to partially replenish liquid-phase OP being depleted by struvite precipitation. However, such conversion seems unlikely under thermodynamic conditions created specifically to precipitate OP, and therefore the dissolved OP as a fraction TP was viewed in these tests as an indicator of phosphorus potentially removable by struvite precipitation.

Likewise, only the dissolved form of Mg and TAN would participate in the precipitation. Therefore, to determine the degree of stoichiometric excess or shortfall for either, the fraction that is dissolved would have to be applied to its overall content in the analysis of the effluent.

To estimate the partitioning among phases, samples of effluent from the Rocky Mount and Clayton sources were centrifuged. The clear centrifugate and the sediment, re-suspended to the original volume, were analyzed for TP, OP, Mg, and TAN. The results of the analyses are shown in Figures 6, 7, and 8.

The analyses indicated that of all the phosphorus in the effluent sample from Rocky Mount, 49% was in the dissolved OP form and thus is potentially removable by struvite precipitation. In the effluent sample from Clayton, 73% was in the dissolved OP form. Dissolved Mg content fell short of stoichiometric equivalence with dissolved OP in both samples. The content in Rocky Mount effluent would need to be nearly tripled to reach equivalence, and the content in Clayton effluent would need to be doubled. The analyses showed that TAN content in samples from both effluents far exceeded stoichiometric equivalence with dissolved OP. The TAN content in the Rocky Mount sample exceeded equivalence with OP by nearly 50 times, and that in the Clayton sample by nearly 80 times.

Magnesium Supplementation Tests

These tests explored means for producing a liquid that can be added to the lagoon effluent for supplementing its dissolved Mg content. The tests focused on magnesium carbonate and MgO, which converts to Mg ion and two hydroxide ions when dissolved in water. The anions (hydroxide, carbonate, and bicarbonate) that these substances impart to water when they dissolve in it are already

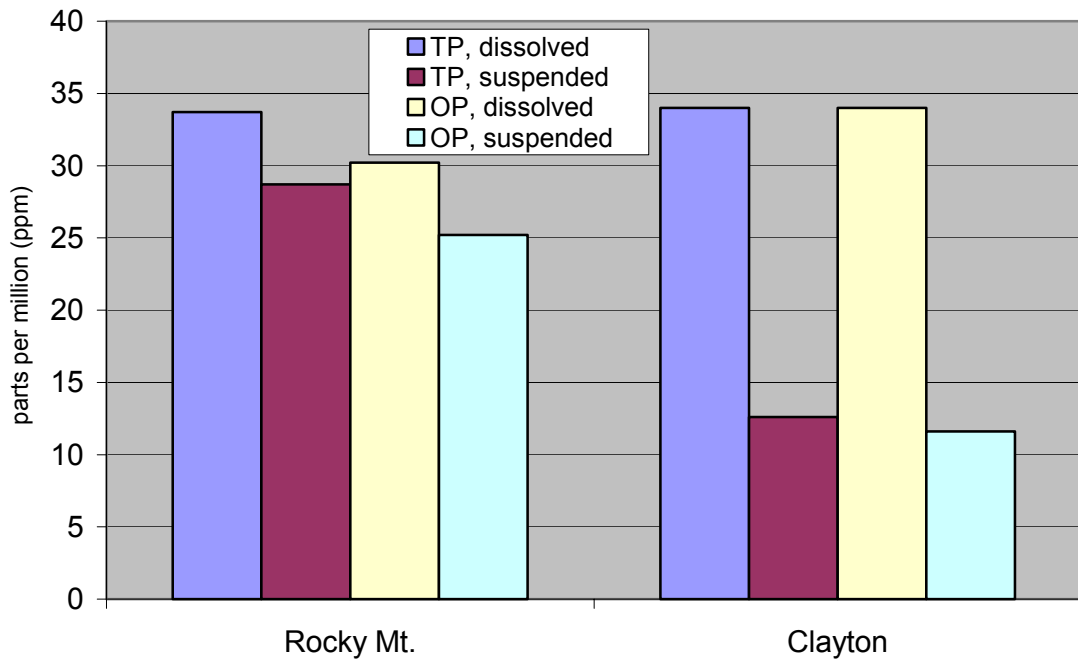


Figure 6: Breakdown of Phosphorus Content (ppm) by Form in Rocky Mount and Clayton Effluent

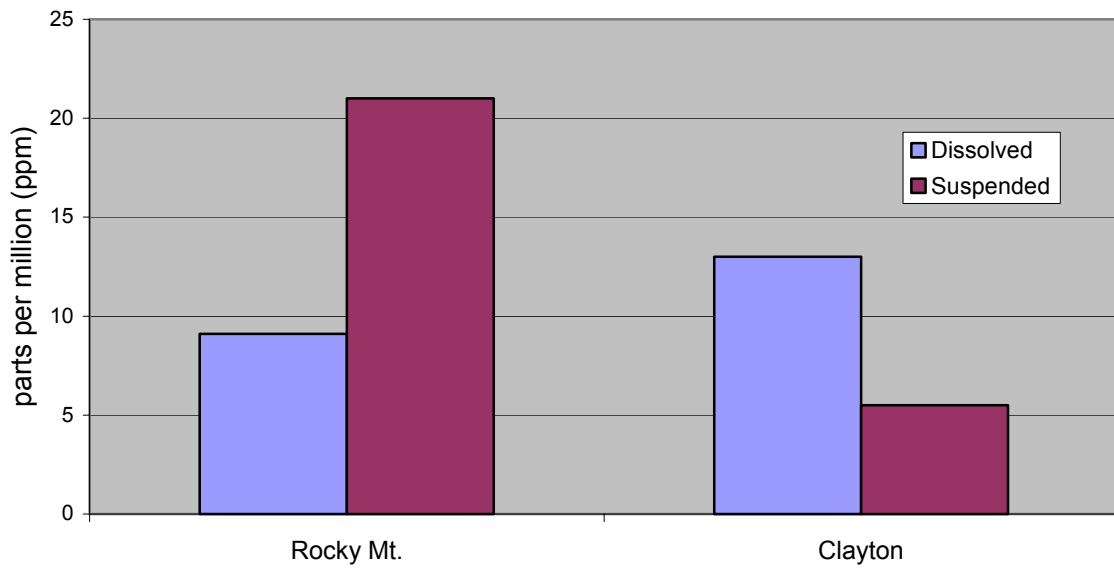


Figure 7: Breakdown of Mg Content (ppm) by Form in Rocky Mount and Clayton Effluents

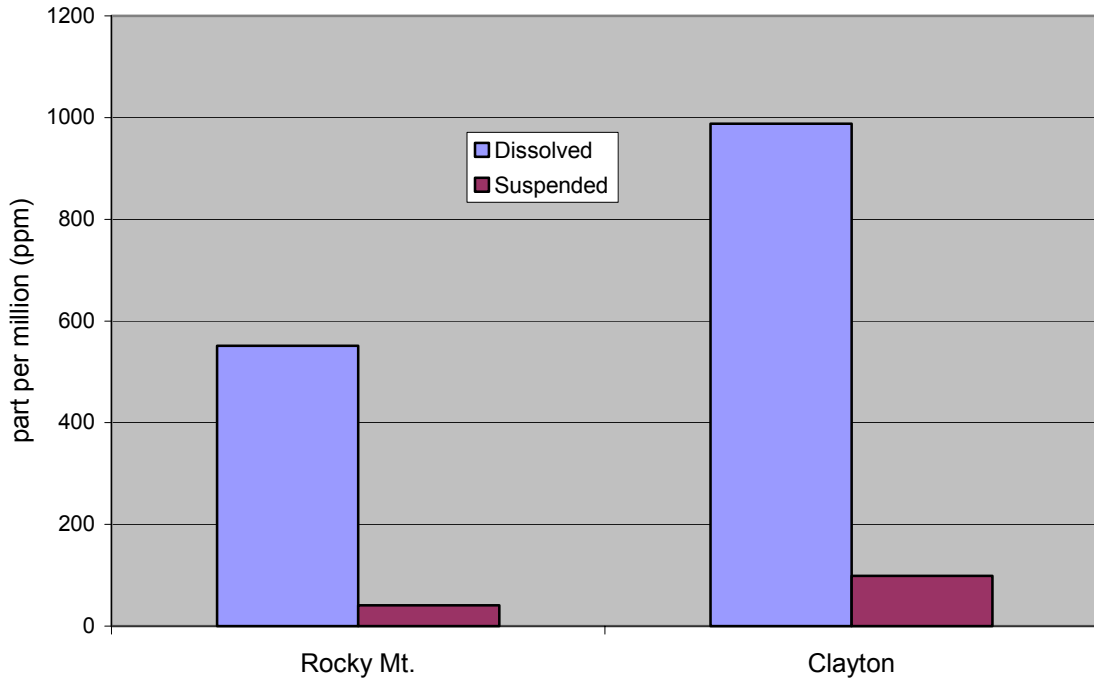


Figure 8: Breakdown of TAN (ppm) by Form in Rocky Mount and Clayton Effluent

present in natural water, and thus the substances pose less environmental concern than do magnesium sulfate and magnesium chloride, which are commonly used for Mg supplementation.

The drawback in using MgO or magnesium carbonate is that they do not dissolve easily in water, and to the extent they do, the pH is raised in the process. Raising the pH is undesirable both because little Mg can dissolve in water above a pH of 10, and because higher pH decreases solubility of struvite, thus potentially interfering with dissolution of the Mg solid and/or creating unwanted suspended particles. In a solubility test, excess MgO was added to de-ionized water. The pH rose to around 10, and magnesium content in the water rose to only 5ppm or less, too low for using as a supplementing solution.

A review of Mg solubility data indicated that Mg solubility is greater in solutions containing species that will lose protons before pH rises as high as 10. Ammonium ion, which has a pKa of 9.2,

fits this description and is of interest because it is present in concentrations of 400 to 1000 ppm in lagoon effluent. Boric acid has the same pKa as ammonium ion and thus should behave similarly in augmenting Mg solubility.

In a test conducted to explore this phenomenon, excess MgO was added to five kinds of solutions. The solutions were then centrifuged and the clear centrifugate was withdrawn and analyzed for Mg content. A control (no MgO added) was also performed for each solution. The five solutions were (1) centrifuged digester effluent; (2) solution of ammonia in water to approximate the TAN content of digester effluent; (3) same as #2 except neutralized with acetic acid; (4) same as #2 except neutralized with sulfuric acid; and (5) solution of boric acid in water to approximate the same molar strength of the other solutions. The results, shown in Table 2, confirm that presence of ammonia makes solution of more than 100 ppm Mg from MgO addition. Consistent with expectations, the ammonia made possible the increased Mg solution only when the ammonia was neutralized, i.e., in its protonated form.

This effect suggests that the enhancement in magnesium solubility results from protonation of hydroxide ions by ammonium ions before the pH rises to 10, around which point the Mg solubility would drop to near zero. Ammonium ions will give up their protons to hydroxide ions when the pH rises to the ammonia pKa, which is 9.2. The similar result with boric acid, which has the same pKa, is consistent with this explanation.

Table 2: Table of Mg Content (ppm) Achieved in Five Liquids

| | Lagoon effluent | Ammonia water | Ammonia water neutralized with acetic acid | Ammonia water neutralized with sulfuric acid | Boric acid |
|-----------------------|------------------------|----------------------|---|---|-------------------|
| Control | 9.6 | 0.0 | 0.2 | 0.1 | 0.0 |
| With MgO added | 106 | 0.6 | 102 | 132 | 103 |

These results indicate that lagoon effluent can be used with MgO to produce a supplementing solution of a little over 100 ppm Mg. However, if supplementation levels of up to, say, 60 ppm are required, a supplementing solution of greater strength is desired in order to decrease the volume of supplementing flow in relation to the main flow of effluent being supplemented. Therefore, another proton-providing substance would have to be added to increase Mg solubility further. Carbon dioxide (CO₂) is a good candidate because it is already produced by biological lagoon activity and is sometimes collected as a component of biogas, and because it adds no ions of environmental concern. In addition, even if CO₂ is not captured from the lagoon, it can be purchased in pressurized cylinders and fed into the system with no need for any other storage or pumping equipment. Finally, because its pKa is only 6.2, CO₂ offers the potential of producing effluent-based supplementing solutions that are low enough in pH to prevent unwanted struvite precipitation despite elevated Mg content.

To test whether CO₂ addition would increase Mg solubility, CO₂ was bubbled via a tube from a chemical CO₂ generator for 45 min. into a suspension of MgO in de-ionized water. The suspension was then centrifuged and the clear centrifugate poured off and analyzed. The experiment was performed three times, and Mg concentrations of 608, 931, and 769 ppm were achieved, demonstrating that the CO₂ does in fact increase MgO solubility.

The least expensive form of MgO for field use that could be identified was calcined magnesite ore. Magnesite ore is predominantly magnesium carbonate, and calcining drives off CO₂, leaving MgO. It was envisioned that, in the field, CO₂ would be admitted under pressure into lagoon effluent in contact with calcined magnesite.

Equipment limitations in the laboratory prevented testing of this process. To approximate it, carbonated water for beverage use was first purchased, as it was considered to approximate the amount of carbonation that could be achieved in the field because the CO₂ cylinders in the field provide the same pressure as those used for carbonating beverages. The purchased water was titrated with 0.1 normal sodium hydroxide to pH 7 (about the maximum allowable without risking

precipitation of pH when Mg content is high) to determine the amount of acidity it contained due to the carbonation. The titration showed carbonation of about 2900 ppm CO₂. This acidity should permit about 800 ppm of Mg to dissolve, assuming each molecule of CO₂ provides one proton and each molecule of MgO abstracts two protons upon dissolving. These approximations appeared valid when supplementing solutions were synthesized later for laboratory use. In the syntheses, calcined magnesite was dissolved with dilute hydrochloric acid. The acid was intended to substitute for CO₂, and thus was added in an amount providing the same acidity as 2900 ppm CO₂. The Mg concentrations reached 700 to 900 ppm, and the pH ranged from 6.7 to 7.3.

Magnesium carbonate was found not to dissolve appreciably in water, even when acidified with CO₂. Low solubility was observed whether the magnesium carbonate was in the form of magnesite gravel or powder. Due to the lack of promising results, no further testing was conducted with magnesium carbonate.

pH Enhancement Tests

These tests explored means for increasing pH in lagoon liquid. Rises of 0.5 to 1.5 pH points will likely be required for stimulating adequate precipitation of struvite. Ammonia was the focus of the tests, because it offers three potential advantages. First, it may be possible to obtain ammonia on-site by stripping it, possibly by vacuum alone, from a lagoon liquid stream other than that flowing to the struvite precipitation system. Second, its pKa appears ideal for achieving adequate pH rise while at the same time minimizing the possibilities for localized areas or brief episodes of pH so high that struvite solubility actually decreases or becomes uncontrolled. Finally, unlike most other additives commonly used to raise pH, ammonia would add no ions of environmental concern not already being addressed. While ammonia itself is of environmental concern because it increases nitrogen content, crop uptake is used for removing it. However, any additional ammonia may require expanded acreage if nitrogen is already being applied to the soil at its maximum loading given the rate of uptake

by the crop. Lime could also be considered because it adds no worrisome ions; however, the increased calcium could promote unwanted calcium phosphate precipitation in lieu of struvite.

Two means for using ammonia to increase pH were tested: pressure manipulation and simple addition.

Pressure Manipulation

The tests aimed to determine whether pH of digester effluent could be increased by exposing it to vapors stripped by vacuum alone from other effluent. Two methods were used in the tests. In one method, vacuum was produced by pumping liquid, and in the other method it was produced by pumping gas.

In the liquid-pumping method, a peristaltic pump withdrew liquid from near the bottom of a sealed flask. At the beginning, the flask was 90% filled with effluent, the remaining 10% being an air space at the top. The withdrawing of the liquid produced vacuum in the flask, and effervescence of the liquid in the flask was observed. The strength of the vacuum increased as more liquid was withdrawn. Five sample bottles received the liquid from the pump discharge, one bottle at a time. The first bottle contained the first liquid withdrawn, which had been exposed to the weakest vacuum. The last bottle contained the last liquid withdrawn, which had been exposed to highest vacuum. Once the flask had been pumped as nearly empty as possible, the liquid outlet to the pump was closed and a valve on another flask port was opened to allow fresh effluent to flow into the flask from a beaker open to the atmosphere. The effluent, which was from the same source as the effluent withdrawn from the flask, was propelled by atmospheric pressure and filled the flask to near the 90% level. The newly admitted liquid was allowed to sit for 30 min to absorb vapor and then was agitated for 2 min to further vapor absorption. The untreated effluent, the five bottles of effluent exposed to increasing degrees of vacuum, and the effluent admitted to the evacuated flask to re-absorb the stripped vapors were all analyzed for TAN and pH. Table 3 presents the results.

Table 3: Results from Liquid-Pumping Method of Increasing Ammonia and pH

| | Untreated effluent | Bottle 1 (very mildly stripped) | Bottle 2 (mildly stripped) | Bottle 3 (moderately stripped) | Bottle 4 (strongly stripped) | Bottle 5 (very strongly stripped) | Re-absorbing effluent |
|-------------------------------|--------------------|---------------------------------|----------------------------|--------------------------------|------------------------------|-----------------------------------|-----------------------|
| pH | 7.43 | 7.44 | 7.4 | 7.48 | 7.47 | 7.54 | 7.46 |
| NH₃-N (ppm) | 1053 | 1020 | 1010 | 1024 | 1016 | 1016 | 1069 |

In the gas-pumping method, the flask was again filled to 90% full with untreated effluent and then sealed. However, the tube leading to the suction of the peristaltic pump was connected to the top of the flask so that gas was withdrawn rather than liquid. The gas discharged from the pump was fed through another tube to the bottom of a graduated cylinder, which was nearly full and contained one-fifth the volume of untreated effluent as was charged to the flask. The pump speed was adjusted to obtain slow bubbling of the gas into the liquid in the cylinder. At the beginning the pump speed was low, and the speed had to be gradually increased to maintain the bubbling. Finally, no bubbling could be obtained even at high pump speed, and effervescence of the liquid in the flask, which had begun soon after the pump was started, had slowed. The experiment was ended at this point. The untreated effluent, the effluent in the flask, which had been exposed to vacuum, and the effluent in the cylinder, which had been exposed to the stripped vapors to absorb them, were all analyzed for pH and TAN.

Table 4 shows the result.

Table 4: Results from Gas-Pumping Method of Increasing Ammonia and pH

| | Untreated effluent | Stripped effluent | Re-adsorbing effluent |
|-------------------------------|--------------------|-------------------|-----------------------|
| pH | 7.43 | 7.5 | 7.55 |
| NH₃-N (ppm) | 1053 | 1047 | 1073 |

Results suggest that, in both methods, some ammonia was stripped from the effluent under vacuum and absorbed by the effluent at atmospheric pressure. Evidence for this conclusion is that, in both methods, TAN content of vacuum-treated effluent was lower than untreated effluent, though in

the gas-pumping method the difference is slight. The TAN content of absorbing effluent, which in both methods was higher than TAN content of untreated effluent, provides more evidence for the conclusion.

The pH results are less clear. In the gas-pumping method, the pH of the absorbing effluent was measured as higher than that of the untreated effluent. Although this difference comports with the hypothesis that ammonia was transferred, the pH difference is small. In addition, the pH of the stripped effluent was measured as slightly higher than that of the untreated effluent, a result apparently inconsistent with the hypothesis. In the liquid-pumping method, the difference between the pH of the absorbing effluent and untreated effluent was again small but consistent with the hypothesis. However, the five samples of stripped effluent in this method exhibit a range of pH from slightly below the untreated effluent to slightly above the absorbing effluent. There appears to be a trend with respect to sample number, with the first two (and least vigorously stripped) samples having the lowest pH, the next two having intermediate pH, and the last having highest pH. This pH behavior may signal that ammonia transfer was accompanied by transfer of acidic gases (CO₂, for example), which limited, or even reversed, the pH fall of the stripped effluent and the pH rise of the absorbing effluent

In any event, the magnitude of the pH rises observed in these experiments fell short of the required range. Pressure manipulation for pH rise was thus pursued no longer.

Direct Addition of Ammonia

An experiment was conducted to determine how much the pH is increased by adding ammonia in various quantities to lagoon effluent mixed with varying amounts of Mg-supplementing solution. This information is needed to plan how much ammonia will be required for adjusting the pH, whether the ammonia is purchased or obtained from lagoon liquid by vacuum stripping with alkali addition.

In the experiment, a liter of lagoon liquid was stirred in a large beaker with a pH meter suspended into it. Water containing 18,000 ppm (as N) ammonia was pipeted into the beaker in increments. After each increment was added and the pH stabilized, the pH and the volume of the increment were recorded. Successive increments increased in size as the effect on pH decreased with accumulated ammonia addition.

This procedure was repeated four more times, each with an increased amount of Mg-supplementing solution added to the effluent. The supplementing solution contained about 200 ppm Mg and was prepared by mixing calcined magnesite into lagoon liquid, settling, and pouring the Mg-enhanced liquid off the settled, excess solid that did not dissolve.

The results are shown in Figure 9. For pure effluent, approximately 40 ppm ammonia addition was required for a 0.5-point rise in pH, and 80 ppm for a one-point rise. For the mixtures of effluent with Mg-supplementing solution, the initial pH depended on how much Mg solution was used, being greater for greater proportions of Mg solution. However, for all mixtures except the one richest in Mg, the amount of pH rise achieved with a given amount of ammonia addition was nearly the same as that for pure effluent. The richest mixture (60% effluent, 40% Mg-supplementing solution) required about twice as much ammonia to raise the pH a half point, and 300 ppm or more to raise the pH one point.

Rate Tests

Tests were conducted to estimate the rate of precipitation as related to available surface area per volume of liquid and to driving force. The goal was to estimate the reaction constant for the rate equation proposed for the reaction. In the equation, the reaction rate, in decrease of molar product (P) per time (t), is equal to the reaction constant (k') times the surface area available per liquid volume (m), times the driving force expressed as excess molar product above the equilibrium (P_e):

$$-\frac{dP}{dt} = mk'(P - P_e) \quad (4)$$

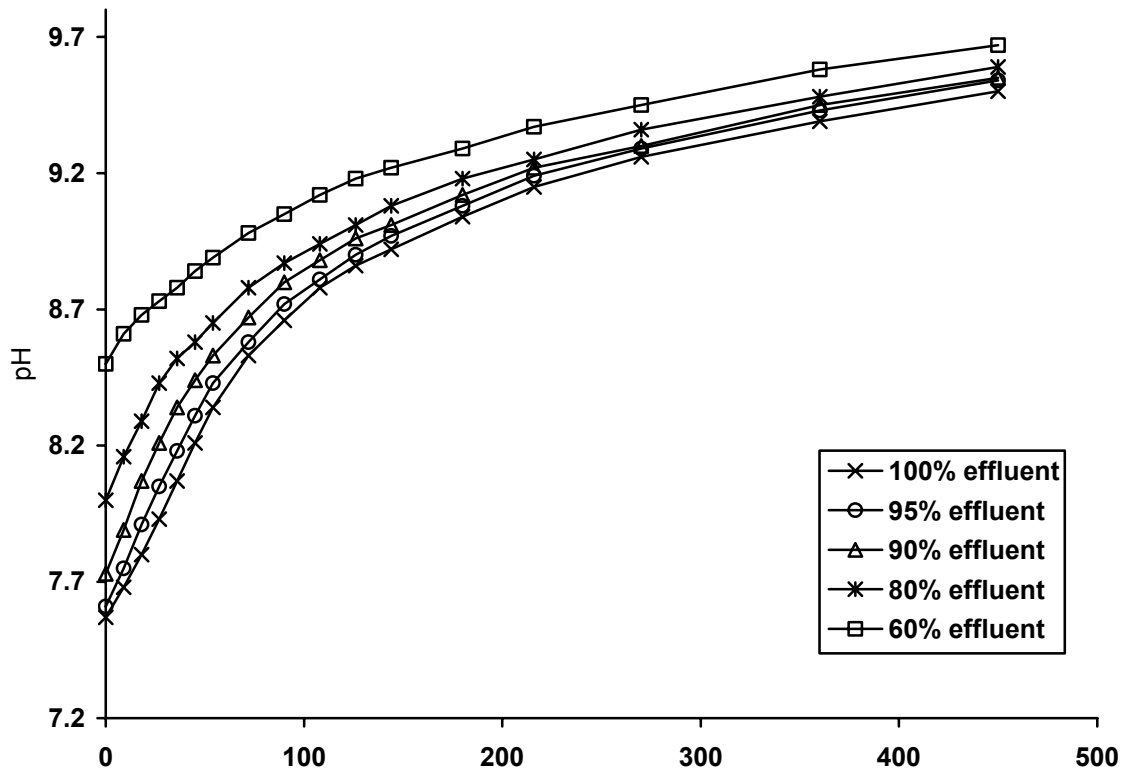


Figure 9: pH versus Amount of Ammonia Added (ppm) for Five Ratios of Effluent to Mg-Supplementing Solution

This information is critical in creating a design for a crystallizing system, because both the choice of reactor type and its dimensions will be influenced by the rate of reaction.

The tests were set up in a manner to allow monitoring of the disappearance of OP, Mg, and TAN from solution as time elapsed. This information allowed calculation at each time increment of the excess molar product, which is the product of total Mg, TAN, and OP molarities minus the equilibrium product at the observed pH. The set-up also allowed calculation of the surface area available per liquid volume at each increment. The surface area was held constant, and the amount of liquid could be calculated at each increment by adding up the total volume of liquid samples removed

by that point in time. Thus, all variables needed for estimation of the rate constant were tracked. A more detailed description of the procedure used is presented below, followed by the results.

Procedure

To provide the surface for reaction, 100 grams (g) of struvite grains of 1.68 to 2.00 mm diameter were prepared by gently grinding large struvite crystals and then using a Tyler screen and shaker assembly to select that range from the ground crystals. The surface area of the grains was estimated, using the assumption the grains were roughly spherical. Several gallons of Rocky Mount lagoon effluent was obtained, and a sample submitted for Mg, TAN, OP, and TP assays.

Mg-supplementing solution was prepared by adding 250 g of Mg ore gravel (washed) to 250 ml of Rocky Mount lagoon effluent, stirring, and allowing to soak overnight in refrigerator. Then the solution was filtered to remove any ore powder and other particulates. A sample was analyzed for OP, Mg, and TAN.

The apparatus was set up for conducting the crystallization reaction. It consisted of a 500-ml beaker, magnetic stirrer, and pH probe mounted in the beaker. Sample bottles marked "1" through "10," each containing the dilute HCl to ensure dissolution of suspended struvite, were prepared. Then, 20 g of the prepared struvite grains were spread and immobilized in a flat stainless steel wire cage. The cage was inserted into the beaker and positioned in such a way to allow the stirring liquid to circulate rapidly through it.

A known volume of lagoon effluent, ranging from 250-350 ml, was placed into the beaker with stirrer. Enough Mg-supplementing solution to provide 50 ppm additional Mg to the lagoon effluent, calculated according to Mg assay of the solution, was prepared, as well as enough ammonia water (3% ammonia as ammonium hydroxide) to add 200 ppm additional TAN. This amount of ammonia served to raise the pH by approximately 1.3 points. The Mg-supplementing solution, ammonia water, and struvite were placed in the beaker quickly and a stopwatch simultaneously turned on. Immediately, a 10-ml sample was pipeted and put into the first sample bottle. Three more

samples were taken in succession as quickly as possible. Two more samples were taken, aiming for 4 minutes between samples, and for the remaining samples approximately 6 minutes was allowed. At the time of pipeting each sample, the time was noted from the stopwatch and the pH of the reacting effluent was also recorded.

After the reaction sequence, the basket holding the grains was removed and the grains allowed to air-dry. The grains were then weighed and found not to have changed in weight perceptibly, thus ensuring that the surface area had remained essentially constant.

The experiment was run a second time, this time augmenting the OP content instead of the Mg content. The OP augmentation was achieved by adding enough potassium dihydrogen phosphate to add 50 ppm OP to the liquid. As in the first run, the pH was raised approximately 1.3 points by adding enough ammonia water to raise TAN by 200 ppm.

The experiment was run a third time, reverting to 50 ppm Mg augmentation with no OP augmentation. Ammonia water equivalent to 200 ppm TAN addition was used as in the other runs to raise pH by approximately 1.3 points. However, in this run, TAN was further increased by 400 ppm (bringing total TAN augmentation to 600 ppm in this run), with no further effect on pH, by adding ammonium chloride.

Results

Figure 10 shows the results for the second run of the experiment. First and third run results are not shown because they were erratic, possibly resulting from contamination or sample mix-ups. The rate constant estimated by averaging its calculated value over the second run is 0.3 dm/hr, roughly twice the estimate drawn from literature and cited in the introductory section on kinetics. To illustrate the calculations used in the estimate, Appendix E shows the calculations for the fifth time segment (0.0422 to 0.1047 hours) in Figure 10.

A careful review of the results and observations made during the run led to the hypothesis that even the 0.3 dm/hr estimate may be low. The hypothesis stems from three ideas.

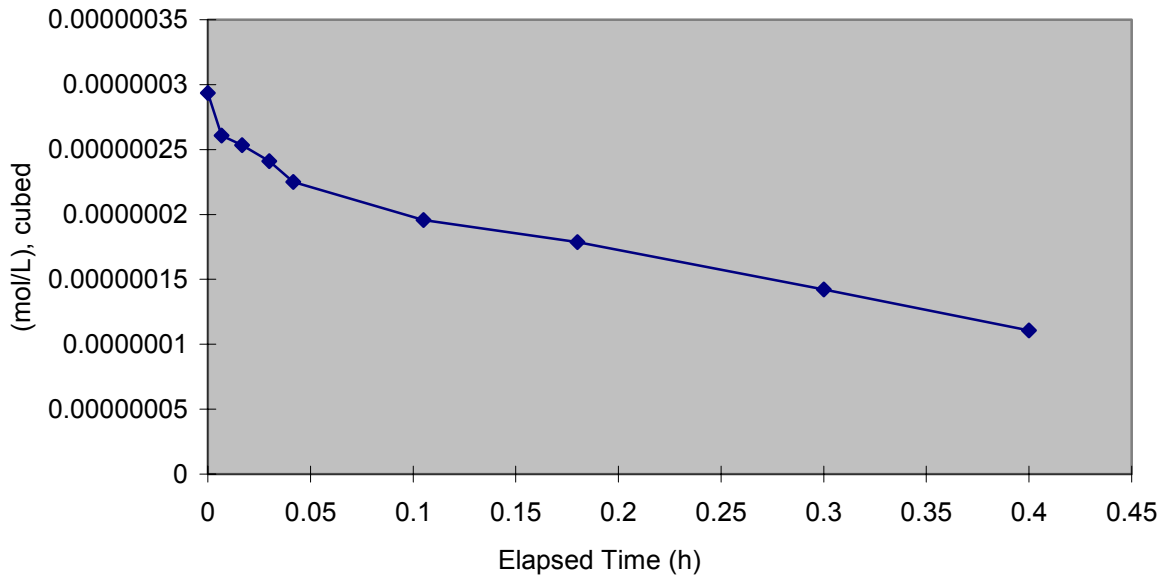


Figure 10: Excess Molar Product (mol/L)³ versus Time (h) Elapsed from pH, OP, and Mg Augmentation

First, a slight clouding of the solution was observed early in the experiment, perhaps 10 to 20 s into the run. This suggests that precipitation may have been occurring by self-nucleation in the bulk of the liquid rather than onto the grains provided. Self-nucleation could occur if the liquid is so highly supersaturated for a long enough period that its self-nucleation time falls short of the average time elapsed before all of the liquid can contact the surface of the provided grains. Precipitation onto nuclei in the bulk liquid would decrease the apparent reaction rate, because the precipitated struvite would be accounted as struvite remaining in the liquid. In fact, precipitation might occur preferentially on the suspended nuclei, because they would be distributed throughout the liquid and thus be more accessible, and also because their surface-to-volume ratio would be high due to their small diameter.

Second, the calculated rate constant during the first time increment, 2.5 dm/hr, was more than eight times greater than the average over the run. For the remaining increments, the calculated constant varied from 0.15 to 0.5 dm/hr in random fashion. Inspection of Figure 10 reveals the

reduction in observed rate at the beginning of the second increment. This rate pattern is consistent with the self-nucleation concept. If some substantial part of the first increment elapsed before nucleation occurred, then precipitation would have had to occur onto the provided grains for that part of the increment, thus removing OP, Mg, and TAN from the liquid. Once nucleation occurred, much of the precipitation could occur on the suspended nuclei, thus reducing the apparent rate.

Third, the amount of OP observed to have been removed from the liquid was only about 20% by the end of the experiment. At the supersaturation achieved, more than half of the phosphorus should have been removed. The shortfall in phosphorus reduction is also consistent with the self-nucleation idea. The phosphorus may actually have been removed from solution, but in the fine, suspended form, thus being included as part of the liquid in the analyses.

To deal with this result and its uncertainty, a safe approach is to design the system with the assumption that the rate constant may really be as low as 0.3 dm/hr, but recognize that the resulting system may be over-designed in the event the rate constant is in fact much higher.

Crystallizer Design Elements

The basic design elements for the system were set forth, drawing on information and ideas developed through the literature review, batch tests, and original thought. The elements are summarized below.

Mode of Reaction. The reaction should take place in the continuous mode rather than batch. Continuous mode systems are generally preferable to batch systems because size, and hence capital cost, is limited. Batch systems may be better if the reaction rate is slow, but that is not the case here.

Type of Reactor. The reactor should be a fluidized bed crystallizer. The reaction rate is high enough that a fluidized bed will work well, and a packed bed reactor would be difficult to manage in the farm environment. However, the nucleation time is so quick, especially at higher levels of supersaturation, that time between chemical adjustment and extensive contact with struvite surfaces

must be minimized. Thus, Mg addition and pH enhancement should occur immediately prior to contact with the fluidized bed.

Shape of Reactor. The reactor should increase in diameter with height, so that the upflow velocity at the bottom is several times greater than that at the top. This will prevent the current from sweeping very small bed particles up and out with the exiting liquid, yet provide enough velocity at the bottom to maintain larger particles in a fluidized state.

Product Removal. Some sort of product collection chamber should be provided at the bottom of the vessel so that product can be removed by gravity, with a simple valve or removable separator between the vessel and the collection chamber to allow movement of bed particles into the chamber when desired. To keep labor cost low, simplicity is key.

pH adjustment. The pH should be augmented by adding ammonia. Batch tests indicated as little as 40 ppm ammonia may be needed. In addition, in the future, ammonia may be available at the site from ammonia stripping operations. Its pKa is ideal for raising pH without risking excessively high pH, and farm waste systems are already designed to remove ammonia. If purchased in pressurized, portable vessels, ammonia can be added through small tubes, without need for pumping equipment or pipes. Finally, ammonia is a common commodity in agriculture and thus should be readily available.

Mg supplementation. Mg should be added by dissolving calcined magnesium carbonate into lagoon effluent with the aid of CO₂. Batch tests indicate this technique will succeed in achieving adequate Mg supplementation. It adds no worrisome cations. This form of magnesium is currently used as a livestock feed supplement, so it also should be readily available. Finally, CO₂ may in the future be available from biogas captured from the lagoon. If purchased in pressurized cylinders, it can be fed to the system through small tubes, thus avoiding need for pumping equipment or piping.