SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS FOR FURTHER WORK

Summary

The work described in the foregoing sections was driven by the question of whether struvite crystallization can be applied practically to remove phosphorus from North Carolina lagoon effluent. A literature review confirmed the potential but uncovered no processes or designs directly applicable to North Carolina lagoons. The review also yielded thermodynamic and kinetic information relevant to struvite crystallization, critical input for design of a practical process. The identified thermodynamic data, which predicts how much phosphorus can be precipitated and whether the precipitation will proceed spontaneously without seeding at various conditions, were in the form needed for design. The information on kinetics, which predicts the time needed, consisted of reports of visual observations on reaction time and also a proposed rate equation and measured rate constant. The visual observations were useful as background but insufficient for design, which requires the rate equation and constant. The reported constant was not in the form needed for design because it was expressed in terms of total reaction volume with no reference to the surface area available for reaction. Using assumptions about the surface area, the reported constant was converted into an estimated constant (0.13 – 0.19 dm/h) in the form required.

Completion of the literature review permitted formulation of goals for the research. Each of the goals, which were all achieved, is restated below, followed by an overview of the results addressing that goal.

(1) Observe precipitation of phosphorus from actual lagoon effluent in batch tests.

Batch-mode tests indicated that phosphorus precipitation was consistent with thermodynamic data identified in the literature review. The tests were inconclusive regarding reaction rate, but suggested that the phosphorus precipitation proceeded at least as fast as predicted by the estimated rate constant.
(2) *Investigate means of magnesium supplementation and pH adjustment in batch tests.*

Batch-mode tests also indicated that, for adjusting pH to precipitate phosphorus, ammonia works well. Also, for supplementing Mg content, a solution created by mixing calcined magnesite with carbonated water was successful. These means are desirable because they offer environmental advantages. The tests were less successful for pH adjustment using pressure manipulation and Mg supplementation using non-calcined magnesite.

(3) *Set forth the basic design for a struvite crystallizer.*

The major features of the crystallizer were specified. These included a continuous-mode fluidized bed reactor with liquid flowing up through a bed of solid particles upon which phosphorus precipitates; Mg solution, produced by carbonating a mixture of calcined magnesite and lagoon water, being injected into the liquid entering the cone; gaseous ammonia also being injected into the inflowing liquid; and a product collection chamber under the cone to accommodate solid particles flowing by gravity from the cone.

(4) *Model the performance of hypothetical crystallizer adhering to the basic design.*

Three models were developed, each predicting, under its own assumption set, the behavior of struvite crystallizers adhering to the basic design set forth under goal (3). The PLCB model assumed plug flow for liquid and a classified bed. The MLMB model assumed perfect mixing both for the liquid and for the bed. The PLMB assumed plug flow for the liquid and a perfectly mixed bed.

(5) *Assemble and operate a laboratory-scale crystallizer adhering to the basic design.*

A laboratory-scale crystallizer was assembled, adhering to the basic design except that, due to laboratory limitation in handling gases, ammonia was added in water solution rather than gaseous form and the Mg solution was created with hydrochloric acid rather than with CO₂. Near-steady state operation was achieved at two different sets of operating conditions. The first used 49.2 L/h of total liquid flow, seeding at 18 particles per second, ammonia addition of 100 ppm, and no Mg addition. The second used 49.2 L/h of total liquid flow, no seeding, ammonia addition of 100 ppm, and Mg
addition of 30 ppm. Factorial experiments were conducted, with flow rate, ammonia addition, and Mg addition varying in ranges centered around the second set of near-steady state conditions.

(6) Characterize the operation of the laboratory-scale crystallizer and compare with modeling.

Estimated reduction in OP and TP was 36% and 24%, respectively, over the first near-steady state period and 74% and 58%, respectively, over the second near-steady state period. Analysis of data indicated that phosphorus reduction exceeded the amount removable by struvite precipitation, suggesting a second mechanism, i.e., one in addition to precipitation of dissolved OP into struvite, for phosphorus reduction. A balance on the number of particles indicated that some nuclei were being produced by some means other than external seeding, especially in the second near-steady state period.

A channel appeared in the bed when it was heavy and/or coarse, and a double top appeared when its particle size distribution had two peaks. The channeling was not associated with noticeable change in final phosphorus reduction, and was associated with only a small difference in the profiles of OP concentration with respect to height.

The profiles of OP concentration with respect to height observed during the near-steady state periods were compared against those predicted by the three models at the same conditions. Rate constants ranging from 0.4 to 15 dm/h were used in the model equations. The actual profiles fit closest to the profiles predicted by the PLMB model using a rate constant of 10 to 15 dm/h.

Statistical analysis of results from the factorial experiments showed high probabilities (p-values less than 0.05) that increasing addition in the range tested (0 to 60 ppm) and increasing ammonia addition in the range tested (0 to 200 ppm) both are associated with increasing phosphorus removal. The probability that flow rate is associated with phosphorus reduction was insignificant (p-value greater than 0.05) in the range tested (41.2 to 56.8 L/h).
(7) Design and operate a field-scale crystallizer by applying results of goal 6.

The laboratory-scale unit was scaled up to a field-scale system designed for 455 L/h, and assembled at a livestock lagoon. Gaseous CO$_2$ and calcined magnesite was used for producing the Mg solution, and gaseous ammonia was used for the ammonia addition. Test runs were conducted, with estimated reductions of 25% to 68% in TP and 22% to 58% in OP being observed when Mg and ammonia were both being added. As in the laboratory-scale experiments, channeling was observed when the bed was coarse and heavy, a double top was observed for a short period, and nuclei were produced in addition to the particles seeded into the reactor.

Obstruction of ammonia flow developed during the test runs and was resolved by removing the diffusing device at the injection point. Composition of the Mg solution was not constant enough for controlled tests, and therefore a switch to magnesium chloride brine was made before beginning factorial experiments.

In the factorial experiments, TP and OP reduction averaged 70.2% and 77.3%, respectively when ammonia and Mg were being added. Peak reductions in TP and OP were 81.9% and 87.1%, respectively. Statistical analysis of results from the factorial experiments showed high probabilities (p-values less than 0.05) that increasing Mg addition in the range tested (0 to 60 ppm), increasing ammonia addition in the range tested (from no pH enhancement to 1 pH point enhancement), and decreasing flow rate in the range tested (341 to 568 L/h) all are associated with increasing phosphorus removal. The data indicated, as in the laboratory-scale experiments, that phosphorus reduction exceeded that explainable solely by precipitation of dissolved OP into struvite.

Conclusions

The system created and evaluated during this course of research performs at least as well as envisioned at the start. The system shows promise for future application in treating effluent from livestock waste lagoons in North Carolina. Based on the results from the research, future systems of this type installed at lagoons can be anticipated to remove most of the phosphorus in the effluent. It is
recommended that further research and development be conducted, working toward full-scale
deployment and fuller characterization of the behavior of the system and its mechanisms of
phosphorus removal.

**Recommendations for Future Work**

Several aspects of the system can be explored. Recommendations for work in areas judged
most important for understanding and developing the system are presented below.

The kinetics could be explored further. The present work did not aim primarily to quantify
the rate constant and therefore the figure of 10 to 15 dm/hr mentioned above should be considered
only a rough estimate. It should also be noted that the constant applies to a rate equation proposed by
previous work by another researcher, and the present work does not address the validity of that
equation. Future work aimed at determining the rate equation and constant more precisely would
yield a better understanding of the kinetics.

The character of the bed and liquid movements could be studied more precisely, also. The
present work found that the results most closely matched those predicted under the assumptions that
the bed is perfectly mixed (instead of perfectly classified) and the liquid moves in perfect plug flow
(instead of being perfectly mixed). However, the bed and liquid motions cannot in reality fit these
assumptions exactly. Understanding the ways in which the movements depart from the assumptions,
and determining the degree of departure, can help in predicting the maximum practical performance
achievable.

The mechanisms of nucleus production and of phosphorus removal can also be explored. The
current work observed that nuclei are being produced in excess of those added as seeds, and that more
phosphorus is being removed than had been expected. Processes are postulated for both observations.
Future work, if successful in identifying the processes more confidently, would allow more precise
design of systems and better understanding of how to best operate them.
Finally, efforts could be devoted toward developing the system for full-scale application, even without further understanding of the kinetics, bed and liquid motions, and mechanisms. Development could focus on achieving smoother and/or simpler operation in some of the currently-included features of the system, such as product removal or production of Mg solution with CO₂. In addition, development could aim to augment the current design by adding new features, such as a means for drying product or a system for storing and/or transporting the treated liquid. Lastly, efforts could focus on pairing the system with complementary systems, such as those that remove nitrogen biologically or chemically, to create a complete nutrient removal system.