

ABSTRACT

BOWERS, KEITH EDISON. Development of a Struvite Crystallizer for Reducing Phosphorus in Effluent from Livestock Waste Lagoons. (Under the Direction of Philip W. Westerman.)

The research successfully met its objectives of designing and characterizing a crystallizer for removing phosphorus from livestock lagoon effluent in North Carolina. A design was created for a struvite crystallizer utilizing a cone-shaped continuous-mode fluidized bed. A laboratory-scale system operating at 49.2 L/h of total liquid flow achieved near-steady state operation at two sets of operating conditions. The first used ammonia addition of 100 ppm and no magnesium (Mg) addition. The second used ammonia addition of 100 ppm and Mg addition of 30 ppm. Estimated reduction in orthophosphate phosphorus (OP) and total phosphorus (TP) was 36% and 24%, respectively, over the first condition set and 74% and 58%, respectively, over the second. Three models were developed to describe crystallizer behavior. The MLMB model assumed perfect mixing of both liquid and bed. The PLCB model assumed plug flow of liquid and perfect classification of the bed. The PLMB model, which best predicted behavior, assumed plug flow of liquid and perfect mixing of the bed. Factorial experiments were conducted to test the effects of Mg addition, ammonia addition, and flow rate on phosphorus removal. Increasing Mg addition in the range tested (0 to 60 ppm) and increasing ammonia addition in the range tested (0 to 200 ppm) were significantly associated with increasing phosphorus removal. The effect of flow rate was insignificant between the values tested (41.2 and 56.8 L/h). A field-scale system was assembled at a lagoon and used to conduct factorial experiments testing the same effects as those in the laboratory. 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 between the values tested (341 and 568 L/h) were all significantly associated with increasing phosphorus removal. Reduction in TP and OP 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.

**DEVELOPMENT OF A STRUVITE CRYSTALLIZER FOR REDUCING
PHOSPHORUS IN EFFLUENT FROM LIVESTOCK WASTE LAGOONS**

by
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TABLE OF CONTENTS

	Page
List of Tables	v
List of Figures	vii
List of Abbreviations and Other Symbols	x
Introduction	1
Need for Removal of Phosphorus from Waste Lagoon Effluent.....	1
Means for Removal of Phosphorus from Anaerobic Treatment Effluent.....	2
Previous Work by Others Relevant to Struvite Precipitation	4
Research Goals for Applying Struvite Crystallization to North Carolina Lagoon Effluent....	23
Experiments in Batch Mode and Resulting Design Elements for Struvite Crystallizer	27
Experiments.....	27
Crystallizer Design Elements	44
Modeling the Behavior of a Cone-Shaped, Fluidized-Bed Struvite Crystallizer (<i>part 1</i>) (<i>part 2</i>).....	46
Purpose of Modeling	46
Simplifying Assumptions for the Crystallizer	46
MLMB Model	47
PLMB Model.....	50
PLCB Model	52
Comparison of the Models	62
Experiments with Laboratory-Scale Continuous Crystallizer (<i>part 1</i>) (<i>part 2</i>) (<i>part 3</i>) (<i>part 4</i>).....	65
Overall Design of Experiments and Reasoning Behind Design.....	65
Equipment, Materials, and Procedures Used.....	70
Results in the FCRs and Discussion	82
Results in the MVRs and Discussion	123
Comparison of Laboratory Results with Model-Predicted Results	139
MLMB Model	139
PLCB Model	142
PLMB Model.....	144
Design and Operation of Field-Scale Crystallizer.....	148
Design of the Field-Scale Crystallizer.....	148
Operating Method for the Field-Scale Crystallizer	154
Results	155

Summary, Conclusions, and Recommendations for Future Work	169
Summary	169
Conclusions	172
Recommendations for Future Work	173
References	175
Appendices	179
Appendix A: Mathematical Relations for PLCB Model	180
Appendix B: Opening Sizes Corresponding with Standard Sieve Numbers	181
Appendix C: Details on Design of Field-Scale Crystallizer	182
Appendix D: Details on Operating Method for the Field-Scale Crystallizer	191
Appendix E: Example Calculations for Estimating Rate Constant	195

LIST OF TABLES

	Page
Introduction	
1. List of Thermodynamic Data.....	10
Experiments in Batch Mode and Resulting Design Elements for Struvite Crystallizer	
2. Table of Mg Content (ppm) Achieved in Five Liquids.....	33
3. Results from Liquid-Pumping Method of Increasing Ammonia and pH.....	37
4. Results from Gas-Pumping Method of Increasing Ammonia and pH.....	37
Experiments with Laboratory-Scale Continuous Crystallizer	
5. Organization of Experiments with Continuous Laboratory-Scale Crystallizer.....	68
6. Results of Analysis of Acid-Dissolved Crystals from Farm.....	75
7. Results of Sieve Analyses to Test for Particle Size Stability Through Wetting, Drying, and Sieving Again.....	81
8. Summary of Samples and Analyses.....	83
9. Concentrations for Near-Steady State Portion of First FCR Series: Raw Liquid, Treated Liquid, and Expected in Treated Liquid at Equilibrium.....	100
10. Concentrations for Near-Steady State Portion of Third FCR Series: Input Liquid, Treated Liquid, and Expected in Treated Liquid at Equilibrium.....	119
11. Analysis of Variance for OP Reduction, Including All Effects of Independent Variables.....	131
12. Analysis of Variance for OP Reduction, Including Only the Significant Effects of the Fixed Independent Variables.....	132
13. Regression of OP Reduction Against Significant Effects of Fixed Independent Variables.....	132
14. Analysis of Variance for TP Reduction, Including All Effects of Independent Variables.....	133
15. Analysis of Variance for TP Reduction, Including Only the Significant Effects of the Fixed Independent Variables.....	134
16. Regression of TP Reduction Against Significant Effects of Fixed Independent Variables.....	134
Design and Operation of Field-Scale Crystallizer	
17. Results from Test Runs with Field-Scale System.....	155
18. Detailed Results from Factorial Experiment with Field-Scale System.....	159
19. Analysis of Variance for Field-Scale TP Reduction, Including All Effects of Independent Variables.....	162
20. Analysis of Variance for Field-Scale TP Reduction, Including Only the Significant Effects of the Fixed Independent Variables.....	163
21. Regression of Field-Scale TP Reduction Against Significant Effects of Fixed Independent Variables.....	163

Design and Operation of Field-Scale Crystallizer (continued)

22. Analysis of Variance for Field-Scale OP Reduction, Including All Effects of Independent Variables	163
23. Analysis of Variance for Field-Scale OP Reduction, Including Only the Effects Indicated as Significant in the Complete Analysis.....	164
24. Regression of Field-Scale OP Reduction Against the Effects Indicated as Significant in the Complete Analysis	164

Appendices

25. Opening Diameter (mm) of Screens with Various Standard Sieve Numbers	181
26. Complete List of Components for Field-Scale Crystallizer	184

LIST OF FIGURES

Page

Introduction

1. Variation of Equilibrium Conditional Solubility Product with pH 12
2. Free Energy versus Number of Particles in a Precipitating Crystal 17
3. Concentration ($-1/3$ log of ionic product, mol/L) versus Induction Time (s) for Struvite Precipitation 20

Experiments in Batch Mode and Resulting Design Elements for Struvite Crystallizer

4. Dissolved OP and TP (ppm) in Untreated and Treated Effluent from Rocky Mount Lagoon 28
5. Dissolved OP and TP (ppm) in Untreated and Treated Effluent from Clayton Digester 29
6. Breakdown of Phosphorus Content (ppm) by Form in Rocky Mount and Clayton Effluent 31
7. Breakdown of Magnesium Content (ppm) by Form in Rocky Mount and Clayton Effluent 31
8. Breakdown of TAN (ppm) by Form in Rocky Mount and Clayton Effluent 32
9. pH versus Amount of Ammonia Added (ppm) for Five Ratios of Effluent to Mg-Supplementing Solution 40
10. Excess Molar Product (mol^3/L^3) versus Time (h) Elapsed from pH, OP, and Magnesium Augmentation 43

Modeling the Behavior of a Cone-Shaped, Fluidized-Bed Struvite Crystallizer

11. Dissolved OP Concentration (ppm) versus Height (cm) in Reactor, Predicted by Three Models 62

Experiments with Laboratory-Scale Continuous Crystallizer

12. Sketch of Laboratory-Scale Continuous Crystallizer 71
13. First Series of FCRs: Bed Weight (g), Broken Down by Particle Size (Standard Sieve), vs. Time Operated (h) 91
14. First Series of FCRs: Bed Height (cm) at End of Run vs. Operating Time (h) 91
15. First Series of FCRs: Production (g/h), Averaged Over Each Run, Broken Down by Particle Size (Standard Sieve) 92
16. First Series of FCRs: Phosphorus Reduction (fraction) vs. Operating Time (h) 93
17. First Series of FCRs: OP (ppm) at Various Sampling Points vs. Operating Time (h) 94
18. Second Series of FCRs: Bed Weight (g), Broken Down by Particle Size (Standard Sieve), vs. Time Operated (h) 104
19. Second Series of FCRs: Bed Height (cm) at End of Run vs. Operating Time (h) 105

Experiments with Laboratory-Scale Continuous Crystallizer (continued)

20. Second Series of FCRs: Production (g/h), Averaged Over Each Run, Broken Down by Particle Size (Standard Sieve).....	106
21. Second Series of FCRs: Phosphorus Reduction (fraction) vs. Operating Time (h)	107
22. Second Series of FCRs: OP (ppm) at Various Sampling Points vs. Operating Time (h)	108
23. Third Series of FCRs: Bed Weight (g), Broken Down by Particle Size (Standard Sieve), vs. Time Operated (h)	113
24. Third Series of FCRs: Bed Height (cm) at End of Run vs. Operating Time (h)	114
25. Third Series of FCRs: Production (g/h), Averaged Over Each Run, Broken Down by Particle Size (Standard Sieve).....	115
26. Third Series of FCRs: Phosphorus Reduction (fraction) vs. Operating Time (h)	116
27. Third Series of FCRs: OP (ppm) at Various Sampling Points vs. Operating Time (h)	117
28. MVRs: OP Removal (%) vs. Mg Addition (ppm) with Zero Ammonia and 41.2 L/h Flow	124
29. MVRs: OP Removal (%) vs. Mg Addition (ppm) with 100 ppm (as TAN) Ammonia and 41.2 L/h Flow	124
30. MVRs: OP Removal (%) vs. Mg Addition (ppm) with 200 ppm (as TAN) Ammonia and 41.2 L/h Flow	125
31. MVRs: TP Removal (%) vs. Mg Addition (ppm) with Zero Ammonia and 41.2 L/h Flow	125
32. MVRs: TP Removal (%) vs. Mg Addition (ppm) with 100 ppm (as TAN) Ammonia and 41.2 L/h Flow	126
33. MVRs: TP Removal (%) vs. Mg Addition (ppm) with 200 ppm (as TAN) Ammonia and 41.2 L/h Flow	126
34. MVRs: OP Removal (%) vs. Mg Addition (ppm) with Zero Ammonia and 56.8 L/h Flow	127
35. MVRs: OP Removal (%) vs. Mg Addition (ppm) with 100 ppm (as TAN) Ammonia and 56.8 L/h Flow	127
36. MVRs: OP Removal (%) vs. Mg Addition (ppm) with 200 ppm (as TAN) Ammonia and 56.8 L/h Flow	128
37. MVRs: TP Removal (%) vs. Mg Addition (ppm) with Zero Ammonia and 56.8 L/h Flow	128
38. MVRs: TP Removal (%) vs. Mg Addition (ppm) with 100 ppm (as N) Ammonia and 56.8 L/h Flow.....	129
39. MVRs: TP Removal (%) vs. Mg Addition (ppm) with 200 ppm (as N) Ammonia and 56.8 L/h Flow.....	129

Comparison of Laboratory Results with Model-Predicted Results

40. Observed and MLMB-Predicted OP (ppm) vs. Height (cm) at Various k' Values (dm/h), For Near-Steady State Portion of FCR Series #1	140
41. Observed and MLMB-Predicted OP (ppm) vs. Height (cm) at Various k' Values (dm/h), For Near-Steady State Portion of FCR Series #3	140

Comparison of Laboratory Results with Model-Predicted Results (continued)

42. Observed and PLCB-Predicted OP (ppm) vs. Height (cm) at Various k' Values (dm/h), For Near-Steady State Portion of FCR Series #1	143
43. Observed and PLMB-Predicted OP (ppm) vs. Height (cm) at Various k' Values (dm/h), For Near-Steady State Portion of FCR Series #1	145
44. Observed and PLMB-Predicted OP (ppm) vs. Height (cm) at Various k' Values (dm/h), For Near-Steady State Portion of FCR Series #3	145

Design and Operation of Field-Scale Crystallizer

45. Schematic Representation of Field-Scale Crystallizer, Showing Principal Components	149
46. TP Reduction (%) vs. Magnesium Added (ppm) at Lower Flow Rate (341 L/h)	160
47. OP Reduction (%) vs. Magnesium Added (ppm) at Lower Flow Rate (341 L/h).....	160
48. TP Reduction (%) vs. Magnesium Added (ppm) at Higher Flow Rate (568 L/h).....	161
49. OP Reduction (%) vs. Magnesium Added (ppm) at Higher Flow Rate (568 L/h).....	161

Appendices

Schematic Diagram of Field-Scale Crystallizer, Identifying All Components	183
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LIST OF ABBREVIATIONS AND OTHER SYMBOLS

Abbreviations

°C	Degrees Celsius
Ca	Calcium
cc	Cubic centimeters
cm	Centimeters
CO ₂	Carbon dioxide
dm	Decimeters
°F	Degrees Fahrenheit
FCR	Fixed-condition run
ft	Feet
g	Grams
gal	Gallons
h	Hours
HCl	Hydrogen chloride (in water solution, hydrochloric acid)
in.	Inches
kg	Kilograms
kPa	Kilopascals
L	Liters
m	Meters
mg	Milligrams
Mg	Magnesium
MgO	Magnesium oxide
min	Minutes

MLMB	Mixed liquid, mixed bed
mm	Millimeters
MVR	Multi-variate run
N	Nitrogen
OP	Orthophosphate phosphorus
PLCB	Plug-flow liquid, classified bed
PLMB	Plug-flow liquid, mixed bed
PVC	Polyvinyl chloride
ppm	Parts per million
psi	Pounds per square inch
s	Seconds
TAN	Total ammoniacal nitrogen
TP	Total phosphorus
%	Percent

Other Symbols

A = Cross-sectional area of the vessel at a given height (area).

$[A]$ = Molar concentration of dissolved ammoniacal nitrogen in liquid in the reaction zone.

$[A]_0$ = Molar concentration of dissolved ammoniacal nitrogen in liquid entering the reaction zone.

AM = Amount of ammonia addition, in ppm as N. Used in regression equations.

AP = Amount of pH adjustment by ammonia addition: zero, 0.5 pH rise, or 1.0 pH rise. Used in regression equations.

C_0 = Concentration of struvite in the liquid phase entering the vessel (dimensionless). Specifically, the sum of the concentration of all OP species, expressed as mass PO_4^{-3} per mass of water; the concentration of magnesium ions, expressed as mass magnesium per mass of water; and the concentration of TAN, expressed as mass NH_4^+ per mass of water.

C = Concentration of struvite in the liquid phase at any height, expressed in the same manner as C_0 (dimensionless).

- F_j = Moles per time of reactant exiting reaction zone of the crystallizer. For struvite, this is the moles per time of dissolved magnesium, ammoniacal nitrogen, and orthophosphate, the sum divided by three.
- F_{j0} = Moles per time of reactant entering the crystallizer. For struvite, this is the moles per time of dissolved magnesium, ammoniacal nitrogen, and orthophosphate, the sum divided by three.
- FL = Liquid flow rate in field-scale crystallizer, in gallons per hour. Used in regression equations.
- G = The rate of deposition of struvite onto a solid struvite particle surface (length per time). It is equal to $\frac{dL}{dt}$.
- g = Acceleration of gravity (9.8 meters per second squared).
- H = Height above bottom of vessel (length).
- H_t = Height at top of vessel (length).
- K = Equilibrium constant.
- k' = Surface-area-specific reaction rate constant. It is the rate of drop in P per unit of surface area density at a given P (volume per time per area).
- L = Radius of a solid struvite particle (length).
- MG = Amount of Mg addition, in ppm. Used in regression equations.
- m = Surface area on bed particles per volume of reaction zone (area per volume).
- $[M]$ = Molar concentration of dissolved magnesium in liquid in the reaction zone.
- $[M]_0$ = Molar concentration of dissolved magnesium in liquid entering the reaction zone.
- n = number of ions in a particle.
- n^* = number of ions in a critical nucleus.
- OPR = % reduction in OP. Used in regression equations.
- pK = Negative base-10 logarithm of an equilibrium constant.
- pKa = pH at which an acid at equilibrium is half protonated and half de-protonated.
- pH = Negative base-10 logarithm of the molar concentration of hydrogen ions.
- P = Conditional solubility product. Equal to the sum of the molarities of all magnesium-containing species, $[Mg]_T$; times the sum of the molarities of all the ammonia-containing

- species, $[\text{NH}_3]_T$; times the sum of the molarities of all the orthophosphate-containing species, $[\text{PO}_4]_T$ (moles cubed per liter cubed).
- $[P]$ = Molar concentration of dissolved orthophosphate in liquid in the reaction zone.
- $[P]_0$ = Molar concentration of dissolved orthophosphate in liquid entering the reaction zone.
- P_e = P at struvite saturation at a given pH (moles cubed per volume cubed).
- R = Universal gas constant.
- r_H = Radius of the cone at height H (length).
- $r_{H+\Delta H}$ = Radius of the cone at height $H+\Delta H$ (length).
- R_T = Reynolds number, indicating the tendency toward turbulent flow (dimensionless).
- Q = Flow rate of liquid phase entering the vessel (volume per time).
- r_A = Reaction rate, expressed as moles of species A generated per time per volume of reaction zone. For struvite crystallization, it is minus one third of the sum of the moles of dissolved magnesium, ammoniacal nitrogen, and orthophosphate that precipitate per time from solution.
- $-r_j$ = Reaction rate, expressed as moles of reactant j consumed per time per volume of reaction zone. For struvite crystallization, it is one third of the sum of the moles of dissolved magnesium, ammoniacal nitrogen, and orthophosphate that precipitate from a volume of solution per time.
- S = Surface area content of the bed material (area per mass).
- T = Absolute temperature.
- t = Time.
- TPR = % reduction in TP. Used in regression equations.
- U_S = Superficial upward velocity of liquid phase (length per time). At a given point in the vessel, it is equal to the volumetric flow rate of the liquid divided by the cross-sectional area of the vessel at that height; i.e., it is the upward velocity the liquid would have if there were no bed.
- U_T = Terminal velocity of a bed particle (length per time).
- V = Volume of the reaction zone. In the crystallizer it is the portion occupied by the bed (volume).
- V_0 = Volumetric flow rate (volume per time).
- W = Diameter of vessel at a given height (length).

W_t = Diameter of vessel at top (length).

W_0 = Diameter of vessel at bottom (length).

x = The number of moles per liter of struvite that have precipitated from solution, defined as:

$$x = \frac{\{([M]_0 - [M]) + ([A]_0 - [A]) + ([P]_0 - [P])\}}{3}.$$

Z = Expansion index (dimensionless).

α = Volume factor for a solid struvite particle (dimensionless). Multiplying it by L^3 gives the volume of the particle. For example, for a sphere, the volume factor is $4\pi/3$.

β = Surface factor for a solid struvite particle (dimensionless). Multiplying it by L^2 gives the surface area of the particle. For example, for a sphere, the surface factor is 4π .

ΔG = Molar Gibbs energy difference between individual ions in solution and ions in an infinite crystal.

ΔG_f° = Standard molar Gibbs energy of formation.

ΔG_r° = Standard molar Gibbs energy of reaction.

ΔH = Difference in height between the upper and lower horizontal surfaces of a horizontal slice of the vessel selected arbitrarily for analysis (length).

Δt_i = Induction time.

ε = Void fraction; that is, the fraction of volume occupied by the liquid phase at a given height in the vessel (dimensionless).

φ = Gibbs energy difference between individual ions in solution and ions in infinite crystal.

γ = Diameter factor for a solid struvite particle (dimensionless). Multiplying it by L gives the diameter of the particle. For example, for a sphere, the diameter factor is 2.

μ = Viscosity of the solution (mass per length per time).

ρ = Density of the liquid phase (mass per volume).

ρ_p = Density of struvite particles (mass per volume).

ρ_p^* = Density of struvite excluding the weight of the water of crystallization (mass per volume).

ψ = Constant of proportionality relating free surface energy to $n^{2/3}$.