

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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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^o = Standard molar Gibbs energy of formation.

ΔG_r^o = 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 $n^{2/3}$.