

PERFORMANCE OF CONE-SHAPED FLUIDIZED BED STRUVITE CRYSTALLIZERS IN REMOVING PHOSPHORUS FROM WASTEWATER

K. E. Bowers, P. W. Westerman

ABSTRACT. A struvite crystallizer design consisting of a continuously operating, cone-shaped fluidized bed was tested for its ability to remove phosphorus from swine lagoon liquid. A laboratory-scale apparatus was first tested, operating at 41 and 57 L h⁻¹ of lagoon liquid, and then a field-scale apparatus was tested, operating at 341 and 568 L h⁻¹. Tests were arranged in a randomized complete block design, with the two cited lagoon liquid flow rates and three levels each of magnesium (Mg) supplementation and pH increase as independent variables. Levels of Mg supplementation were 0, 30, and 60 ppm. Ammonia was used to increase pH, and in the laboratory-scale tests, levels of this variable were set at 0, 100, and 200 ppm as nitrogen (N) of ammonia. In the field-scale tests, pH was controlled directly, and increased by 0, 0.5, and 1.0 pH units. In the laboratory-scale tests, orthophosphate phosphorus (OP) removal ranged from 1% to 80%, and total phosphorus (TP) removal ranged from -5% to 56%. In the field-scale tests, OP removal was 13% to 82%, and TP removal was 0% to 80%. The laboratory-scale apparatus exhibited greater removal with increasing Mg supplementation and pH augmentation, but flow rate showed no significant effect. The effects of the independent variables were similar in the field-scale apparatus, except that decreasing flow rate was associated with greater removal.

Keywords. CAFO, Crystallizer, Fluidized bed, Livestock, Phosphorus, Struvite, Waste, Wastewater.

Cropland near concentrated animal feeding operations sometimes is irrigated with wastewater from treatment/storage lagoons associated with those operations. In many cases, the wastewater is applied to the crops at a rate calculated to balance the nitrogen (N) applied via the wastewater with the N uptake rate of the crops. In such cases, phosphorus (P) applied via the wastewater typically exceeds the P uptake by the crops, resulting in unwanted accumulation of P in the soil. Removing P from the wastewater by precipitating struvite can address the P imbalance. Struvite, also known as magnesium ammonium phosphate hexahydrate, or MgNH₄PO₄·6(H₂O), is a crystalline salt that has been observed to form in livestock wastewater. Several researchers have examined struvite formation in swine manure wastewater (Beal et al., 1999; Brionne et al., 1994; Liao et al., 1995; Webb and Ho, 1992). Buchanan et al. (1994) examined the thermodynamics of struvite formation in the context of livestock wastewater. Ohlinger et al. (2000) studied struvite precipitation from wastewater from a public treatment plant. A novel design concept for an effective crystallizer, consisting of a continuously operating cone-shaped fluidized bed, and a model and kinetics useful for applying

the concept have been elaborated by Bowers (2002) and Bowers and Westerman (2005).

A cone-shaped fluidized bed crystallizer offers advantages over other means for precipitating the struvite because its range in upflow velocity (high velocity at the bottom, diminishing to a low velocity at the top) retains a broad range of particle sizes in a dense bed. The broad particle size range permits large particles (important for a granular product that is inexpensive to handle) to be produced, while simultaneously suspending the fine particles required to achieve a high ratio of crystal surface area to reactor volume. The high ratio permits use of a small reaction vessel, further lowering costs. In the design, supplementation with Mg and/or augmentation of pH are used to increase the concentrations of the constituent ions of struvite, thus increasing the thermodynamic driving force for struvite crystallization.

The experiments described in the present article aimed at evaluating the performance, in terms of OP removal and TP removal, of crystallizers adhering to the novel design concept. In particular, the experiments sought to reveal, through a factorial design, the ways in which TP and OP removal varies with respect to the three main operating variables that can be controlled in an installed system, namely: (1) flow rate of wastewater, (2) degree of supplementation with Mg, and (3) amount of pH augmentation. Two crystallizers, a laboratory-scale apparatus and the other at field-scale, were evaluated.

MATERIALS AND METHODS

LABORATORY-SCALE EXPERIMENTS

A cone 39.7 centimeters (cm) high with inner diameters of 1.27 cm and 10.2 cm, respectively, at the bottom and top

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The authors are **Keith Edison Bowers, ASAE Member Engineer**, President, Multiform Harvest, Inc., Seattle, Washington; and **Philip W. Westerman, ASAE Member Engineer**, Professor, Department of Biological and Agricultural Engineering, North Carolina State University, Raleigh, North Carolina. **Corresponding author:** Keith E. Bowers, Multiform Harvest, Inc., 3109 South Frontenac St., Seattle, WA 98108; phone: 206-725-3305; e-mail: keithebowers@yahoo.com.

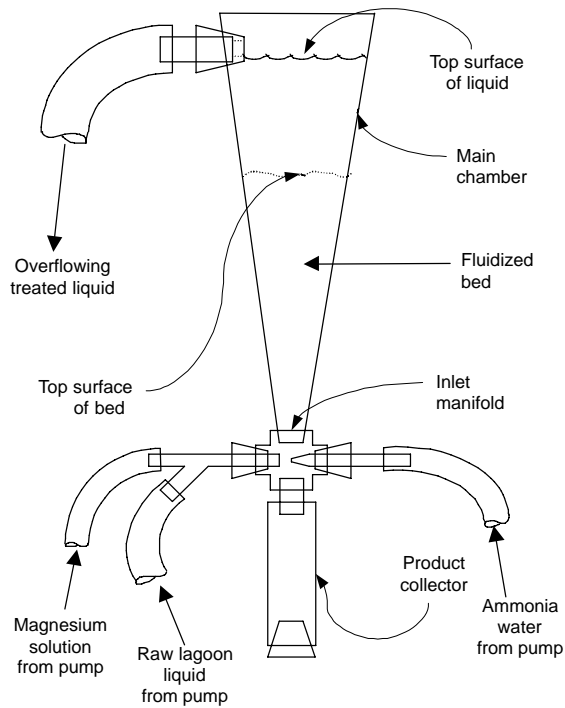


Figure 1. Sketch of laboratory-scale continuous crystallizer (U.S. Patent Application No. 10/659,239).

served as the main chamber, containing the fluidized bed (fig. 1). The cone was of transparent polystyrene, and a hole centered 1.9 cm from the top was drilled to accommodate the overflow connection. The conduits for fluids and the product collector were of flexible tubing. Rubber stoppers were used to close the bottom of the product collector and, along with short tubes of glass or plastic, to connect the fluid conduits. A plastic four-way pipe connector serving as the inlet manifold was cemented to the cone and connected to the product collector with a short plastic tube.

Fisher Scientific Variable Mini-Flow peristaltic pumps were used to meter in ammonia to raise pH and magnesium solution to raise the magnesium concentration and thus increase the driving force for struvite precipitation. Lagoon liquid was metered from a 455 L tank with an IDEX model 120-000-110 variable-speed gear pump, and was kept agitated in the tank by recirculating it with a Little Giant model PE-1 submersible centrifugal pump. The pH of the liquid in the upper part of the cone, above the top of the bed, was monitored with a pH probe that extended into the liquid from the top and was clamped to an external support.

Lagoon liquid was brought to the laboratory in a 455 L tank from the swine lagoon at the Upper Coastal Plain Research Station in eastern North Carolina. The Mg solution was prepared by dissolving magnesium oxide into hydrochloric acid and then diluting with lagoon liquid to obtain a liquid containing 800 ppm Mg and pH of 7.0 to 7.5. Ammonia solution was prepared by diluting ammonium hydroxide to 8500 ppm as nitrogen (N). A struvite particle bed with particle size distribution summarized in table 1 was loaded into the crystallizer at the beginning of each block of tests. The bed was made up from struvite particles produced during the fixed-condition runs in the experiments described in Bowers and Westerman (2005). During operation of the crystallizer, the top surface of the bed was observed at 26 to

Table 1. Particle size distribution of struvite bed loaded into crystallizer for each block.

Particle Size Fraction (sieve number range)	Particle Diameter (mm)	Grams in Bed (g)
16 to 18	1.00 to 1.19	0.0
18 to 20	0.84 to 1.00	0.8
20 to 25	0.71 to 0.84	0.9
25 to 30	0.59 to 0.71	6.6
30 to 35	0.50 to 0.59	27.8
35 to 40	0.42 to 0.50	40.1
40 to 50	0.297 to 0.42	49.7
50 to 60	0.25 to 0.297	20.9
>60	<0.25	20.2
Total		167.0

29 cm above the bottom of the cone, and the bottom of the bed stayed near the bottom of the cone.

The experiments were organized into three blocks, each block consisting of a sequence containing all eighteen combinations, in random order, of two levels of lagoon liquid flow rate (41 and 57 L h⁻¹) and three levels each of Mg (0, 30, and 60 ppm) and ammonia (0, 100, and 200 ppm as N) supplementation. Each block was completed within a 4 h period, using the same sample of raw lagoon liquid in the feed tank. A separate, fresh tank of liquid was obtained for each block. Four samples, spaced evenly in time, were taken from the liquid tank during each block and combined into one composite sample of raw liquid. For each of the eighteen treatment combinations, a waiting period of at least 10 min, equating to a minimum of seven residence times, was allowed after setting the treatment conditions before collecting the treated liquid sample from the overflow. To maintain a nearly constant bed mass, product was drained four times during each block. To drain product, the flow rate was reduced to 15 to 20 L h⁻¹ for the time required (generally about 1 min) to allow sufficient product to settle into the product collector to return the bed level to its height measured at the normal flow rates (26.6 cm at 41 L h⁻¹ and 28.2 cm at 57 L h⁻¹) at the beginning of the block. The conditions for each treatment following product drainings were not set until the bed had completely re-fluidized to its normal form. The maximum bed height deviation from mean for a given block and flow rate averaged 1.0%.

The composite raw liquid sample and eighteen treated liquid samples from each block were analyzed for OP and TP content. The composite raw liquid samples from the first two blocks were also analyzed for total ammoniacal nitrogen (TAN) and Mg content. The OP analyses were by EPA Test Method 365.1 (EPA, 1979), with the ascorbic acid method for automated analysis. The TP analyses used the same method, except that samples were subjected to persulfate digestion before automated analysis. The TAN analyses used EPA Test Method 351.2 (EPA, 1979), and the Mg analyses used Standard Method 3111 B (APHA, 1995).

Product of crystallization was harvested from the laboratory crystallizer during the various tests, and a subsample of the mixed accumulated product was analyzed by x-ray diffraction. Powdered samples were run on the Rigaku D-Max/B X-Ray Diffractometer in the XRD Laboratory, Department of Marine, Earth and Atmospheric Sciences at North Carolina State University. Operating conditions were 35 kV and 30 mA, using CuK-alpha radiation and a graphite monochromator. Samples were scanned from 10° to 50°

tio of bed growth rate to bed mass, limiting bed growth during blocks despite the lower draining frequency. As a result, the maximum bed height deviation from mean for a given block and flow rate averaged only 1.8%. Particle size distribution of the full-sized bed was not evaluated, but from visual observation appeared similar to that seen in the laboratory-scale system.

It should also be noted that the scale-up resulted in an increase in residence time. To keep upflow velocity range (and thus bed particle size distribution) nearly the same in the field-scale apparatus as in the laboratory-scale apparatus, the cross-sectional area of the cone needs to increase proportionally (the power of 1) with the volumetric flow rate. The cross-sectional area varies as the square of the diameter; therefore, the diameter must only be increased proportionally to the square root (the 1/2 power) of the volumetric flow rate. However, to maintain similar bed shape and side slope, the height of the bed must increase proportionally with the diameter; that is, with the square root of the volumetric flow rate. The volume of the bed, proportional to the cross-sectional area times the height, thus increases with the 3/2 power (1 + 1/2) of the volumetric flow rate. The residence time (volume divided by volumetric flow rate) therefore increases with the square root (3/2 - 1 = 1/2) of the volumetric flow rate. As a result, the field-scale apparatus, designed for a volumetric flow rate ten times greater, provided about 10^{1/2}, or about three times greater, residence time than did the laboratory-scale apparatus. This change means that a minimum of about 2.5 residence times elapsed between setting conditions and taking the treated liquid sample in the field-scale experiments. However, for plug flow of liquid (demonstrated in Bowers, 2002, to likely be the case), any elapsed time greater than one residence time would be sufficient for the changes to work through to the treated liquid exit.

The PLMB (plug-flow liquid, mixed bed) model used by Bowers and Westerman (2005) to predict the P removal performance of the laboratory-scale system can also be used for the field-scale system. The model is described by the equation:

$$S = \frac{v_0}{k'} \int_0^{x_f} \left\{ 3x^2 - 2([M]_0 + [A]_0 + [P]_0)x + ([M]_0[A]_0 + [A]_0[P]_0 + [P]_0[M]_0) \right\} + \left\{ ([M]_0 - x)([A]_0 - x)([P]_0 - x) - P_e \right\} dx \quad (1)$$

where S represents the total surface area of the bed; v_0 is the volumetric flow rate of the entering liquid; k' is the surface-area specific rate constant; x and x_f are the number of moles of struvite that have precipitated per liter of solution at any point and in the exiting liquid, respectively; $[M]_0$, $[A]_0$, and $[P]_0$ represent the molarity of magnesium, ammonium (as total ammoniacal nitrogen), and phosphate in the liquid entering the reaction zone; and P_e is the struvite conditional solubility product.

To predict the P removal that will be achieved by a system of a given design, equation 1 is solved for x_f after inserting estimates for all other variables. For the present case, two predictions are made here: one for operation at the middle levels of pH rise and Mg addition (0.5 and 30 ppm, respectively) with the lower flow rate (341 L h⁻¹), and

another at the same conditions except for the higher flow rate (568 L h⁻¹).

For both predictions, an estimate of 3,990 square decimeters for S is calculated after assuming that the bed in the field-scale system will occupy the same fraction of cone volume and have the same particle size distribution as the bed in the laboratory-scale system. The lab-scale value of S (163 square decimeters) can then be multiplied by the field-to-lab ratio of cone volume (24.5) to estimate the field-scale S . The two values of v_0 are 341 and 568 L h⁻¹. The constant k' was estimated at 10 to 15 dm h⁻¹ in Bowers and Westerman (2005), so 12.5 dm h⁻¹, the midpoint of the range, is used here. The values for $[M]_0$, $[A]_0$, and $[P]_0$ are estimated using the expected composition of the raw wastewater after pH and Mg adjustment. Raw wastewater averaged 62 ppm Mg before and thus would be 92 ppm Mg after adjustment, equating to 0.0030 molarity for $[M]_0$. For $[A]_0$, the raw wastewater TAN averaged 184 ppm as N. Approximately 50 ppm was needed to produce a 0.5 increase in pH, and therefore the entering liquid contained approximately 234 ppm TAN, equating to 0.017 molarity. (The TAN addition can be estimated either by water chemistry calculations or by simply observing the ammonia quantity needed to raise the pH of a wastewater sample to the desired value.) Estimating $[P]_0$ is more difficult because, as Bowers and Westerman (2005) suggested, the amount of P available for precipitation may exceed that reflected in the OP analysis alone. For the present case, each prediction will be made for a range of $[P]_0$, the range bracketed by the average OP and TP analyses (respectively 41 and 89 ppm, equating to 0.0013 and 0.0029 molarity). The value of P_e (10⁻⁸) can be read from the graph of conditional solubility product vs. pH in Ohlinger et al. (2000) at pH = 8.2 (raw wastewater pH 7.7 plus the 0.5 desired rise).

Using numerical integration, equation 1 is solved to find a predicted value for x_f of 0.00099 when using the OP analysis for $[P]_0$ and 0.00213 when using the TP analysis. Because x , the moles per liter of struvite precipitated, is also equal to the moles per liter of P removed, these predicted x_f values can be converted to predicted TP reduction by dividing them by 0.0029, the TP molarity of the raw wastewater. The resulting predictions are 34% TP removal when using the OP analysis and 73% TP removal when using the TP analysis. The predictions at the lower value of v_0 , the liquid flow rate, differ only negligibly from those at the higher value, a result of the fact that the amount of bed surface area is great enough in comparison with the flow rate that the reaction is predicted to proceed almost completely to equilibrium in both cases.

RESULTS

QUALITATIVE OBSERVATIONS

During the experiments, the lower portion of the bed in both the laboratory-scale and field-scale crystallizers appeared to swirl rapidly (moving about 5 cm s⁻¹ or faster, in approximately circular patterns) and randomly (the circular patterns forming and dissipating unpredictably and moving in unpredictable directions). This portion was also very loosely packed with bed material, i.e., there was more wastewater than bed material visible. Above this zone was a region where churning was slower, but still random, and the bed appeared dense (more bed material than wastewater

visible). Finally, in the highest portion of the bed could be seen a zone where the bed was dense and churning in a more predictable manner. Specifically, the bed appeared to move generally downward at the periphery and upward in the center. No channels could be seen in any of the zones, and the bed did not look any finer or coarser in any one place than it did in another. The exiting, treated liquid appeared identical to the raw liquid in color and opacity.

LABORATORY-SCALE QUANTITATIVE RESULTS

The laboratory-scale results are summarized in table 2, which shows OP and TP removal rates, averaged across the three blocks, for each combination of the three independent variables (flow rate, Mg addition rate, and ammonia addition rate). The limits of the 95% confidence intervals are also indicated. When both ammonia and Mg were being added, OP removal of 72% to 80% and TP removal of 49% to 56% were achieved. Addition of 100 and 200 ppm ammonia raised the pH by about 0.8 and 1.2 points, respectively. The TP content of the raw liquid was 90.6, 81.7, and 82.6 ppm, respectively, for blocks 1, 2, and 3; OP content was 45.5, 46.4, and 48.9 ppm, and pH was 7.60, 7.56, and 7.68. The TAN content was 278 and 271 ppm as N for blocks 1 and 2, and Mg content was 16.3 and 15.3 ppm.

In table 2, it can be seen that TP and OP removal tends to increase with increasing Mg and ammonia addition rate. The effect is strongest for ammonia, moving from the lowest to the middle level of ammonia addition. All differences between these two levels at a given Mg level exceed the least significant difference. Little or no effect is observed in moving from the middle to high ammonia level. A similar, though less pronounced, trend can be seen with respect to Mg addition. A greater block-to-block variation within treatments for TP results than for OP results led to the greater confidence intervals and least significant differences for TP than for OP.

Analyses of variance were performed on the data, using OP reduction and TP reduction as dependent variables. All linear, quadratic, and interaction effects of the three fixed independent variables were tested. The two dependent variables were then regressed against the effects that the analyses of variance revealed to be significant at a *P* level of 0.02. Statistical analysis software (SAS, 2001) was used to

complete the analyses of variance and regressions. The resulting model equations for predicting P removal were:

$$\begin{aligned} OPR = & 3.43 + 0.725(AM) + 0.83(MG) \\ & - 0.00122(AM \times MG) \\ & - 0.00224(AM \times AM) \\ & - 0.0048(MG \times MG) \end{aligned} \quad (2)$$

and

$$\begin{aligned} TPR = & -2.81 + 0.605(AM) + 0.275(MG) \\ & - 0.00202(AM \times AM) \end{aligned} \quad (3)$$

where

OPR = percent reduction in orthophosphate phosphorus

TPR = percent reduction in total phosphorus

AM = ppm (as N) ammonia addition

MG = ppm Mg addition.

The *R*² values (fraction of all variation in the data that is captured by the equation) for equations 2 and 3 are 0.93 and 0.74, respectively.

Some of the data trends that are described by the terms in equations 2 and 3 can be seen in the data. The tendency in table 2 for P removal to increase with increasing Mg and ammonia addition are reflected in the equations in the positive coefficients for terms containing simply *AM* or *MG*. The tendency of P removal to increase more in going from the low to middle addition level than in going from the middle to high level is seen in the negative coefficients for terms containing *AM* × *AM* or *MG* × *MG*. The effect of flow is not apparent in the data and neither does it appear in the equations.

The highest OP removal predicted by equation 2 is 83.7%, which occurs at 143 ppm ammonia addition and 68 ppm Mg addition. Equation 3 has no quadratic term for Mg addition. Therefore, the usual technique for locating a maximum (simultaneously solving the two equations that result from setting equal to zero the two partial derivative functions and selecting the solution for which the second partial derivatives are both negative) can locate no maximum other than at infinite Mg addition. However, if Mg is set at its highest

Table 2. Phosphorus reduction in laboratory-scale system.

Ammonia Addition Rate	41 L h ⁻¹ Liquid Flow Rate			57 L h ⁻¹ Liquid Flow Rate		
	0 ppm Mg Addition Rate	30 ppm Mg Addition Rate	60 ppm Mg Addition Rate	0 ppm Mg Addition Rate	30 ppm Mg Addition Rate	60 ppm Mg Addition Rate
Orthophosphate phosphorus (OP) removal ^[a]						
0 ppm	9%	21%	35%	1%	21%	40%
100 ppm	52%	72%	79%	52%	72%	80%
200 ppm	59%	72%	76%	56%	76%	76%
Total phosphorus (TP) removal ^[b]						
0 ppm	4%	0%	8%	-5%	10%	15%
100 ppm	31%	49%	56%	34%	52%	51%
200 ppm	30%	49%	50%	39%	51%	53%

^[a] 95% confidence limits are ±8.7% OP removal, and least significant difference at 95% confidence is 12.4% removal. Therefore, at the 95% confidence level, there is a significant difference between zero and any value greater than 8.7% removal and also between any two values that differ by more than 12.4% removal.

^[b] 95% confidence limits are ±15.7% TP removal, and least significant difference at 95% confidence interval is 22.3% removal. Therefore, at the 95% confidence level, there is a significant difference between zero and any value greater than 15.7% removal and also between any two values that differ by more than 22.3% removal.

Table 3. Comparison of x-ray diffraction results for product from laboratory tests for top ten peak heights and the results for pure struvite from software database.

Product from Laboratory Tests			Struvite (from software database)	
% of Maximum Peak Height	2-theta Angle (°)	d-spacing (Å)	2-theta Angle (°)	d-spacing (Å)
100.0	33.381	2.6821	33.400	2.6806
98.2	21.598	4.1112	21.571	4.1162
96.5	15.960	5.5487	15.930	5.5591
73.0	21.001	4.2267	20.970	4.2329
55.9	32.060	2.7895	32.033	2.7918
52.0	16.584	5.3413	16.590	5.3394
38.8	30.303	2.9471	30.309	2.9466
34.6	27.218	3.2737	27.209	3.2748
24.8	30.740	2.9062	30.722	2.9079
24.6	14.582	6.0698	14.534	6.0896

tested value (60 ppm), maximum TP removal (59%) is predicted at 150 ppm ammonia addition.

LABORATORY-SCALE X-RAY DIFFRACTION RESULTS

Subsample of product collected from several laboratory tests compared very well to the characteristics of struvite from the software database in terms of the d-spacing at various 2-theta angles. Table 3 shows data for the top ten peak heights.

FIELD-SCALE QUANTITATIVE RESULTS

The field-scale results are summarized in table 4, which shows OP and TP removal rates, averaged across the three blocks, for each combination of the three independent variables. The limits of the 95% confidence intervals are also indicated. When both ammonia and Mg were being added, OP removal of 70% to 82% and TP removal of 63% to 80% were achieved. Composite raw liquid samples contained 90.7, 82.3, and 93.1 ppm TP, respectively, for blocks 1, 2, and 3; 45.6, 37.6, and 40.7 ppm OP; 197, 180, and 176 ppm TAN as N; and 65.6, 53.4, and 67.4 ppm Mg. The pH of the raw liquid remained between 7.69 and 7.72 during all three blocks.

In table 4, trends can be seen similar to those noted in the factorial data for the laboratory-scale system. However, the

maximum TP reductions achieved are greater for the on-site system. The average TP removal during treatments that included both Mg and ammonia addition was 71% for the field-scale system versus only 51% for the laboratory-scale system, a large difference in comparison with the 95% confidence intervals for these averages ($\pm 2.8\%$ and $\pm 5.6\%$, respectively).

The same statistical analysis as that described for the table 2 data was performed on the table 4 data, resulting in the following model equations for predicting OP and TP reduction:

$$TPR = 11.0 + 140(AP) - 0.0673(FL) + 0.641(MG) - 80.5(AP)^2 - 0.00681(MG)^2 \quad (4)$$

and

$$OPR = 10.1 + 145(AP) + 0.580(MG) - 89.3(AP)^2 - 0.00486(MG)^2 - 0.0650(AP)(MG) \quad (5)$$

where AP is the pH rise achieved, and FL is the liquid flow rate (gal h^{-1}). Other symbols appearing in equations 4 and 5 have the same meaning as in equations 2 and 3. The R^2 value for each equation is 0.94.

Equation 4, unlike any of the other statistically derived predictive equations, includes a term with FL . The negative coefficient indicates that, in the range tested, TP removal increased with decreasing flow in the on-site system. However, from table 4 it can be seen that the increase was small when Mg was added and pH was increased.

Within the ranges of independent variables tested, equation 4 predicts maximum TP removal of 87% at 0.87 points of pH rise, 47 ppm Mg addition, and 341 L h^{-1} flow rate. Equation 5 predicts maximum OP removal of 84% at 55 ppm Mg addition and 0.78 point of pH rise.

FIELD-SCALE X-RAY DIFFRACTION RESULTS

Subsample of product collected from several field-scale tests compared very well to the characteristics of struvite from the software database in terms of the d-spacing at various 2-theta angles. Table 5 shows data for the top ten peak heights.

Table 4. Phosphorus reduction in factorial experiments with field-scale system.

pH Rise Achieved	341 L h^{-1} Liquid Flow Rate			568 L h^{-1} Liquid Flow Rate		
	0 ppm Mg Addition Rate	30 ppm Mg Addition Rate	60 ppm Mg Addition Rate	0 ppm Mg Addition Rate	30 ppm Mg Addition Rate	60 ppm Mg Addition Rate
Orthophosphate phosphorus (OP) removal ^[a]						
None	13%	23%	24%	13%	22%	27%
0.5 point	61%	73%	82%	56%	70%	78%
1.0 point	68%	78%	76%	64%	81%	80%
Total phosphorus (TP) removal ^[b]						
None	0%	14%	23%	7%	12%	14%
0.5 point	59%	70%	69%	41%	63%	67%
1.0 point	64%	80%	72%	63%	75%	73%

^[a] 95% confidence limits are $\pm 8.3\%$ removal, and least significant difference at 95% confidence is 11.7% removal. Therefore, at the 95% confidence level, there is a significant difference between zero and any value greater than 8.3% removal and also between any two values that differ by more than 11.7% removal.

^[b] 95% confidence limits are $\pm 7.8\%$ TP removal, and least significant difference at 95% confidence interval is 11.0% removal. Therefore, at the 95% confidence level, there is a significant difference between zero and any value greater than 7.8% removal and also between any two values that differ by more than 11.0% removal.

Table 5. Comparison of x-ray diffraction results for product from field-scale tests for top ten peak heights and the results for pure struvite from software database.

Product from Laboratory Tests			Struvite (from software database)	
% of Maximum Peak Height	2-theta Angle (°)	d-spacing (Å)	2-theta Angle (°)	d-spacing (Å)
100.0	33.460	2.6760	33.400	2.6806
94.9	21.020	4.2230	20.970	4.2329
43.4	32.062	2.7894	32.033	2.7918
41.5	15.979	5.5420	15.930	5.5591
41.4	16.638	5.3238	16.590	5.3394
37.8	21.599	4.1110	21.571	4.1162
34.7	30.780	2.9025	30.722	2.9079
33.5	30.360	2.9417	30.309	2.9466
25.1	33.802	2.6496	33.786	2.6508
21.2	33.079	2.7058	32.997	2.7124

DISCUSSION

CONSISTENCY OF RESULTS WITH THEORY

The underlying theory of phosphorus removal in this system is that phosphorus dissolved as OP in the liquid phase is removed from the waste stream by precipitating onto the particles in the fluidized bed. Most aspects of the results conform with expectations based on this theory, but one aspect does not.

Based on this theory, the simple effects of magnesium addition and pH rise (or ammonia addition) on phosphorus removal would be positive. Both agents serve to increase the concentration of struvite constituent ions, leading to greater driving force for precipitation of phosphorus. All four regression equations did indeed contain both these terms, all with positive coefficients. From this theory, one would also expect that quadratic effects of magnesium and pH rise (or ammonia addition) may be negative. Once a driving force sufficient to precipitate phosphorus to near-equilibrium is reached, further increases in magnesium addition and pH rise (or ammonia addition) would produce little or no additional phosphorus removal. The results are consistent with this logic, as all four equations contain one or both these terms, all with negative coefficients.

The degree of P removal achieved does not conform well with the theory because it appears to exceed the theoretical maximum in some cases. By the theory, only the dissolved OP could be removed. In the laboratory-scale experiments, total OP content of the raw liquid ranged from 50% to 59% of TP. In the eight treatment combinations that included addition of both Mg and ammonia, OP removal ranged from 72% to 80%. Therefore, if P removal occurred by OP removal alone, then the expected TP removal range could be calculated at 36% to 47% by multiplying the OP content range by the OP removal range. However, observed TP removal in these eight combinations ranged from 49% to 56%. Given the breadth of the 95% confidence intervals for the removal values, the lack of overlap between the expected and observed removal ranges can only suggest, rather than indicate convincingly, that some non-orthophosphate P in the raw liquid is being removed. A similar look at the field-scale data is more convincing. Total OP content in the raw liquid ranged from 44% to 50%, and OP removal ranged from 73% to 82% in the eight treatment combinations that included addition of both Mg and ammonia. The expected TP removal

range would thus be 32% to 41%, as compared with the observed range of 63% to 80%. The difference between expected and observed removal is large compared with the confidence intervals, imparting confidence in concluding that the observed removal really is greater than that expected. This conclusion favors the hypothesis that some P other than that accounted for as OP in the raw liquid is being removed.

Three hypotheses can be offered for how non-orthophosphate P is being removed. First, the bed may be entrapping, by adsorption or agglomeration, some of the suspended non-orthophosphate P, though no sludge-like component was observed in the bed or product. Second, some dissolved non-orthophosphate P may be precipitating onto the bed particles. Third, some non-orthophosphate P may be converted to OP that was lost by precipitation to maintain equilibrium between the non-orthophosphate P and the OP. This new OP may then be precipitated and thus removed. The close match of the product to struvite by x-ray diffraction offers some evidence in favor of the third hypothesis.

The fact that the field-scale apparatus, which had a greater residence time, exhibited a greater excess of P removal beyond the theoretical removal hints that the secondary mechanism may be slower than the primary, theoretical one. A slow secondary mechanism could also explain why the flow rate appears in the regression equation for TP removal in the field-scale, but not the laboratory-scale, apparatus. The amount of time needed before the slow mechanism can achieve additional TP removal of the degree required for statistical significance may exceed that provided in the laboratory-scale apparatus. The field-scale apparatus, with approximately triple the residence time, may have provided enough additional time, and enough difference in time between the lower and higher flow rates, to reveal statistically significant differences.

COMPARISON WITH PLMB MODEL PREDICTIONS

Table 6 compares the PLMB-predicted TP reductions with observed reductions. The observed reductions fall in the high end of the ranges defined by the predictions assuming only OP is available for precipitation (using raw OP for $[P]_0$) and assuming all P is available (using TP for $[P]_0$). In contrast, the Bowers and Westerman (2005) results for the laboratory-scale apparatus at the same k' were near and just above the value predicted assuming only OP is available, that is, near the low end of the range. The difference may be that the ratio of reactor volume to volumetric flow rate (residence time) and the ratio of bed surface area to volumetric flow rate were both about three times greater in the field-scale system. The greater ratios may provide more time for the hypothesized slow, secondary mechanism to make the non-orthophosphate P available for precipitation. The fact that the observed reduction for the 341 L h⁻¹ case was nearer the high end of the range than the observed reduction for the 568 L h⁻¹ case, which has lower ratios, is consistent with this trend.

Table 6. Observed vs. predicted TP reduction in field-scale apparatus at 30 ppm Mg addition and 0.5 pH rise.

Flow Rate (L h ⁻¹)	PLMB-Predicted TP Reduction		Observed TP Reduction
	Assuming Only OP is Available	Assuming All P is Available	
341	34%	73%	70%
568	34%	73%	63%

FURTHER DEVELOPMENT AND PRACTICAL MANAGEMENT

The degree of P removal demonstrated in the experiments could be sufficient to correct the over-application of P at many livestock operations where it is a problem. However, the field-scale system used in the tests was smaller than would be required for most of these livestock operations. In addition, it was intended mainly for the type of experiments described here, rather than for long-term operation. As a result, it lacked some features likely to be required in a system meant for long-term practical operation. Therefore, future development work addressing these issues is envisioned. In particular, larger systems could be developed and tested, with emphasis on product handling, treated liquid storage, and freeze protection. Effort could be directed into achieving long-term trouble-free operation. In addition, testing could be expanded to include wastewater at dairy farms, the other main type of operation in the U.S. using lagoons for storage and treatment of livestock waste.

Another stream of effort could address the above-suggested hypothesis that a second mechanism is achieving the P removal in excess of that achievable by the primary theoretical mechanism. Identifying the mechanism and characterizing it thermodynamically and kinetically would aid in further development of P removal systems of this novel design.

CONCLUSION

A system of this design, operating in the field on raw liquid similar in content to that used in these experiments, can be expected to remove most of the phosphorus. Therefore, this design concept shows promise for future use in removing phosphorus from livestock lagoon liquid.

Wastewater from different sources will have different characteristics, so the results of the experiments described here may not apply to other wastewater. For example, higher viscosity in the wastewater, as a result of higher concentrations of suspended and/or dissolved solids, could lead to fine bed particles being swept out of the bed, resulting in lower phosphorus removal. Removal could also be lower if a greater proportion of the phosphorus in the wastewater exists in forms that do not participate in the crystallization reaction. Wastewater that contains little ammonia nitrogen may not exhibit much phosphorus removal because the amount of ammonia added in these experiments, while sufficient to achieve adequate pH rise, may not push the struvite concentration (product of the three constituent ion concentrations) high enough. Finally, the system may not be able to remove as much phosphorus from wastewater that has significantly higher pH or Mg content, because phosphorus may have already precipitated into fine suspended struvite particles that will pass through the crystallizer with the treated water.

However, as a starting point for lagoons that do have similar characteristics, a rise of about 0.8 in pH and Mg addition of about 50 ppm should be used, although a rise of only 0.5 points in pH and Mg addition of only 30 ppm may achieve 60% to 70% TP removal. Note that Mg content of the lagoon liquid in the field-scale experiments was within

10 ppm of molar equivalence with TP content. In cases where Mg content falls shorter of molar equivalence, corresponding increases in Mg addition requirements may be expected for achieving comparable TP removal.

The increase in TP removal performance with increases in Mg and pH rise slows or reverses itself at higher levels of Mg addition and pH rise. Therefore, in applying the system to other wastewater, care should be taken to avoid excesses in this aspect. The Mg content and pH of the raw wastewater should be determined. The pH in the crystallizer should be set not necessarily at the crystallizer pH reported in these experiments, but rather at a pH of 0.5 to 1.0 above the raw wastewater pH. If the Mg molarity of the raw wastewater exceeds that of phosphorus, then Mg addition should be kept in the low part of the range reported in these experiments or not used at all.

Finally, the experiments reported here did not find an optimal flow rate, only that phosphorus removal improved with decreasing flow rate. Therefore, lower flow rates through a given bed, or a larger bed at a given particle size distribution and flow rate, may increase TP removal beyond the range reported here.

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