PHOSPHORUS REMOVAL AND RECOVERY FROM HIGH CALCIUM HOG LAGOON SUPERNATANT USING A GRAVITY SETTLED STRUVITE REACTOR

JOE N. ACKERMAN[1], NAZIM CICEK[2]

[1]Joe Ackerman Dept Biosystems Engineering E2-376 EITC University of Manitoba Winnipeg MB R3T-5V6, joe.ackerman@gmail.com
[2]Nazim Cicek Dept Biosystems Engineering E2-376 EITC University of Manitoba Winnipeg MB R3T-5V6, nazim_cicek@umanitoba.ca

ABSTRACT In Canada, the majority of swine waste is stored in open lagoons and land applied according to crop nitrogen requirements. This practice over-applies phosphorus (P) two to five fold, leading to runoff and a loss of P to the environment. Removing P from liquid hog wastes is an important step in correcting the N:P ratio of manure applied to cropland. Reclaiming this P as struvite ($MgNH_4PO_4$) would ease environmental concerns of eutrophication, provide a saleable fertilizer, and help address the limited global supply of phosphate. Most struvite reactors are capital and operationally intensive, making the process too expensive to be implemented by the average farmer. In addition, high calcium levels found in some supernatants compete with Mg and struvite formation is impaired. We have used a low energy, low capital approach to P removal by employing two 400 litre gravity settled batch reactors. Lagoon supernatant with total phosphate (TP) concentration of 190 mg/l and pH of 6.7 was adjusted to pH 8.5 and allowed to settle with no addition of magnesium chloride. Results show TP was reduced by 70%, total suspended solids by half, and soluble P was reduced by 90% (94.5 to 10.3 mg/L). Particulate mineral forms of P were removed from the liquid (reduction from 83 to 26 mg/L), perhaps by flocculation. The dried precipitate had a TP concentration of 5.6%, total nitrogen of 6.3%, and potassium of 3.8%. Struvite content in the dried sludge was estimated at 30% and calcium phosphates comprised the remainder of the mineral P compounds. Half of the precipitate was estimated to be organic solids. These results indicate nutrient rich supernatants with high SS are good targets for P recovery but product purity is a challenge.

Keywords: Phosphorus, manure, struvite, nutrient recovery.

INTRODUCTION In Manitoba, Canada, the majority of swine waste is stored in open lagoons and land applied according to crop nitrogen requirements. Because swine manure has a low plant available N/P ratio, this practice over-applies phosphorus 2 to 5 fold, leading to runoff and a loss of nutrients to the environment, and contributing to eutrophication of surface waters. Reclaiming this wasted phosphate as struvite ($MgNH_4PO_4$) would ease environmental concerns, provide economic resources as saleable fertilizer containing two macronutrients, and help address the limited global

supply of phosphate. Several researchers have targeted hog lagoons for struvite precipitation (Burns et al. 2003; Bowers and Westerman 2005; Laridi et al. 2005; Suzuki et al. 2007) leading to pilot scale struvite reactors. The most successful of these reactors used hog waste supernatant low in total solids (TS) and total suspended solids (TSS) to produce high purity struvite. This was accomplished by upstream processes that settled TSS in an anaerobic covered lagoon (Bowers and Westerman 2005); digested TSS in a trickling filter (Laridi et al. 2005; Buelna et al. 2008); or used a suspended metal surface for struvite crystallization (Suzuki et al. 2006). No researcher has studied calcium (Ca) as an important factor in the viability of using hog wastes to make struvite, although it has been determined as an inhibitor in wastewater supernatants (Moerman et al. 2009) and in synthetic supernatant studies (Le Corre et al. 2005). Many hog farms use ground water high in Ca and have no upstream process to reduce TSS from supernatant. Before P can be reclaimed from these kinds of farms at an economical scale, it must be determined if supernatants high in TSS and Ca can produce fertilizer precipitate of high purity and value.

Struvite formation readily occurs under conditions where soluble magnesium (Mg), ammonium (NH_4) and phosphate (PO_4) reach super saturation. Solubility decreases as pH increases, forming struvite crystals that can increase in size by crystal growth (Britton et al. 2005) or by agglomeration (Le Corre et al. 2007) and settle out of solution. Most pilot reactors use upflow fluidized bed configurations but these are capital and operationally intensive, increasing the cost of P removal. In theory, a nutrient rich supernatant in a simple batch reactor needs only alkali pH adjustment and adequate settling time for a low energy, low capital, reactor system.

High concentrations of Ca have been reported to compete with Mg and form calcium phosphates (Le Corre et al. 2005) lengthening crystal induction time and growth rate of struvite. Calcium phosphates are a group of compounds with varying Ksp values and formation kinetics (Valsami-Jones 2001) and include $Ca_3(PO_4)_2$, $Ca(HPO_4)_2$, $CaHPO_4$, and others. As a precipitate, it has less value as a fertilizer when compared with struvite because the lack of NH_4. Using synthetic supernatant Le Corre et al. (2005) found Mg:Ca ratios below 2:1 inhibited struvite purity and at 1:1 and lower, produced only amorphous calcium phosphate and no struvite at all. Particle size analysis and XRD showed struvite crystals in the range of 13.4 to 15.1 µm formed with no Ca present, while particles of 2.7, 3.1, and 4.5 µm sizes formed at Mg:Ca ratios of 2:1, 1:1 and 1:2 respectively. Since standard TSS measurement records all particles larger than 10 µm, the presence of Ca may produce particles that are not recorded as TSS and would be lost to effluent in most upflow struvite reactors. P-PO_4 measurement is defined by all reactive P passing through a 0.45 µm filter. Calcium phosphate particles would escape detection either as TSS or P-PO_4. Similar Ca effects were found in a commercial struvite reactor processing anaerobically digested potato waste water. Ca:P ratios of 2.69 resulted in 70-75% P-PO_4 reduction, but no struvite was produced and a flocculent matter was evident (Moerman et al. 2009). Struvite formed again when the ratio was established at 1.36 as a result of increases in P concentration in the influent feed. Reduction in P-PO_4 may have been related to the formation of calcium phosphates that were lost to the effluent. No Mg data was collected in this study.

Struvite reactors using hog manure supernatant report varying degrees of P removal efficiency (Table 1) and unfortunately, incomplete data collection restricts full

comparisons between studies. The most efficient reactors use supernatant low in TS and a high proportion of TP as P-PO$_4$. It may be noted that high P-PO$_4$ removal is not always reflected in TP removal. This may be from loss of P-PO$_4$ resulting from calcium phosphate formation but subsequent loss of the particles to effluent. Identification of these particulate mineral forms of P would help in identification of appropriate supernatants for efficient P removal and to improve reactor design.

Table 1. Pilot scale struvite reactors using hog manure and potato wastes. Initial and final adjusted pH is noted as pH$_i$ and pH$_f$. Data not collected is denoted as NA.

Author	Reactor volume (L)	Liquor	% TS	TP	P-PO$_4$	Mg	NH$_4$	Ca	pH$_i$ pH$_f$	% TP removal	% PO$_4$ removal
(Bowers and Westerman 2005)	40?	Hog	0.5	88	41	NA	NA	NA	7.7 8.2	59-70	61-82
(Shepherd et al. 2009)	3785	Hog[DP]	2.2	800	22	NA	3200	NA	7.83 7.93	9-14	14-91
(Shepherd et al. 2009)	3785	Hog[C]	2.1	420	130	NA	NA	NA	7.04 7.3	18	92
(Laridi et al. 2005)	15	Hog* manure	1.1	NA	159	362	2282	260	6.3 8.5	NA	90
(Suzuki et al. 2007)	3720	Hog	0.4	138	70	46	532	80	7.4 8.0	73	63
(Moerman et al. 2009)	200	Potato [AD]	NA	64	60	NA	110	140	7.1 8.5	78	85

[DP] Deep Pit storage, not agitated before extraction

[C] Concrete storage, agitated before extraction

*Manure was flocculated, then run through peat trickle filter to lower TSS

[AD] Anaerobically digested potato wastes

Implementing economical P removal at farms requires use of existing infrastructure without additional processes. High strength supernatants with high TSS and dissolved solids may keep struvite crystals and calcium phosphate in suspension even after they have precipitated. For phosphorus reclamation to be adopted on a wide scale the process of precipitation must be simple and inexpensive, so that common farmers can operate the equipment with a minimum of capital expenditure. This study takes a low capital, low energy input approach to precipitation of phosphorus from lagoon supernatant and uses a gravity settling system that removes the majority of TP and produces a nutrient rich sludge that can be processed into a dry fertilizer. The focus was on the function of the system and the precipitated product in terms of nutrient content and struvite purity.

METHODS A commercial feeder barn in southern Manitoba using a primary and secondary lagoon system was selected to install the struvite precipitation reactor system. Two 410 litre cone bottomed plastic tanks equipped with two-way drain valves were installed adjacent to a full scale primary lagoon. Tanks were filled from the top with a hand operated diaphragm pump, dosed with KOH (45%) to reach pH 8.5 and allowed to settle for 24 hrs. Settled precipitate sludge was drained into separate containers and the remainder of the effluent was released to the secondary storage (Fig. 1). It was found that an additional 24 hr. settling would further stratify the thicker grey sludge layer. The collected sludge was stored in the lab at 4° C and later dried in the sun in flat shallow trays and then pulverized in a ball bearing mill to produce the final product.
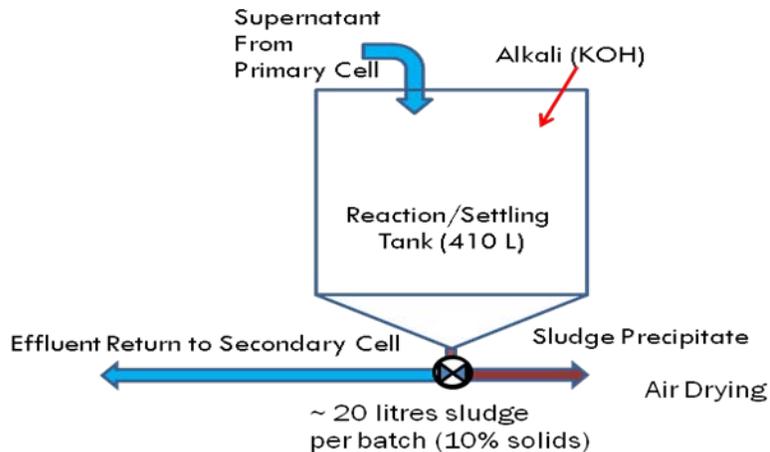

Fig. 1. A schematic drawing of the gravity settling batch reactor. The tank is filled with lagoon supernatant, dosed with KOH to pH 8.5 and allowed to settle for 24 hrs. A two way valve allowed precipitate to be collected and effluent to be released to the secondary lagoon. Collected precipitate was dried and milled to a powder.

Samples of influent and effluent were measured for TS, TSS and alkalinity according to Standard Methods (Clesceri et al. 1998). Nutrients were measured as follows: P-PO$_4$ with ascorbic acid method on an Ultrospec 4300Pro and elemental Mg, Ca, K, and P by Varian 700 ICP-OES. Nutrient forms were determined by nutrient analysis of filtered (0.45 µm membrane filter), unfiltered and digested supernatant. Digestion of samples was conducted in a Hach Digesdahl using concentrated H$_2$SO$_4$ and hydrogen peroxide (50%). Using TP from digested samples, unfiltered samples diluted in weak acid (0.5% HNO$_3$) to dissolve mineral particulate P, P-PO$_4$ analysis from filtered (0.45 µm filter), and ICP determination of total dissolved P, a determination of soluble reactive, soluble organic, particulate mineral and particulate organic forms of P was possible. This method also enabled quantification of particulate and soluble forms of Ca and Mg.

Three representative samples of the dried precipitate were mixed and further ground in a mortar and pestle. Total digestion of triplicate 0.5 gram portions was conducted as described above. To dissolve all struvite and calcium phosphates, 1 gram portions of dried sludge were added to a weak HNO$_3$ solution and adjusted several times over 24 hrs to a final pH of 1.5. These solutions were analyzed for Mg, Ca, P, and K. Ammonium was determined on a LaChat QuikChem 8500 flow injection analyzer. Organic carbon in the sludge was removed by loss on ignition at 550° C for 2 hrs using replicate 10 g

samples. Analysis of crystalline mineral forms in the precipitate was conducted using X ray diffraction (XRD) on a Phillips PW 1710.

RESULTS Lagoon nutrient levels fluctuated considerably over time. Fall and spring sampling revealed significant changes, as did sampling from mid and late summer (Fig. 2). A 4 week period elapsed between two reactor operation events in July and August 2009. During this time, concentrations of P, Mg and Ca in unfiltered reactor influent increased by 281, 278 and 299 percent. Reactor performance was essentially unchanged however, removing 79 vs 82 % of P, 68 vs 67% Mg and 31 vs 35% Ca in unfiltered samples, respectively. Replicate samples were from consecutive batches of influent (n=3 in July and n=4 in August) and effluent samples (n=6 July and n=4 in August).
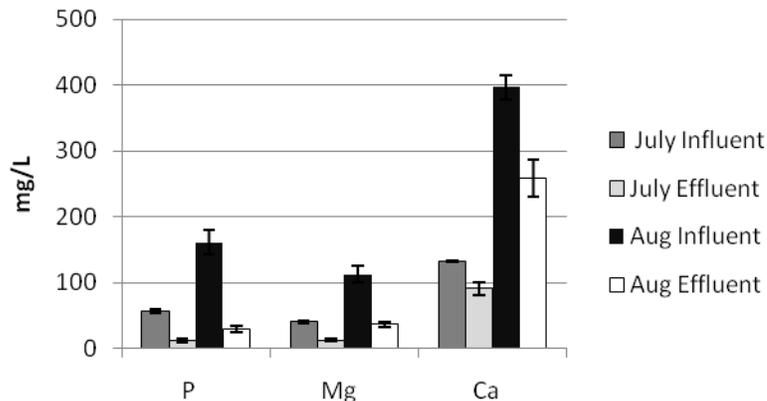

Fig. 2 Reactor performance with supernatant of different nutrient concentrations. Over a 4 week period nutrients in unfiltered influent samples increased by 280, 278 and 300% for P, Mg and Ca. Dosing with KOH to pH 8.5 reduced effluent concentrations of the nutrients by similar percentages.

A possible cause of the summer nutrient increase was a floating straw cover placed over the lagoon by the farmer to reduce odours. Small daily changes in nutrient content appeared to correspond with the extent of straw cover at the reactor intake pump. Straw moved in the lagoon according to wind direction.Reactor operation removed the majority of supernatant P at the lower and higher P levels, reducing TP by 70% in digested samples (Table 2) and P by 80% in unfiltered samples.

Table 2. Nutrient removal in the struvite reactor as determined by total digestion of influent and effluent (n=3).

	TP (mg/L)	Mg (mg/L)	Ca (mg/L)
Influent	216 ±4	142 ±3	467±21
Effluent	63.6 ± 12.3	48.3±8.6	335±117
% reduction	70	66	28
Removed nutrients (mM)	4.9	3.9	3.3

The use of three different sampling methods (total digestion, unfiltered and filtered) enabled differentiation of the P forms present in supernatant of a limited number of batch samples. Precipitation reduced all forms to some extent but the greatest reduction was found in the dissolved P and mineral particulate forms (Table 3).

Table 3. Phosphorus forms present in reactor influent and effluent.

	Influent (mg/L)	Effluent (mg/L)
Dissolved reactive P	95	8
Dissolved organic P	9	3
Particulate mineral P	83	26
Particulate organic P	30	26
Total P	216	64

The majority of P-PO$_4$ and mineral particulate P was removed in the reactor, whereas particulate organic P remained almost the same during the process. This is similar to the forms of Ca present in supernatant revealed by the same sampling process (Fig. 3). In the case of Ca, a decrease in the soluble form was countered by an increase in particulate mineral forms.
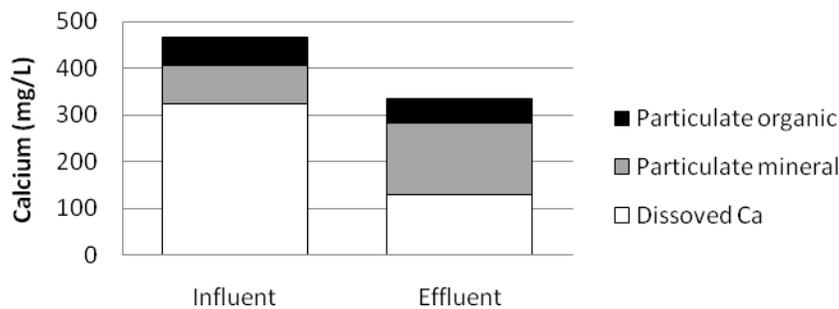

Fig. 3 Forms of calcium present in reactor influent and effluent.

Total suspended solids were reduced by reactor operation. Typical influent TSS was 4.9 ± 0.4 g/L and effluent was 2.17 ± 0.53 (N=3). Inorganic solids remained about the same (0.6 g/L) in both influent and effluent, indicating the loss to the precipitate fraction was mostly organic solids.

Supernatant total solids increased from influent to effluent from 18.05 ± 1.7 to 22.47 ± 3.2 g/L (Fig. 4). Sampling was taken from the top of the reactor before alkali dosing, and again after 24 hours of settling. Samples were the average of 3 influent and 3 effluent batches. An increase in inorganic solids also occurred in effluent as determined from loss on ignition of dried solids at $550°$ C (Fig. 4).
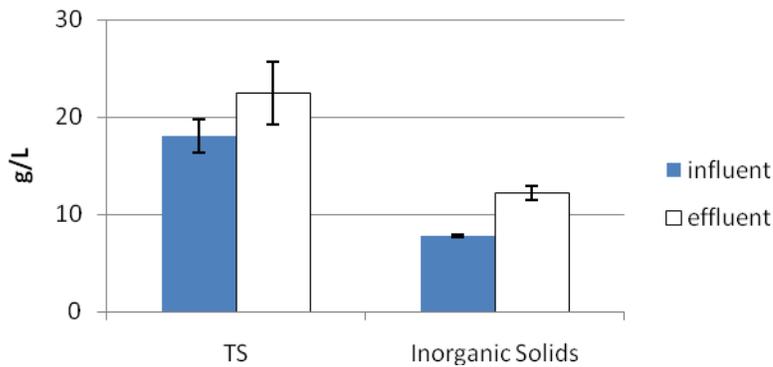
Fig. 4. Total solids and inorganic solids contained in reactor supernatant. Inorganic solids are solids remaining after volatile solids are lost during heating to 550° C for 2 hrs.

Analysis of the air dried precipitate showed mass loss was 65.9% ±0.14 (N=6) by ignition at 550° C. There is difficulty in assessing organic carbon loss because mass is also lost from hydrates and other volatiles such as ammonia. For example, if all water molecules and NH_4 of pure struvite ($MgNH_4PO_4 \cdot 6 H_2O$) are volatilized at 550° C, mass would be reduced by 48.6%. If struvite content could be estimated, carbon determination would be easier. XRD analysis detected presence of struvite and sylvite (KCl), but is not quantitative.

Elemental analysis of dried precipitate showed concentrations of K, P and N to range from 3.8 to 6.3 % (Table 4). Determining the content of pure struvite formed in the reactor is difficult and can only be approximated by measuring the content of struvite constituents. To accomplish this, precipitate was mixed with distilled water and the pH adjusted with HNO_3 and allowed to equilibrate at pH 1.5 for 24 hrs. This allowed mineral particulates to dissolve into solution. When comparing results to nutrients measured by total digestion, all Mg dissolved at pH 1.5, suggesting no Mg was associated with organic particulate forms, as in the case of P and NH_4. For these reasons Mg was taken as the indicator of struvite and total struvite content was calculated according the Mg concentration. Other mineral Mg compounds may be present in the precipitate, but were not found using XRD analysis indicating an absence of crystalline Mg minerals.

Table 4. Elemental analysis of air dried reactor precipitate. Values are given as a percentage of total mass and the percentage soluble at pH 1.5. Maximum possible struvite content is estimated as the mole fraction of the least abundant soluble struvite constituent. Struvite molar wt is 244 g/mole.

	P	Mg	Ca	TN	K	Na
% total digestion	5.6 ± 0.08	3.3 ± 0.05	4.2 ± 0.34 %	6.3 ± 0.19	3.8 ± 0.04	1.5 ± 0.02
% soluble at pH 1.5	4.5 ± 0.12	3.3 ± 0.13	3.9 ± 0.15	2.5 ± 0.08	3.4 ± 0.03	1.3 ± 0.01
Moles in 100 g of ppt	0.146	0.135	0.098	0.178		
Possible struvite (g) in 100g ppt	35.6	33.1		43.4		

DISCUSSION A variance was found in nutrient concentration of lagoon supernatant over time but the proportion of P removed from precipitation remained similar. The diet and age of the pigs producing the waste was not considered in this study but differences in manure nutrient content does change with pig age (Westerman and Arogo Ogejo 2006). High P levels in the latter half of the summer may have been due to the straw cover, producing anaerobic conditions and increased gas production from the solids on the lagoon bottom. Bubbling gasses are likely responsible for bringing high nutrient solids to the surface and changing the nutrient content in the surface supernatant. Even though TP content fluctuated by almost 300% between the two sampling periods, the percentage of P removed was almost identical.

Precipitation within the reactor removed most of the P-PO_4 in the supernatant (92%) and additionally, 68% of the mineral particulate P settled out of suspension. It is possible that mineral particles settled by flocculation along with newly formed precipitate or by organic solid settling. A common assumption is that only P-PO_4 can be removed from supernatant because it can precipitate, but this data indicates other processes play an important role in P removal.

 Identification of precipitate compounds is difficult, but can be inferred by the molar mass of removed nutrients (Table 2). If only struvite were produced, equal molar mass removal of P and Mg would be evident. However, P was removed from supernatant in excess of Mg by one mM/L, indicating other phosphorus compounds were produced, the most likely being calcium phosphates. The suite of calcium phosphates do not have a specific Ca:P molar ratio but an approximate ratio of 1.5 can be assumed (Valsami-Jones 2001). Formation of calcium phosphates creates a floc that is difficult to settle in a reactor due to its small particle size. Calcium phosphate floc formation may account for the anomaly in the lower TSS and yet higher TS of reactor effluent. The TSS filter size is 10 µm, allowing most newly formed floc to pass through, yet organic solids have already settled with larger precipitate particles yielding a lower effluent TSS while maintaining small

mineral particulates in suspension. Higher TS in reactor effluent than influent, even with loss of organic carbon and struvite may be from an inverse stratification of lighter particles, such as calcium phosphate floc and calcium carbonate. An increase in particulate calcium forms in effluent can be seen in the calcium form chart (Fig. 3), adding evidence to this theory.

Struvite and calcium phosphate precipitate in very different forms, affecting their ability to settle and be removed from the supernatant. Struvite forms a crystal that increases in size from agglomeration or crystal growth, potentially forming large particles (50 to 500 μm are common depending on the reactor configuration). Calcium phosphates precipitate as floc, a fractal structure of low density and extreme fragility. Flocs easily break apart and settle very slowly, if at all. Preliminary laboratory work with high calcium lagoon supernatants showed increased settling of precipitate with reduced mixing time. Maximum settling was found with zero mixing time whereas 10 minutes of mixing produced no settled precipitate at all in 4 hrs. This suggests mixing destroys the floc structure and the floc particles do not settle out. Other researchers have noted similar problems when the Ca:P ratio was 2.67 (Moerman et al. 2009) or the Mg:Ca ratio less than 1 (Le Corre et al. 2005). In this experiment, the dissolved Ca:P ratio was 3.42 and Mg:Ca ratio 0.4, suggesting Ca is too high to effectively produce struvite.

Composition of the precipitate sludge was deduced to be no higher than 33% struvite if all Mg soluble at pH 1.5 is from struvite. There may be quantities of other Mg precipitates that are also present and soluble at pH 1.5, but no evidence of these were found with XRD analysis. Determining organic carbon content requires an assumption that loss on ignition removed all carbon and mass loss of volatile hydrates and NH_4 was only from struvite. Theoretical mass loss of 33 g (the assumed struvite content in 100g of precipitate) of struvite from heating to 550° C would leave 16 g of inorganic solids and remove 17 g of volatiles. Total solids without struvite volatile loss would then be 51 g per 100 g of precipitate, yielding 49 g of organic solids. So assuming no other hydrated or volatile species, about half of the dried sludge was organic carbon. When comparing the nutrient analysis with that of pure struvite, the precipitate contains 5.6 vs 12.7% P, 6.3 vs 5.7% N and 3.8 vs 0% K. The precipitate N content was not impaired due to calcium phosphate precipitation but was probably high due to the high organic solids content. Table 3 shows 60% of NH_4 in the dry precipitate was not soluble at pH 1.5 and thus is assumed to be related to the organic fraction. The use of KOH instead of NaOH had a favourable effect on total K content of the final product.

CONCLUSION The gravity settling batch reactor removed 70% of TP with a 24 hr settling period. P was removed by precipitate formation as well as other settling processes. The settled sludge was difficult to dry and unpleasant to work with, due to the high (~50%) organic solids content. The struvite purity was estimated to be 33% assuming all of the Mg content was attributable to struvite crystals. As far as total nutrient content is concerned, the precipitate contains 5.6% P, 6.3% N and 3.8% K. Pure struvite would have 12.7 % P, 5.7% N and 0% K. High Ca concentration in the supernatant did not impair the N content of the product and the use of KOH as an alkali contributed favourably to the value as a fertilizer.

REFERENCES

Bowers, K. E. and P. W. Westerman (2005). Performance of cone-shaped fluidized bed struvite crystallizers in removing phosphorus from wastewater. *Transactions of the Asae* 48(3): 1227-1234.

Britton, A., F. A. Koch, D. S. Mavinic, A. Adnan, W. K. Oldham and B. Udala (2005). Pilot-scale struvite recovery from anaerobic digester supernatant at an enhanced biological phosphorus removal wastewater treatment plant. *Journal of Environmental Engineering and Science* 4(4): 265-277.

Buelna, G., R. Dube and N. Turgeon (2008). Pig manure treatment by organic bed biofiltration. *Desalination* 231(1-3): 297-304.

Burns, R. T., L. B. Moody, I. Celen and J. R. Buchanan (2003). Optimization of phosphorus precipitation from swine manure slurries to enhance recovery. *Water Science and Technology* 48(1): 139-146.

Clesceri, L. S., A. E. Greenberg and A. D. Eaton, Eds. (1998). Standard Methods for the Examination of Water and Wastewater. Washington D.C., American Public Health Assn., American Water Works Assn., Water Environment Federation.

Laridi, R., J. C. Auclair and H. Benmoussa (2005). Laboratory and pilot-scale phosphate and ammonium removal by controlled struvite precipitation following coagulation and flocculation of swine wastewater. *Environmental Technology* 26(5): 525-536.

Le Corre, K. S., E. Valsami-Jones, P. Hobbs, B. Jefferson and S. A. Parsons (2007). Agglomeration of struvite crystals. *Water Research* 41(2): 419-425.

Le Corre, K. S., E. Valsami-Jones, P. Hobbs and S. A. Parsons (2005). Impact of calcium on struvite crystal size, shape and purity. *Journal of Crystal Growth* 283(3-4): 514-522.

Moerman, W., M. Carballa, A. Vandekerckhove, D. Derycke and W. Verstraete (2009). Phosphate removal in agro-industry: Pilot- and full-scale operational considerations of struvite crystallization. *Water Research* 43(7): 1887-1892.

Shepherd, T. A., R. T. Burns, D. R. Raman, L. B. Moody and K. J. Stalder (2009). Performance of a pilot-scale air sparged continuous flow reactor and hydrocyclone for struvite precipitation and removal from liquid swine manure. *Applied Engineering in Agriculture* 25(2): 257-267.

Suzuki, K., Y. Tanaka, K. Kuroda, D. Hanajima, Y. Fukumoto and T. Yasuda (2006). The technology of phosphorus removal and recovery from swine wastewater by struvite crystallization reaction. *JARQ* 40(4): 341-349.

Suzuki, K., Y. Tanaka, K. Kuroda, D. Hanajima, Y. Fukumoto, T. Yasuda and M. Waki (2007). Removal and recovery of phosphorous from swine wastewater by demonstration crystallization reactor and struvite accumulation device. *Bioresource Technology* 98(8): 1573-1578.

Valsami-Jones, E. (2001). Mineralogical controls on phosphorus recovery from wastewaters. *Mineralogical Magazine* 65(5): 611-620.

Westerman, P. W. and J. Arogo Ogejo (2006). Swine anaerobic lagoon nutrient concentration variation with season, lagoon level, and rainfall. 2006 ASABE Annual International Meeting. Portland Oregon, ASABE.