

## Phosphorous Recovery Technology in Conjunction with Dairy Anaerobic Digestion

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### Introduction

Phosphorous (P) is a non-renewable resource and an important non-substitutable macronutrient, which exists in nature as phosphates in various inorganic or organic forms. Agriculture, through its reliance on inorganic fertilizers, is the primary user of commercially-produced P, and there is concern that current exploitation is unsustainable. Total annual global production is currently 20 million tons of P, derived from approximately 140 million tons of rock concentrates (IFA, 2002; Rockstrom et al., 2009). Nearly all the P used globally is mined from a relatively small number of commercially-exploitable deposits, and it has been estimated that the global economic P reserves may last only about 100 years at the current rate of extraction (Driver et al, 1999).

More efficient agricultural use of P, and recycling of existing P resources, has been suggested as possible solutions to unsustainable P-mining practices. Animal manure represents a potentially important source of recycled P, with as-excreted dairy manure typically yielding 0.16 lbs P/cow day (Nennich, 2004). As noted in earlier chapters, anaerobic digestion (AD) technology is notable in its ability to produce saleable biogas while stabilizing organic solids, removing pathogens and mitigating methane emissions on farms. Unfortunately, the AD process does not remove any nutrients during the waste transformation process, so the digested effluent still has a high P concentration (Sung and Santha, 2003; Zhang et al., 2000). Ideally, the excess P in the effluent would be recovered before the effluent is stored or spread on fields. This would recycle P, reduce environmental concerns about water quality, eutrophication, excess P-loading, and improve dairy economics through a saleable P fertilizer.

Characterization of the form of P in dairy manure, and in particular digested dairy manure, is an important first step for determining appropriate P-extraction and recovery technologies. He et al. (2004) characterized P from dairy manures representing a range of bedding options and storage strategies, into inorganic, organic, phospholipid and extracted fractions. They found that the largest portion of total P (TP) was in the water-extractable fraction, with an inorganic P content of 12-44% and an organic P content of 2-23%. Importantly, the majority of the inorganic P was particulate-bound (Gerritse and Vriesema, 1984; Zhang et al., 2008). Several other studies on P extraction show that the particulates are predominantly Ca-P and/or Mg-P (Chapuis-Lardy et al., 2004; Dou et al., 2000; Gungor and Karthikeyan, 2005; Gungor and Karthikeyan, 2005; Kleinman et al., 2002; Zhang et al., 2008; Zhang et al., Submitted) that result from the high Ca:P molar ratio (1.66-2.43) of a dairy cow's diet (Gungor and Karthikeyan, 2008). Recently, Gungör and Karthikeyan (2008) evaluated P dynamics during AD of dairy manure to determine P speciation

and phase distribution in both the influent and effluent. They reported that total dissolved P constituted about 12% and 7% of TP in the influent and effluent, respectively. Through inference then, the majority of phosphate ions ( $\text{PO}_4^{3-}$ ) in digested dairy effluent are sequestered in finely-suspended, intractable calcium-phosphate solids, and effectively unavailable for many current recovery methods.

Based on this previous research, the purpose of the P research component of the CFF dairy component was to advance the basic understanding of phosphorous in digested dairy manure and subsequently develop and evaluate a new generation of P-removal technologies that could be economically applied to dairy farms with ADs. Importantly, manures are not homogeneous, with dairy manure varying in important physicochemical characteristics depending upon animal diet, farm location, and manure handling and digester systems utilized. As a result, a matrix of potential P recovery technologies is preferred, with particular options within the matrix applicable to specific manure and farm conditions. Processes and technologies devised and studied during this project include:

- Struvite Crystallization
- Polymer/Coagulant Dosing with Belt Press
- Decanting Centrifuge with or without Polymer Dosing
- Aeration/lime Settling
- Electro-coagulation Settling

Each of the above studied processes is discussed individually in the described order. Projected capabilities and comparisons of all methods, along with potential greenhouse gas impacts, are discussed in a concluding section.

## **Struvite Crystallization**

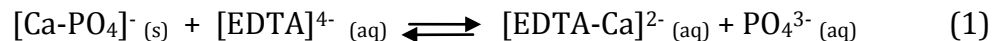
### *Background*

An emerging commercially-viable P removal and recovery process is crystallization in the form of struvite (magnesium ammonium phosphate hexahydrate or  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) (Battistoni et al., 2001; Battistoni et al., 1997; Battistoni et al., 2006; Burns et al., 2001; Jeong and Hwang, 2005; Liberti et al., 1986; Wrigley et al., 1992). Struvite formation requires that three soluble ions in the wastewater solution,  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$ , react to form precipitates with low solubility (pKsp of 12.6). The resulting struvite product can be marketed as a slow release fertilizer and its crystalline structure formation is well suited to be produced in a crystallizer. Different types of crystallization reactors have been tested, including a mechanically stirred reactor (Pastor et al., 2008; Stratful et al., 2004; Yoshino et al., 2003), a gas agitated fluidized bed reactor (Bowers and Westerman, 2005; Bowers and Westerman, 2005; Jaffer et al., 2002; Le Corre et al., 2007), and a water agitated fluidized bed reactor (Adnan et al., 2003; Battistoni et al., 2001).

Several factors can affect struvite precipitation, such as pH, super-saturation of the three ions in the solution, and the presence of impurities (e.g., calcium) (Doyle and Parsons, 2002; Nelson et al., 2003). For instance, higher pH (e.g., pH 8.5) is favorable to struvite formation (Doyle and Parsons, 2002) while calcium impurities, such as those present in synthesized wastewater, can negatively impact struvite formation because calcium-phosphorus precipitates can also be formed (Le Corre et al., 2005).

Although struvite precipitation has not been proven effective in digested dairy wastewater, others have studied the process using similar materials. P recovery using a struvite crystallization process has been successfully demonstrated in lab, pilot, and full scale models using swine wastewater (Adnan et al., 2003; Bowers and Westerman, 2005; Bowers and Westerman, 2005; Suzuki et al., 2005), with high TP removal (~80%) in full-scale tests (Bowers and Westerman, 2005). Unfortunately, WSU research has shown that application of struvite technology to dairy manure is not nearly as effective with a cone-shaped fluidized-bed reactor yielding less than 15% TP removal (Harris et al., 2008). The majority of the manure P used in their study was verified by X-ray diffraction (XRD), scanning electron microscopy, and elemental analysis, as being in the form of calcium phosphate, not struvite. These results suggested that struvite formation was inhibited by the calcium bond that Le Corre et al. (2005) predicted.

One logical hypothesis is that struvite fertilizer could still be produced with the digested dairy wastewater if the Ca-P suspended solids could be converted to dissolved-phosphate ions that become available for struvite formation. This in theory can be accomplished by adding a chelating agent, such as ethylenediaminetetraacetic acid (EDTA). EDTA could sequester calcium because EDTA has a high stability constant for chelating calcium, with a  $[EDTA-Ca]^{2-}$  of  $10^{10.7}$  (Martell and Hancock, 1996). If calcium were present in the solid form of  $[Ca-PO_4]^-$ , EDTA added into the solution would react with the calcium, creating  $[EDTA-Ca]^{2-}$  and  $PO_4^{3-}$ . The release of P can be predicted according to Equation 1 below.



In our work on struvite crystallization, we tested the hypothesis that P could be released into solution as reactive phosphate ions, enabling struvite precipitation from dairy effluent. Several different methods, including acidification and sequestering calcium with a chelating agent were tested for their efficacy in liberating P from calcium-phosphate solids. Based on the results of these tests, an improved process for P recovery through struvite crystallization from digested dairy effluent was proposed and tested at a pilot-scale reactor. In addition, the solid product obtained after P liberation and struvite precipitation was analyzed using X-ray diffraction (XRD), confirming struvite phase structure.

## *Materials and Methods*

### Dairy Effluent and Prepared Treatments

AD dairy effluent from an axial-mixed plug-flow, mesophilic digester (GHD Inc., Chilton, WI) operated on a Washington State scrape dairy was mechanically screened (0.3 cm) for fibrous solids (US Farms, Tulare, CA) and then collected and stored for use in this project. Two treatments were performed to liberate P in the dairy effluent, acidification and EDTA addition.

- *Acidification* aimed at negating the interfering effect of calcium, by protonating the phosphate ions, thus breaking up the solid calcium phosphate and dissolving the P into the solution as soluble phosphate ions. Concentrated HCl (36.5-38.0%) was added to the effluent samples to depress the pH to various targeted degrees, from its original pH 7.8 to 3.8. The reaction was allowed to continue with stirring for one hour, after which samples were centrifuged at 10,000 rpm for 10 minutes. It was noted that acidification typically dissolved inorganic P into solution. Although the majority of TP is in inorganic P form, the specific P speciation present in dairy effluent was not clear. Güngör and Karthikeyan (2008) have suggested that dicalcium phosphate dihydrate (DCPD,  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ), dicalcium phosphate anhydrous (DCPA,  $\text{CaHPO}_4$ ), octacalcium phosphate (OCP,  $\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 3\text{H}_2\text{O}$ ), newberyite ( $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ ), and struvite are probable solid phases in the AD digester effluent.
- *EDTA addition* sought to sequester calcium from the Ca-P solids. EDTA, with final concentrations from 0-70 mmol/L, was added to the effluent samples. Samples were mixed at about 120 rpm for 1 hour on a shaker to ensure complete reaction between EDTA and calcium-phosphorous, and then centrifuged at 10,000 rpm for 10 min. Later, the pH in the effluent was increased to 8.5 to encourage formation of phosphate solids and then centrifuged again prior to analysis. In order to evaluate the effect of the treatment, the concentrations of TDP, DRP, calcium, and magnesium in the supernatants were determined.

### Struvite Formation

It was anticipated that at high EDTA levels, magnesium would also be tied up and unable to contribute to precipitating the P as struvite. Thus, magnesium chloride at different levels from 0-155.4 mmol/L was added to increase the  $\text{Mg}^{2+}$  ion molarity at two EDTA levels of 40 and 70 mmol/L. The TDP concentrations in the solutions were analyzed after centrifugation. The resulting concentrations of TDP in solution decreased significantly after precipitation of struvite enabled by excess  $\text{Mg}^{2+}$  ions. In order to verify struvite formation, the precipitated solid was collected after centrifugation and subjected to X-ray diffraction (XRD) analysis for phase structure. In addition, the composition of the solid was determined according to the contents of  $\text{PO}_4^{3-}$ ,  $\text{NH}_4^+$ , magnesium and calcium, according to the analytical methods described below.

### Pilot Study for Struvite Crystallization

Struvite formation was further investigated at the pilot-scale using a cone-shaped fluidized bed struvite crystallizer (Bowers and Westerman, 2005; Bowers and Westerman, 2005) previously developed for reducing P content of swine wastewater. The system achieves a fast reaction and produces a desirable, granular product by keeping both the small and the large particles well-fluidized in the reaction zone. For swine lagoon wastewater, the crystallizers were operated at residence times ranging from 4.8 minutes down to as low as 1.2 minutes at the lab scale and in a field-scale test system at a research swine farm. Removal of TP reached 65% in the lab tests and 82% in the field test (Bowers and Westerman, 2005; Bowers and Westerman, 2005).

Based on the swine wastewater system, the CFF pilot-scale dairy system used a main crystallizer cone that was 2.3 m in height and 0.46 m in diameter at the top. Pretreatment with acids, EDTA, caustic soda and/or ammonia was done in either three 1,235 L tanks or one 5,700 L plastic tank, metered for the appropriate dosages with peristaltic pumps and stirred with clamp-on agitators. Struvite material, screened to include only particles between #8 and #24 standard sieve size, was loaded into the cone to serve as the initial bed material. The flow rate of the cone was between 1.7-2.1 liters/minute. The struvite bed granules grew as the system operated and were periodically harvested by opening a valve at the bottom of the cone.

### Analytical Methods

Standard Methods for the Examination of Water and Wastewater Analytical methods were used to determine TDP (P mmol/L as  $\text{PO}_4\text{-P}$ ), DRP (P mmol/L as  $\text{PO}_4\text{-P}$ ), TP (P mmol/L as  $\text{PO}_4\text{-P}$ ), ammonia nitrogen (N mmol/L as  $\text{NH}_4\text{-N}$ ) and pH (APHA, 2005). The concentrations of calcium and magnesium were measured using the atomic absorption method with air-acetylene flame on a Spectrometer (Varian 220, USA). Before the analysis of calcium and magnesium, concentrated HCl was added to the samples to adjust the pH to 1.0-2.0. This adjustment should have solubilized calcium and magnesium into solution if they were present in a particulate form. XRD analysis was run on an X-Ray Powder Diffractometer (Siemens D500). Operation conditions were 35kV and 30mA with CuK $\alpha$  radiation. Samples were scanned from  $10^\circ$  to  $70^\circ$  (2-theta) with 0.02 degrees and 1.5 sec per step.

### *Results and Discussion*

#### Liberation of P by Acidification

Figure 7.1 presents the results of the acidification to dissolve P and  $\text{Ca}^{2+}$  ions in solution. As shown in the figure, concentrations of  $\text{Ca}^{2+}$ , TDP, and DPR increased significantly as pH decreased due to acid addition; evidence that the acid indeed released P and  $\text{Ca}^{2+}$  into the solution. These results demonstrate that more P was

placed into solution as pH decreased and confirm that the majority of P was in a suspended solid form in the original dairy manure effluent.

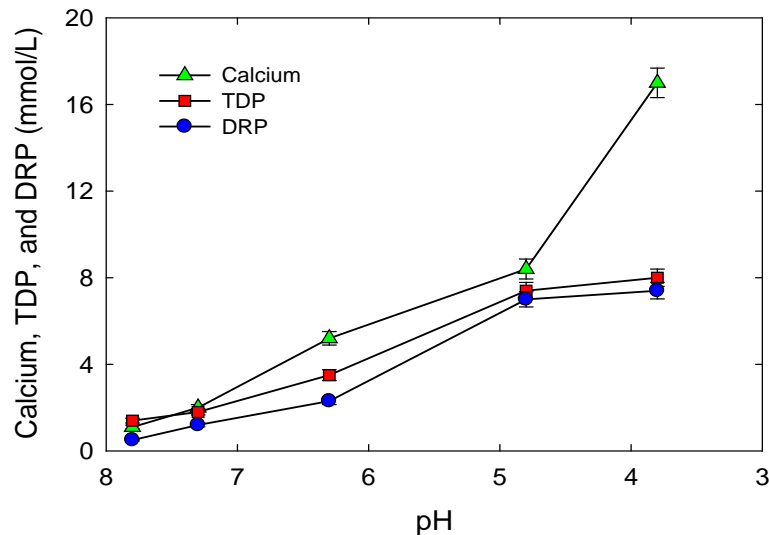


Figure 7.1: Concentrations of calcium, TDP, and DRP in the supernatant after acidification

As the pH of the low pH solution was raised back to the original pH of 7.8, the P that was present in phosphate ions in the low pH solution could either form struvite or return back to calcium-phosphate particles. In essence, the equilibrium of the probable Ca-P species competes with that of struvite for released phosphate ions. If the calcium content is so high that the equilibrium moves toward the Ca-P compounds, Ca-P solids would be formed. On the other hand, struvite is formed if high concentrations of the constituent ions necessary for struvite ( $\text{NH}_4^+$  and  $\text{Mg}^{2+}$ ) are present in the solution, as well as crystal seeds that would support spontaneous formation of new particles.

Several modeling studies (Gungor and Karthikeyan, 2008; Musvoto et al., 2000) have predicted the probable P phase within AD dairy manure as being struvite, but their studies were performed at relatively low calcium ion concentrations, much lower than the concentrations seen in this particular manure stream. Although manure characteristics (such as calcium ionic composition) can vary among different dairy operations, and even seasonally within the same operation, it is likely that dairy manure has larger concentrations of calcium compared to other animal manures, and results from Le Corre et al. (2005) show that the presence of calcium ions has a significant impact on struvite crystallization. Higher calcium concentrations (1:1 molar ratios and above of Ca:Mg) inhibit struvite growth and lead to the formation of an amorphous calcium phosphate rather than a crystalline struvite. In the current study, the molar ratio of Ca:Mg was about 1:2.1, suggesting that it was difficult to form crystalline struvite.

### Effect of EDTA Addition on P Liberation

The EDTA results demonstrated that EDTA successfully liberated P into solution. As more EDTA was added, more calcium and P dissolved (Figure 7.2).

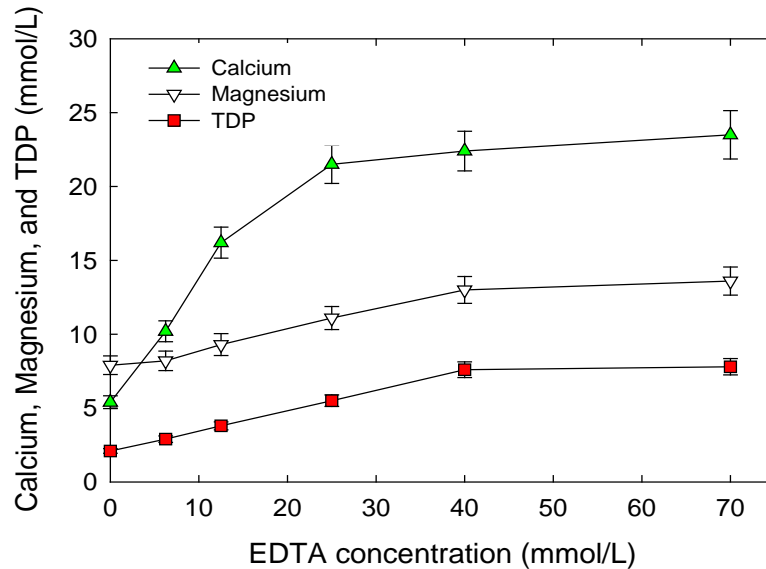


Figure 7.2: Concentrations of calcium, magnesium and TDP in supernatants after EDTA addition, without pH adjustment

These results are consistent with the hypothesis that EDTA reacts with calcium, releasing both calcium and the P into solution. Accordingly, without EDTA addition, most of the calcium and P were present in the solids, leaving little in the final treated liquid. However, with the addition of 40 mmol/L EDTA, slightly exceeding the sum of the calcium and magnesium molarity in the raw sample, most of the calcium (93%) was released. The TP in the raw effluent was 8.6 mmol/L.

Most of the TP was released into the solution by adding EDTA, with more complete liberation (up to 91%) shown at high levels of EDTA addition. It should be noted that high doses (40-70 mmol/L) of EDTA is too expensive to use in a commercial system and was used here only to test the concept of calcium binding.

Struvite formation also requires free  $Mg^{2+}$  ions. Unfortunately, EDTA in high concentration binds with magnesium as an  $[EDTA-Mg]^{2-}$  complex with stability constants  $10^{+8.7}$ , resulting in the reduction of free  $Mg^{2+}$  ions available for struvite formation. The release profiles of P and magnesium were similar, but magnesium lagged behind somewhat. This lag can be explained by the fact that EDTA preferentially binds to calcium first, since the stability of the  $[EDTA-Ca]^{2-}$  complex is two orders of magnitude greater than that of the  $[EDTA-Mg]^{2-}$  complex.

To verify that struvite formation with dairy effluent required free  $Mg^{2+}$  ions, magnesium chloride was added to increase the magnesium ion molarity to different levels. Figure 7.3 shows the effect of three levels of additional  $Mg^{2+}$  ions added (0,

14.5, and 94.5 mmol/L) and two different levels of EDTA concentrations (40 and 70 mmol/L) on TDP concentrations.

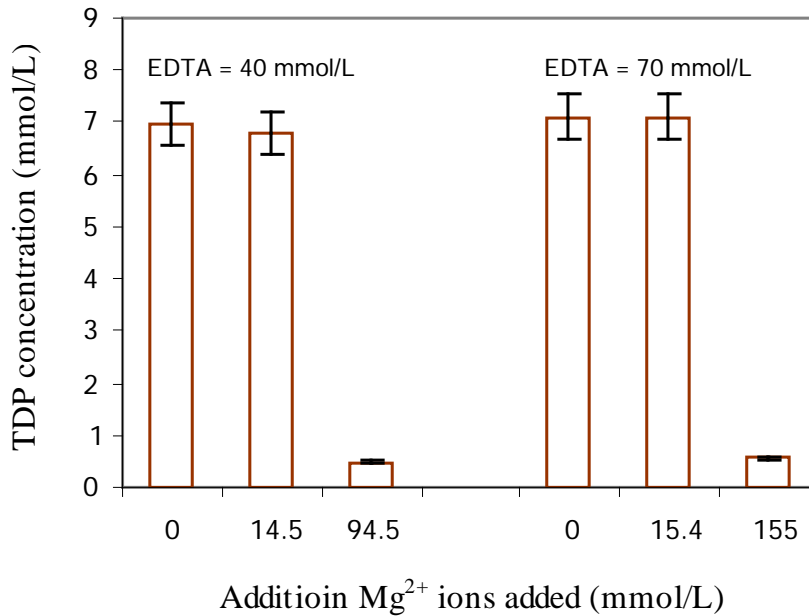


Figure 7.3: TDP in supernatant after both EDTA and additional Mg<sup>2+</sup> ions added (pH=8.5)

The addition of 14.5 mmol/L Mg<sup>2+</sup> ions had no impact on TDP concentration at EDTA concentration of 40 mmol/L. These results indicate that EDTA tied up all of the Mg<sup>2+</sup> ions, leaving no free Mg<sup>2+</sup> ions for struvite reaction. However, when the Mg<sup>2+</sup> ion concentration increased to 94.5 mmol/L, much higher than EDTA of 40 mmol/L, the excess Mg<sup>2+</sup> ions combined with the P to form struvite precipitates, resulting in a sharp reduction of P concentration in the solution. Similar results were obtained at an even higher EDTA level of 70 mmol/L.

#### Precipitate Identification

Figure 7.4 shows the XRD result for the precipitated solid, compared with that of standard struvite, clearly showing that the pattern of the precipitated solid matches the unique pattern of standard struvite (JCPDS, 1986) very well for both angles (diffraction angles 2θ) and intensities.



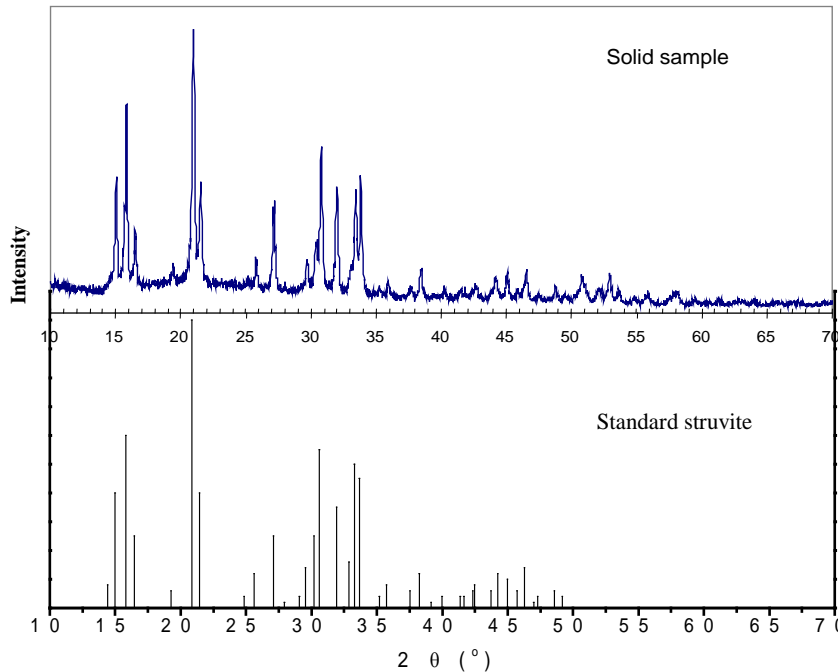


Figure 7.4: X-Ray Diffraction pattern from the solid product compared with standard struvite

A solid composition analysis supported the results of the XRD analysis, in that the composition of the solid product was similar to that of pure struvite (Table 7.1). The molar ratio of P:N:Mg was 1:1.02:1.02, very close to the theoretical ratio of 1:1:1. The relative purity compared with pure struvite was about 78%.

Table 7.1: Composition of the solid sample compared with pure struvite

Sample	P (% wt)	N (% wt)	Mg (% wt)	Molar ratio of P : N : Mg	Ca (% wt)	Product purity (%)
Solid product	10.1	4.6	7.8	1 : 1.02 : 1.02	0.9	78
Pure struvite	12.9	5.9	9.9	1 : 1 : 1	0	100

### Struvite Production at the Pilot Scale

Initial P removal results (without pre-treatment) of the pilot crystallizer are summarized in Table 7.2. TP reduction was generally poor, never exceeding 15%. Acidification of the raw effluent below pH 7.0 seemed to improve performance slightly. These poor P reduction results with the dairy AD effluent contrasts sharply compared with the high reduction (82%) achieved with swine wastewater (Bowers and Westerman, 2005) using the same crystallizer. These results are consistent with

our bench-scale studies, suggesting that the P in the dairy effluent was locked up in calcium-phosphate solids and not available for struvite formation.

Table 7.2: Phosphorus removal in crystallizer from dairy effluent

Run No.	Sample	TP (mg/L)	% TP reduction	Flow rate (L/min)	pH (raw)	pH (crystallizer)
1#	raw	275	3	1.7	7.0	7.9
	treated	268				
2#	raw	302	11	1.7	6.4	8.0
	treated	270				
3#	raw	293	4	1.7	6.5	7.5
	treated	281				
4#	raw	293	11	1.9	6.5	8.5
	treated	262				
5#	raw	290	13	1.9	6.0	8.0
	treated	251				
6#	raw	317	1	2.1	8.0	8.0
	treated	315				
7#	raw	317	5	1.9	8.0	8.25
	treated	300				
8#	raw	288	1	2.1	7.5	7.5
	treated	285				
9#	raw	288	8	1.9	7.5	8.0
	treated	265				

For the pilot-scale study, a modified process was proposed to free P into the phosphate ion form and improve struvite crystallization. A pretreatment unit was added, so that acidification and/or EDTA treatment could happen prior to entry into the cone. Digester effluent, flowing at 7.5-7.7 liters per minute, was directed into the pre-treatment tank(s), where it was mixed with EDTA to bind calcium and hydrochloric acid to prevent premature precipitation of struvite.

Table 7.3 summarizes operating conditions and results for the first four runs from which samples were taken and analyzed. The first two runs used nearly identical operating conditions, whereas the third run used a higher raw pH, and the fourth run used a lower pH in the cone. The results of these four operating runs (measured by % reduction in P) show a drastic improvement compared to the initial runs in Table 7.2, with the first two runs performing particularly well.

Table 7.3: Phosphorus removal in crystallizer from dairy effluent, using EDTA

Run No.	Sample	TP (mg/L)	% TP reduction	Flow rate (L/min)	pH (raw)	pH (crystallizer)
E-1#	raw	239	70	7.4	5.2	7.3
	treated	71.5				
E-2#	raw	169	82	7.6	5.1	7.5
	treated	31.1				
E-3#	raw	122	30	7.5	5.75	7.6
	treated	84.8				
E-4#	raw	149	62	7.4	5.1	6.75
	treated	57.2				

Compared to our bench-scale tests, relatively low dosages of EDTA were added in the pilot tests, in consideration of the cost of EDTA. We used a molar ratio of EDTA to calcium of 1:1, amounting to an EDTA concentration of roughly 7.3 g/L if the calcium concentration is the typical dairy AD effluent concentration of 25 mmol/L. The 2008 U.S. market price for EDTA was \$0.95/kg according to Chemical Marketing Reporting (2008). Under these prices, EDTA would cost about \$6.90/1000 liters of effluent. Even at the low dosages used in our pilot tests, the EDTA is too expensive to be commercially viable. Other more inexpensive organic acid anions, such as citric acid, citrate containing substances, oxalic acid, and oxalate-containing substances might be commercially viable, but their effectiveness would need to be tested, both in laboratory tests and at the pilot scale.

In addition to the cost concerns surrounding EDTA, another critical issue is whether it would have any environmental impact on the dairy farm when it is added into the effluent. However, its other uses suggest that this would not be a particular concern. EDTA is used in a variety of industrial applications involving the sequestration of metal ions in aqueous solution, such as in textile, pulp and paper, food, and cosmetics industries. For example, EDTA is added to some food as a preservative to prevent catalytic oxidative decoloration which is catalyzed by metal ions. In addition, EDTA is on the U.S. Environmental Protection Agency (EPA)'s list of inert pesticide ingredients (List 4B). This list includes only products that the EPA has concluded will not adversely affect public health or the environment under current pesticide product use patterns.

### *Conclusions*

Our work confirmed suggestions in the existing literature that the phosphorus in dairy manure is primarily in suspended particulate solid form, attached to calcium that is high in concentration within the manure. Acidification and addition of EDTA as a calcium chelating agent proved useful in releasing this bond and freeing the phosphorous in an active, dissolved form for subsequent struvite production. The addition of EDTA released 91% of the TP and 93% of calcium. The liberated P was precipitated as struvite as long as sufficient free  $Mg^{2+}$  ions remained present in the solution. Pilot-scale testing on AD-treated dairy manure yielded similar TP removal

results to previous non-pretreated studies on swine (~80% removal). Unfortunately, while EDTA is chemically successful, the additional costs necessary for the equipment and pretreatment chemicals cause the cost of struvite production to be higher than is commercially feasible. Inexpensive chelating chemicals other than EDTA will need to be further explored for their potential technical and economic viability.

## **Polymer/Coagulant Dosing with Belt Press**

### *Introduction*

While the fact that phosphorous in AD effluent is primarily in the form of suspended micro-solids complicates struvite production, it may be possible to avoid struvite production altogether if the phosphorous can be isolated using another method. Based on this, we explored the use of typical wastewater flocculation techniques to settle and isolate the phosphorous-containing solids, taking advantage of the fact that the phosphorous is in colloidal (suspended, small particle) form.

Flocculation is the process by which these small suspended particles can clump together, a process that is dictated by the behavior of colloids in water which in turn is strongly influenced by their electro-kinetic charge. Each colloidal particle carries a like charge, which in nature is usually negative. With a force known as electrostatic repulsion, the negative charges cause adjacent particles to repel each other and prevent effective flocculation. As a result, charged colloids tend to remain discrete, dispersed, and in suspension. On the other hand, if the charge is significantly reduced or eliminated, then the colloids will gather together, forming small groups of particles, then larger aggregates and finally visible floc particles which settle rapidly.

DLVO Theory explains why some colloids agglomerate while others will not by studying the balance between two opposing forces - electrostatic repulsion, which prevents flocculation, and van der Waals attraction, which promotes it. If electrostatic repulsion is larger than the van der Waals attraction, then the size of the difference indicates the height of the energy barrier, a measure of how resistant the system is to effective flocculation. In order to agglomerate, two particles on a collision course must have sufficient kinetic energy overcome this barrier. Once the energy barrier is cleared, the net interaction energy is all attractive. For effective flocculation to take place, the energy barrier is generally lowered or completely removed so that the net interaction is attractive without additional energy input into the system. This can be accomplished by reducing the surface charge. In water treatment, this is accomplished by adding cationic flocculants (also known as coagulants) such as Alum or Ferric Chloride to reduce the surface charge.

The process is a little more complicated in the case of AD effluent because of the presence of supersaturated gases that are evolving out of solution as the effluent leaves the digester and experiences changes in mixing, temperature and pH. These micro-bubbles provide a buoyant force which can counteract or overwhelm the

coagulation that is resulting from the addition of coagulants. Overcoming the disruptive potential of the gas micro-bubbles requires either additional coagulant or a polymer, another typical wastewater chemical.

Polymers are long, branched, high-molecular weight chemicals that trap small coagulated particles and intensify flocculation. Beyond enmeshing particles, some polymers are charged, in which case they may serve a dual role as a surface charge neutralizer. In theory, this has the potential to lower cost (because only a polymer is needed, rather than a cationic coagulant plus a polymer). However, in practice, many wastewater flocculation processes add both coagulants and polymers as the cost of the coagulant is comparatively low and its use can notably reduce the amount of polymer required. Because of the high cost of polymers, considerable research is being conducted to determine the optimal charge, branching and molecular weight (MW) needed for effective flocculation of particular wastewaters. A great deal of research has been carried out on effective polymer use with municipal wastewater, but less exists for animal manure wastewaters. Because of the high cost of commercial polymers and their combined use with coagulants, many in the industrial community question whether wastewater chemical technologies can ever be economically implemented for phosphorous recovery on animal farms.

#### *Evaluation of a Commercial Flocculent Process for Application to Dairy AD Effluent*

Fortunately, we were able to work with industry contacts to evaluate the performance of a commercial scale flocculation system and develop a baseline cost (Kemira Systems, Kennesaw GA and AL-2 Teknik, Hovborg, Denmark) for a dairy farm in southern Idaho. The system involved a controlled infusion of Alum coagulant (195 mL/m<sup>3</sup> @ \$1.72/L) with Superfloc polymer (1,250 mL/m<sup>3</sup> @ \$3.84/L) into a mixing chamber containing dairy AD effluent (from which the fibrous solids have not been removed). After a specified residence time in the mixing chamber and on the belt, the resulting flocs were pressed into a cake for subsequent compost treatment. Table 7.4 summarizes the performance and cost analysis of the commercial process.

Table 7.4: Kemira/AL-2 commercial performance and cost analysis (100 gallons per minute)

	<i>TS Reduction (%)</i>	<i>TP Reduction (%)</i>	<i>TN Reduction (%)</i>
Performance	72.3 ± 3.0	83.1 ± 3.7	38.2 ± 2.4
	<i>Chemical Cost</i>	<i>Electrical Cost</i>	<i>Capital Cost</i>
Cost Analysis	\$2.90/m <sup>3</sup>	\$0.07/m <sup>3</sup>	\$80-100/cow

A simple cost analysis of this system shows that total cost is \$2.97/m<sup>3</sup> of effluent treated, or roughly 1¢/gallon treated. At first read, this is reasonably effective

performance for a relatively low cost, yielding over 70% and 80% removal of total solids and phosphorous, respectively, producing almost 300 kg of cake (22.6% moisture and 0.53% P) per m<sup>3</sup> of treated effluent.

Unfortunately, in order to reduce the required coagulant and polymer input to the system, the Kemira/AL-2 system technology must utilize AD effluent which has not had the fibrous solids removed. Put another way, the system uses the binding effect of the fibrous solids as a means to intensify the flocculation process and reduce the chemical input to the system. While innovative and effective, the result is a process which binds the otherwise desirable fibrous solids (bedding replacement and/or value-added soil amendment) into a cake that needs additional composting to make a marketable product. But this product is also less desirable for end users because of the inclusion of industrial chemicals and polymers. Therefore, a more realistic price for this process rises to about \$6.95/m<sup>3</sup> or \$0.026/gallon, due to loss of marketable fiber (\$1.92/m<sup>3</sup>) and additional compost treatment (\$2.06/m<sup>3</sup>). To offset these costs the resulting compost product would require a minimum selling price of nearly \$15/MT which is potentially achievable.<sup>1</sup>

Our commercial-scale evaluation found very reliable, effective performance with the technology. Economies of scale, achieved in this case by using the technology on a large CAFO facility (~3,500 wet cow equivalents), resulted in an approximate production cost that was quite minimal. Drawbacks primarily included the fact that significant farm labor was needed to manage the process (labor costs were not included in our cost analysis), as well as its reliance on fibrous solids that cannot be used for on-farm bedding or value-added products. In our judgment, chemical costs simply become too high without the use of fibrous solids and if application is to be on smaller farms, reductions in polymer dosage or completely new technology approaches will be required.

#### *Laboratory Polymer Optimization*

Polymer adsorption is crucial to flocculation as other effects, including charge neutralization and bridging, are dependent on the adsorption, which in turn is impacted by differences in polymer structure and architecture. In this study, a new method was researched to evaluate polymer flocculation, and specifically the role of polymer architecture and structure on performance. Results could identify new classes and/or sizes of polymers that work more effectively on dairy AD effluent, allowing for a reduction in chemical input needs and cost.

Low concentrations of anionic dye (Cibacron Blue F3GA) were added to the dairy wastewater prior to cationic polymer addition. Cationic polymers are electrostatically attracted to both the negative dye and the suspended particles (in this case, the phosphorous-calcium solids). If the polymer adsorbs both particles and dye, it takes dye out of solution. This results in a color change as the dye has a strong blue color in solution. We hypothesized that this color change might reflect

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<sup>1</sup> MT = metric tons (1 MT = 1 Mg); MMT = million metric tons (1 MMT = 1 Tg)

polymer performance. Through the use of visible light spectrometry, it is possible to quantify the color change and thus develop a standard curve and statistical model that predicts the relationship between polymer type/dosage and adsorption. The adsorption in turn is directly related to polymer flocculation capability in a given wastewater. We hypothesized the following results, dependent on dosage:

(a) At low dosages of polymers, all the polymers are adsorbed on the particle surfaces and no free polymer is left in solution. The particles still remain negatively charged because the few polymers added do not have enough positive charges to neutralize the negative particle charges. The dye is still dissolved in solution due to electrostatic repulsion between the dye and the particles, so the color of the solution does not change significantly. These results indicate that neutralization is not complete, and that the particles will be difficult to aggregate because they still have significant electrostatic repulsion.

(b) At medium dosages of polymers, all the polymers are adsorbed on the particle surfaces and no free polymer is left in solution, similar to at low dosages. However, in contrast to low dosages, the particles become positively charged because the polymers have enough positive charges to neutralize the negative particle charges. The adsorbed polymer adsorbs some free dyes from solution because it has sufficient electrostatic attraction available for both the particles and the anionic dye. Thus, the solution has a lighter color as some amount of dye is pulled from solution. Depending on the amount of polymer added, the solution will range from slightly lighter in color to almost colorless. A nearly colorless solution suggests that polymer dosage is high enough that charge neutralization is complete and aggregation will be successful. For flocculation purpose, no further polymer is needed to add into the wastewater.

(c) At high dosage of polymer, polymer adsorption reaches saturation and some amount of polymers is free in solution. These free cationic polymers attract the negatively charged dyes, and some amount of dye captured to form a polymer-dye complex with no adsorbed particles. This polymer-dye complex dissolves in solution and color is again observed. The reappearance of color suggests excess polymers have been added into wastewater.

Using these hypotheses, we added varying types of polymers to the manure wastewater and tested for the lowest level of concentration to achieve effective adsorption.

### Materials and Methods

Cationic polymers and dye selected for this study are summarized in Table 7.5. Cationic PEI polymers, a group of branched polymers with different molecular weights and positive charges, are widely used in the paper industry for increasing paper strength and flocculating waste streams for recycling. Their application to treatment of animal manure wastewater has not yet been fully investigated. Three PEIs, with molecular weights varying from a low of 25,000 to a high of 2,000,000,

were evaluated in this work. A cationic commercial flocculant from GE Company was also used to evaluate flocculant adsorption.

Table 7.5: Molecular weights of chemicals

Designated Name	Full Name	Average Molecular Weight (M <sub>w</sub> )	Source
PEI-25k	Polyethylenimine	25,000	Aldrich
PEI-750k	Polyethylenimine	750,000	Aldrich
PEI-2000k	Lupasol® SK	2,000,000	BASF
PC1195	Commercial flocculant	500,000	GE
Dye	Cibacron Blue F3GA	840.10	Fluka

In order to evaluate polymer adsorption on solid particles, solids from the dairy effluent were obtained through centrifugation of 50 mL of dairy effluent at 10,000 rpm for 20 minutes. The CB dye was diluted to 60 mg/L with deionized water (DI water), and the pH was adjusted to about 8.0 using diluted NaOH. 50 mL of this CB solution was added into the solids obtained from centrifugation, and then the polymer (at 5% wt concentration) was added at different dosages to the sample. The polymer dosage varied from 0 to 4,000 mg/L. The sample was mixed in a sonicator bath (19H Ney from Ultrasonik) for about 60 minutes in order to ensure complete mixing and adsorption. After that, the sample was centrifuged again at 10,000 rpm for 20 minutes, and the supernatant solution was collected. Absorbance of the supernatant solution was measured at 610 nm (the point of maximum absorbance of the dye) in a spectrometer (Spectronic 20 Genesys from Spectronic Instruments).

### Results and Discussion

As expected, increases in the polymer dosage led to significant color changes in solution, from colored, to colorless, and then back to color. An example using the polymer PEI-25k is shown in Figure 7.5. At a PEI dosage of 1,400 mg/L, the solution became almost colorless, indicating all the dye was adsorbed by the particles. For flocculation purposes, the dosage of this particular polymer would likely therefore be most efficient at 1,400 mg/L.



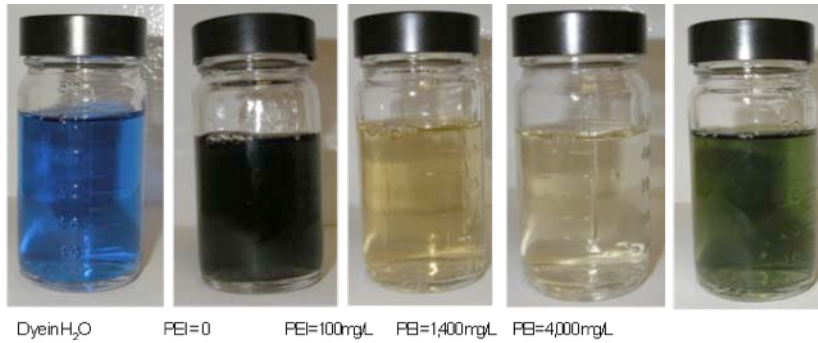


Figure 7.5: Samples in color change with different dosage of polymer PEI-25k addition

Spectroscopic analysis quantifies this color relationship. Figure 7.6 (a, b) shows the correlation of absorbance against dosages for PEI-25k and PEI-2000k, respectively. As expected from the qualitative results shown in Figure 7.5 above, the dosage of PEI-25k should be below 1,400 mg/L as the free soluble polymers that develop above that concentration are not necessary for flocculation and thus adds cost without improved performance.

Interestingly, Figure 7.6 (b) shows a different trend of absorbance for the high molecular weight polymer PEI-2000k. Here, the solution absorbance decreased with increases of the polymer dosage, indicating that the polymer performance continued to improve (albeit only marginally) as polymer concentration increased. This was true even at very high concentrations of 4,000 mg/L, a concentration that is unlikely to be economically feasible. Absorbance never reached the same lows as the polymer PEI-25k, suggesting that PEI-25k performs better than the high molecular weight polymer. These results support work from other authors regarding the influence of molecular weights on flocculation (Timby et al., 2004; Krumpelman et al., 2005).

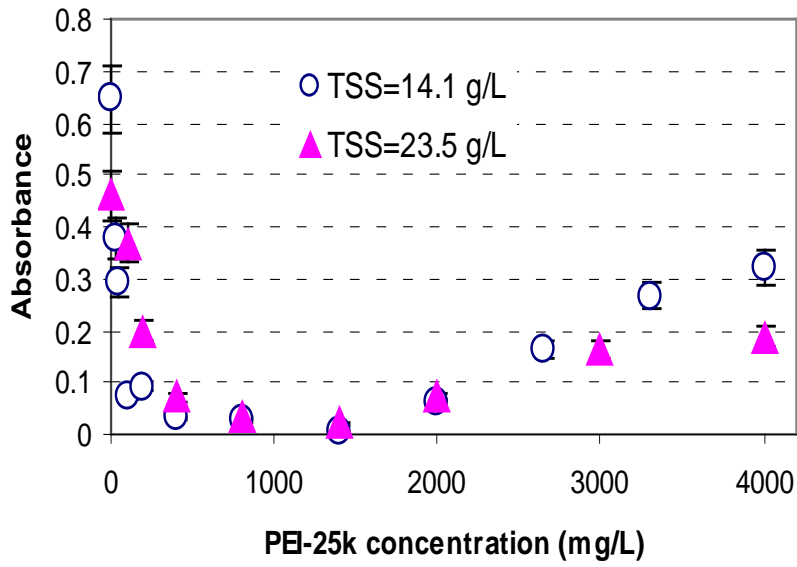


Figure 7.6(a): Effect of PEI-25k dosages on the solution absorbance

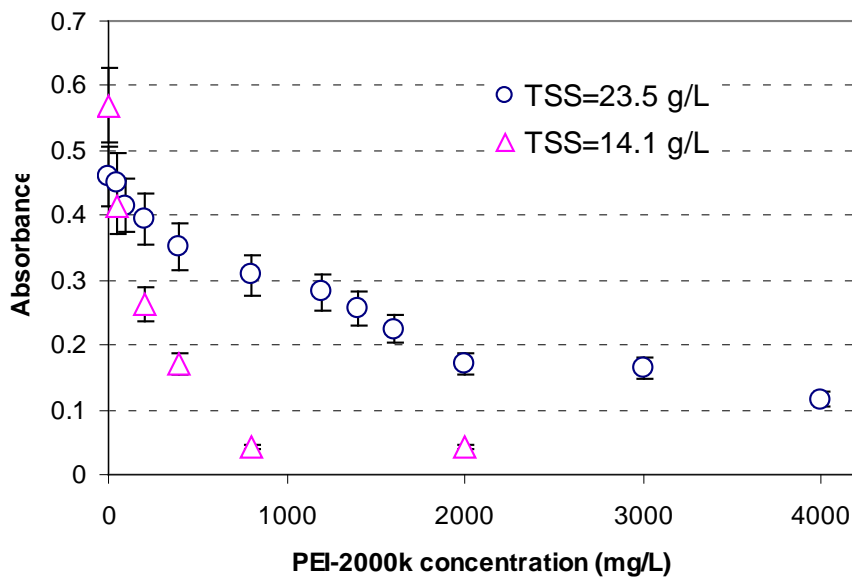


Figure 7.6(b): Effect of PEI-2000k dosages on the solution absorbance

This study also shows that dye spectrometric experiments can assist in determining suitable polymers for manure wastewater treatment, and thus can assist in developing polymers that can achieve the desired flocculation at lower concentrations. Use of these new polymers could eventually lead to lower costs for commercial systems such as the Kemira system we evaluated.

## **Decanting Centrifuge With or Without Polymer Dosing**

### *Introduction*

Early laboratory studies we conducted with coagulant and polymer additions to dairy AD effluent indicated that, surprisingly, coagulants did not have as much of an effect on flocculation and removal of solids and phosphorous as would be expected (data not shown). This contradicts the prediction of DLVO theory that the colloidal solids stay suspended because of surface charge repulsion, in which case coagulant addition to overcome that surface charge repulsion should result in improved flocculation and solids and phosphorous removal. However, we also knew that effective flocculation was seen when coagulants were paired with polymers, particularly cationic polymers. From these observations, we hypothesized that surface charge might not be the most intensive barrier to flocculation. Instead, although some charge repulsion might be present (indicated by the observed small benefits to coagulant addition), attractive forces are also significant, with other forces such as gas buoyant forces present within AD effluent preventing attractive forces from being realized.

Based on this hypothesis, a pilot-scale study utilizing a decanting centrifuge with or without coagulant and polymer dosing was completed. The decanting centrifuge attempts to create additional forces to assist in overcoming the barriers to effective flocculation via a simple, mechanical mechanism that does not require the addition (and expense) of chemicals.

### *Material and Methods*

A SWECO (Florence, KY) Model 518 pilot-scale decanting centrifuge was contracted for testing at a commercial dairy with an AD unit in southern Idaho. The pilot centrifuge could monitor amperage loading to its scroll, bowl and overall unit, while allowing for 10-50 gallon per minute flow rates from the AD unit. After the primary screening for fibrous solids, AD effluent was sent to the centrifuge unit for testing at three flow rates (10, 30 and 45 gpm) and at various scroll and bowl speed ratios. After preliminary testing, it was noted that an even scroll and bowl speed ratio (60:60 hz) led to the production of a relatively dry and usable cake at each of the flow rates studied. This ratio was then used for all subsequent tests with results for the 45 gallon per minute flow rate reported in Table 7.6.

### *Results and Discussion*

As can be seen from the results in Table 7.6, centrifuge alone can result in nearly 60% TP removal, in comparison to the earlier reported coagulant/polymer belt

press operation that resulted in over 83% TP removal. However, for centrifugation, this total does not include fibrous solids which in themselves represent approximately 5-10% of total TP. Capital costs are similar for the two processes while the electrical draw is somewhat higher for the decanting centrifuge (21 amps versus 18 amps at similar flow rates). We also tested the use of the decanting centrifuge with added alum or polymer. Interestingly, just as observed in our previous experiments, use of Alum as a coagulant either alone or in conjunction with polymer had zero or a deleterious effect on solids and phosphorous removal thus in part corroborating our early hypothesis that surface charges might not be the most intensive barrier to flocculation. On the other hand, polymer dosing did increase both solids and phosphorous removal, with higher removal rates at higher dosages. However, even at the highest polymer dosing, ultimate TP removal percentages were below or near that seen from the Kemira/AL-2 belt press operation.

Table 7.6: Decanting centrifuge removal percentages (45 gallon per minute)

<i>Influent = 750 ppm TP and 5.1% TS</i>	TS Removal (%)	TP Removal (%)
Centrifuge alone	51.0	56.0
Alum (625 ml/m <sup>3</sup> )	51.0	53.3
Alum (1,250 ml/m <sup>3</sup> )	51.0	56.0
Polymer (100 ml/m <sup>3</sup> )	61.0	56.9
Polymer (200 ml/m <sup>3</sup> )	60.8	65.3
Polymer (300 ml/m <sup>3</sup> )	62.8	74.7
Alum (625 ml/m <sup>3</sup> ) + Polymer (100 ml/m <sup>3</sup> )	54.9	57.3
Alum (1,250 ml/m <sup>3</sup> ) + Polymer (200 ml/m <sup>3</sup> )	58.8	58.7

### *Conclusion*

The main benefit of decanting centrifugation without any chemical addition is that a moderately effective TP removal rate (~60%) can be accomplished at similar electrical and capital costs of flocculent systems but at reduced operating costs due to no chemical inputs. In addition the fibrous solids can be used directly for bedding and are not contaminated by chemical additions. Use of centrifuge plus polymer dosing raises the TP removal to near that of commercial flocculent/belt press systems but at the added cost of inputting chemical polymers which makes the system almost identical in overall input costs to that of the flocculent/belt press systems, save the advantage of a useable, pure bedding. As with the earlier studied flocculent/belt press system, costs can prove to be economically viable and removal performances required by the farm can be accomplished but at costs that are only affordable because of economies of scale to large CAFO operations.

## **Aeration/Lime Settling**

### *Introduction*

With confirmation that Alum coagulant addition did not significantly increase TP removal, a new technical approach was studied in an attempt to simplify solids and phosphorous removal and reduce costs. Assuming that surface charge neutralization was not an overriding concern, efforts were targeted towards overcoming the forces within the AD effluent that were disrupting the existing attractive forces that encourage flocculation. It is well known that during AD digestion significant amounts of CO<sub>2</sub> and even some CH<sub>4</sub> produced during the biological process can become dissolved and/or super-saturated within the effluent. This is particularly true of CO<sub>2</sub> which is stored within the liquid effluent as bicarbonates or carbonates. Upon release from the digester, changes in temperature, pressure, pH, air and agitation can lead to a release of these super-saturated gases (Battistoni et al., 1997; Cecchi et al., 1994).

Figure 7.7 shows a microscope image of micro-bubbles within liquid AD effluent, emphasizing that these bubbles occur in numbers high enough to disrupt attractive forces with the buoyant forces and micro-turbulence they might induce. In an attempt to reduce the number of micro-bubbles and investigate whether they were contributing to the suspension of phosphorous particles, we aerated the AD effluent. Because this process also increases pH as it drives off gases, optimized flow rate and reaction time for aeration can be inferred by recording a pH/aeration profile.

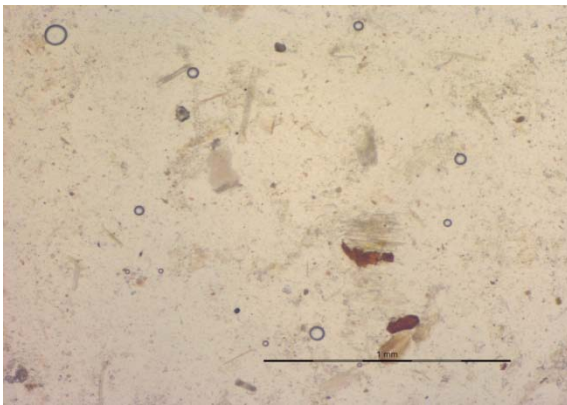


Figure 7.7: Microscope image of micro-bubbles of gas present and evolving within AD effluent

Figure 7.8 is a pH/aeration profile for a laboratory test on AD dairy effluent. As can be seen from the figure, aeration of only 30 minutes increased the pH of the AD effluent by nearly a half of a pH point, indicating the removal of significant amounts of super-saturated CO<sub>2</sub>.

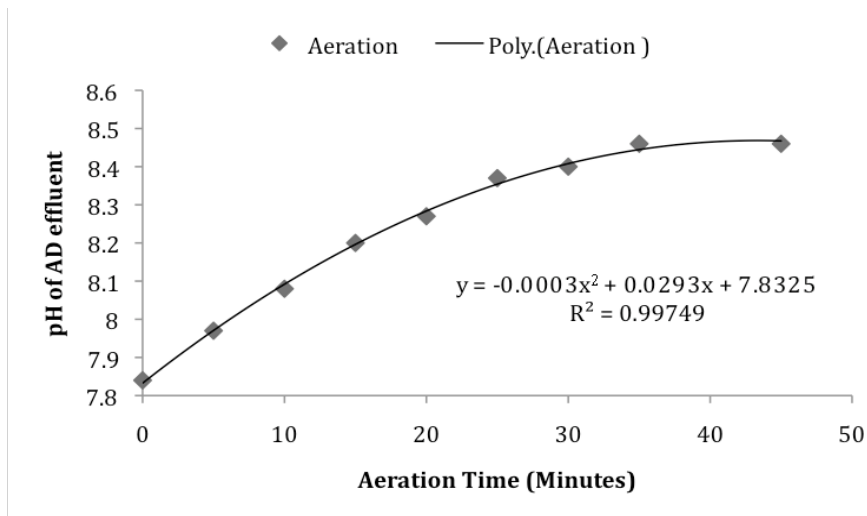


Figure 7.8: pH and aeration profile

### *Results and Discussion*

Aeration, with its subsequent gas removal and pH increase had notable effects on the quantity of micro-bubbles present within the AD effluent, in effect completely removing bubbles within the microscopic image (Figure 7.9). Removal of these interfering gases led to significant improvement in settling capability and solids/phosphorous removal. Without aeration, only 28.4% of TP was settled during a 24-hour period. This is in comparison to the performance after aeration and subsequent 24-hour settling which achieved 52.3% TP removal. This removal, although a strong improvement, simply is not comparable to removal percentages from other technologies. In an effort to further improve the performance without too much added cost, an additional step comprised of lime addition was completed. Previous research with the ammonia stripping technology showed that lime addition not only led to a required increase in pH but also significant settling of solids and phosphorous, due primarily to the formation of insoluble calcium phosphate salts. Table 7.7 summarizes the results of the different sequential steps, ultimately leading to a nearly 80% TP removal through a combination of aeration, lime addition and 24 hour settling. This performance compares favorably with the aforementioned Kemira/AL-2 operation but with significant reductions in chemical and energy inputs while also preserving a fibrous product for use as bedding and/or value-added sales. Notably, the aeration can be easily completed using blowers, and effluent pits available with standard, biogas-mixed plug-flow digesters and the lime input fits in nicely with an ammonia recovery operation as well as with existing farm practices that often use slaked lime for bedding treatment. Commercial-scale validation of the bench-scale results is on-going with an industry partner at a Southern Idaho dairy.

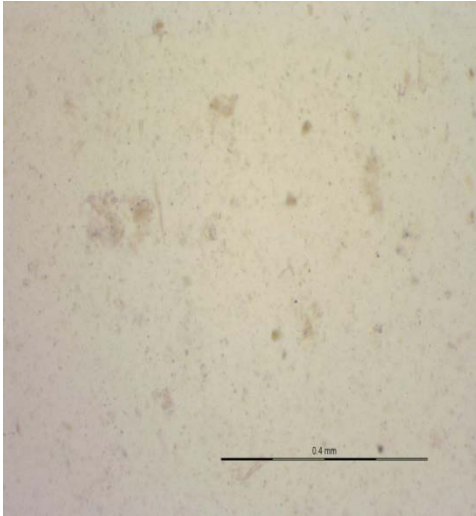


Figure 7.9: Removal of micro-bubbles through aeration

Table 7.7: TP removal percentages with aeration, lime treatment and aeration

Fiber-separated, digested manure TP (mg/l)	Settling for 24h		Aeration for 40min and settling for 24h		Aeration for 40min, lime (2g/l), settling 24h	
	TP (mg/l)	TP removal (%)	TP (mg/l)	TP removal (%)	TP (mg/l)	TP removal (%)
1760	1260	28.4	840	52.3	380	78.4

## Electro-Coagulation Settling

### *Introduction*

Electro-coagulation (EC) has been used in wastewater treatment although it has not been a main component in animal wastewater treatment systems. The EC process is potentially very suited to phosphorous and solids removal as the effluent has high enough electrical conductivity that the electrochemical process can provide an electrical field and/or produce a field 'in situ' by sacrificial electrodes without adding additional ionic species. The process alters the surface charge in the effluent and enhances P and solid settling. EC has demonstrated its superior performance in treating effluents containing suspended solids, oil and grease, and other similar substances.

### *Materials and methods*

#### E C Cell Set-up

A bench-scale EC system with mono-polar electrodes in parallel connections was designed and set up in lab as shown in Figure 7.10. EC treatment was carried out in

both batch and continuous flow electrolytic cell systems. The electrode sets (both anode and cathode) comprised six parallel pieces of metal plates (304 stainless steel) situated 1.0 cm apart, and submerged in the effluent. The anode and cathode sets were, respectively, connected to the positive and negative outlets of a DC power source (model CM-1 from HY Charge) at an open circuit potential of 6.0 V. Current was held at a constant of 1.0 A for each run.



Figure 7.10: Bench-scale EC system with mono-polar electrodes in parallel connections

Batch experiments show that TP reduction increased sharply during the first 30 minutes of EC time, and then remained constant with no significant increase. The maximum TP reduction achieved was 83%. Thus the majority of TP was removed by this EC system in less than 30 minutes. TSS reduction increased sharply before 15 minutes of EC time and then remained constant. The maximum TSS reduction was about 88%, indicating that majority of TSS was removed by the EC process.

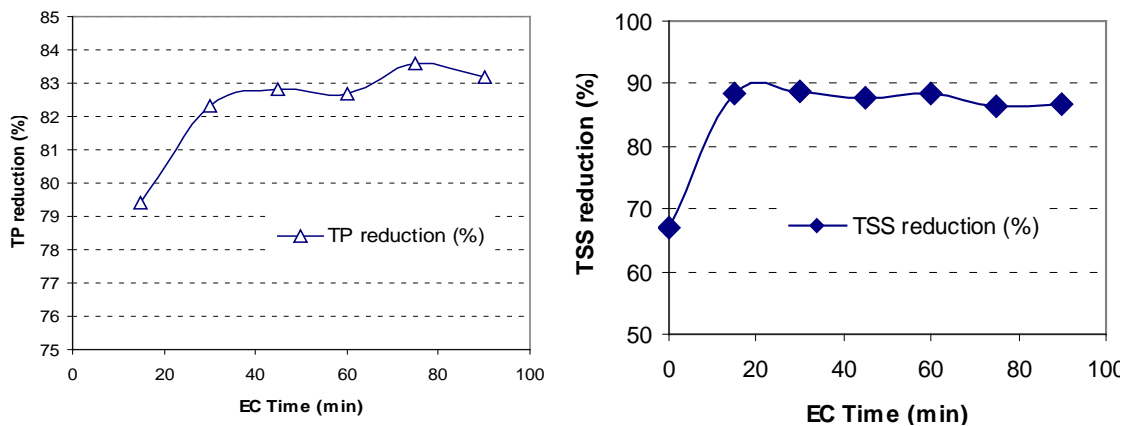


Figure 7.11: TP and TSS removal by EC cell

### Pilot EC System Set-up

A continuous-flow pilot-scale EC system with mono-polar electrodes in parallel connections was designed and set up in lab as shown in Figure 7.12. EC treatment was carried out in both batch and continuous flow electrolytic cell systems. Each electrode sets (both anode and cathode) comprised ten parallel pieces of metal



plates (304 stainless steel) situated 1.0 cm apart. A peristaltic pump was used to transfer manure into the EC.

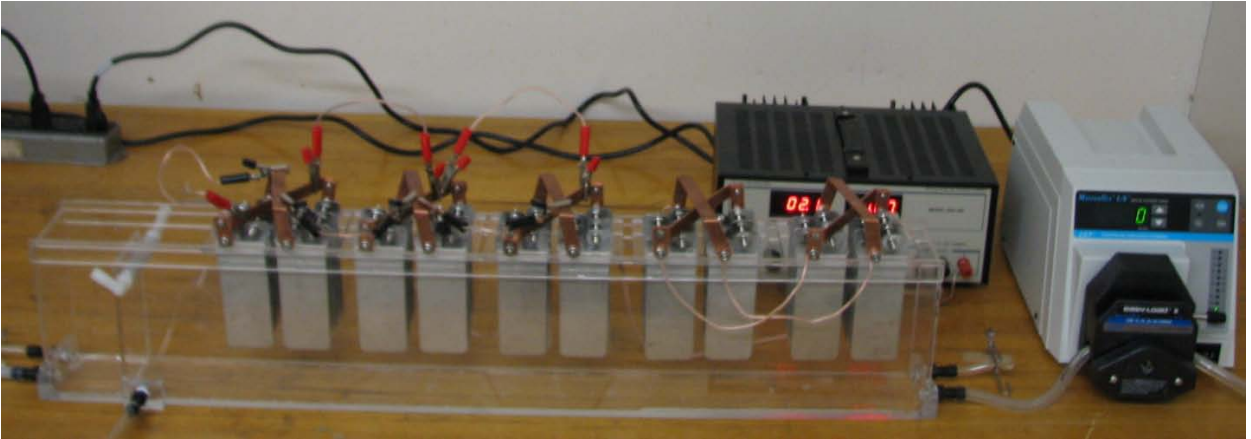


Figure 7.12: Pilot-scale continuous-flow EC reactor setup

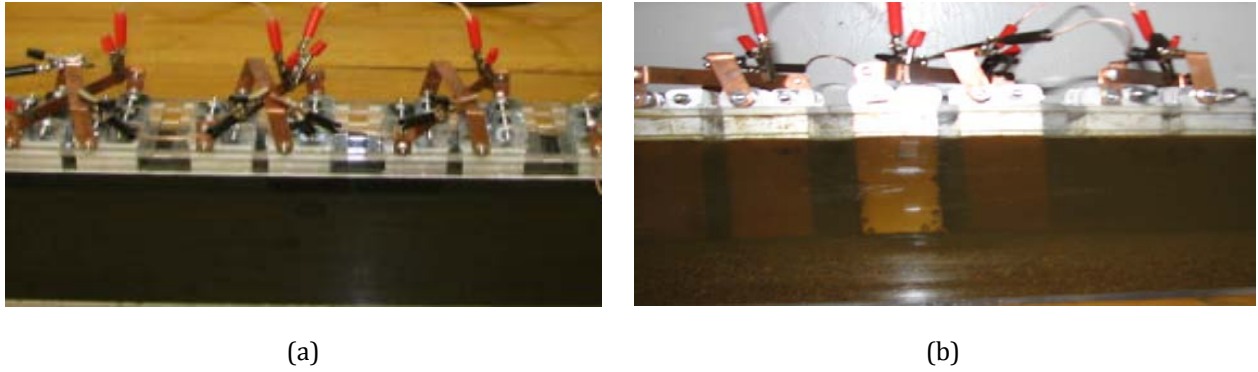


Figure 7.13: Anaerobic digested manure (a) settled (b) after EC treatment at 5 A

Six liters of anaerobic digested manure, which is shown in Figure 7.13a, was treated at 5A for 30 min in the EC reactor. After one hour naturally settling, a perfect solid liquid separation phenomenon was found (Figure 7.13b). To optimize TP removal efficiency, a series of current density (3.0A to 6.0 A) were tested at the flow rate of 40 ml/min. The raw manure sample was taken at the beginning and of each run. Liquid and solid samples were taken from the EC reactor after 2 hours running.

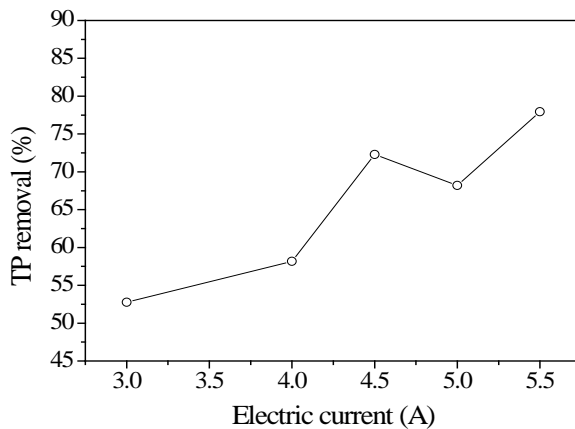


Figure 7.14: TP removal efficiency by EC with different amperage

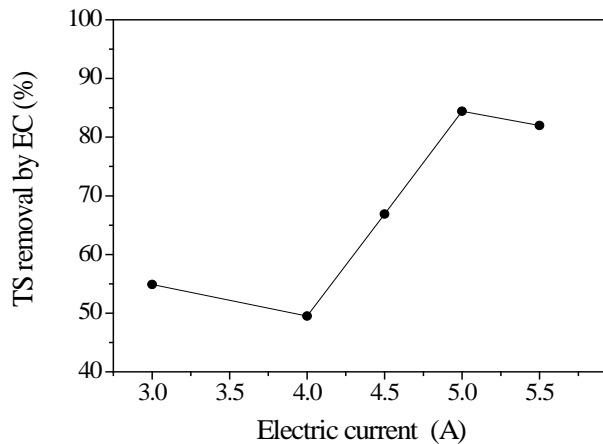


Figure 7.15: TS removal from manure by EC at different amperages

The figures above show TP and TS removal from manure with different electric currents. 78% TP removal was accomplished using an amperage of 5.5 A. It is anticipated that the removal efficiency could be higher if the settling time is longer.

Nutrients (TN, TP and K) in the solid part and liquid part after EC were analyzed (Figure 7.16). The solid part has a higher concentration of nitrogen. Although EC removed part of the nitrogen from manure, but there is a high level of nitrogen (1600-2000 mg/l) in liquid part which need to be treated. The TP concentration of solid is two times than that of liquids. There is no difference of potassium concentration in these two phases.

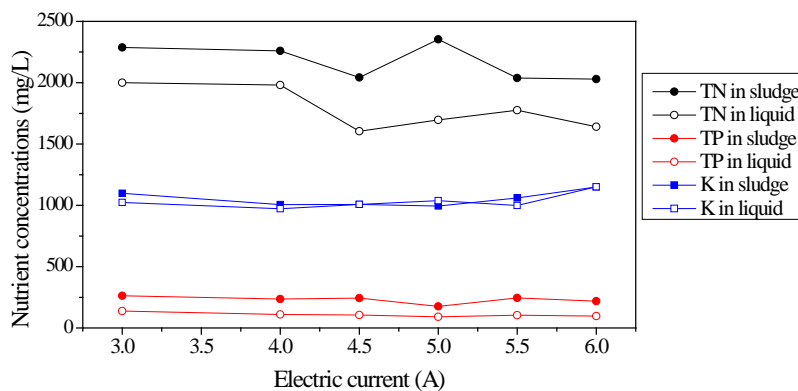


Figure 7.16: Nutrients in anaerobic digested manure post EC

Metal profiles are shown in Figure 7.17. The concentration of Ca in the solid is two times more than that of liquid. The concentrations of Al and Fe in solid are also much higher than that in liquids.

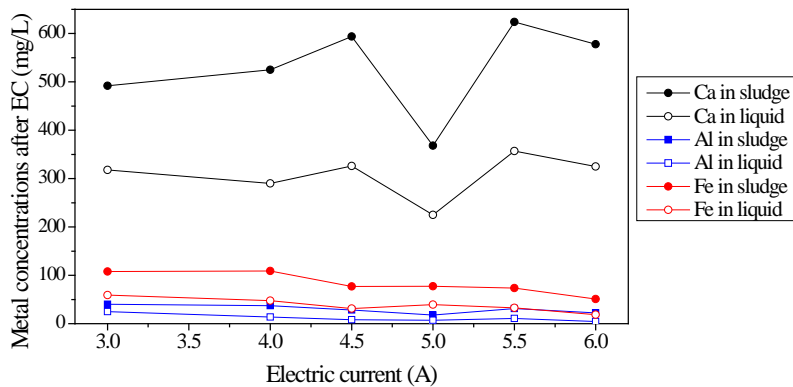


Figure 7.17: Metals in anaerobic digested manure post EC

### Conclusion

EC is effective at removing phosphorus and solids from digested manure without any chemical addition. The settled solids resulting from EC contain a higher level of nitrogen, phosphorus and minerals, which can be used as fertilizer. Although the solids separated from the EC unit still contains considerably high water content, they can be dried in the open air or by waste heat from the electric generator which is generally set up near the anaerobic digester.

### Overall P-Recovery Conclusion

During the phosphorous recovery work several key conclusions were developed, including:

- Each manure produced within varying manure management systems and under disparate scales and available working infrastructure make the development of P-recovery technology problematic and most-likely user dependent, requiring the availability of a suite of options;
- Confirmation was made and information extended regarding the fact that dairy manure is unique among other manures in regard to the physico-chemical structure of the phosphorous, particularly within AD treated effluents. The micro-solid, colloidal form of the solid makes crystallization strategies particularly problematic and leads researchers towards coagulant/polymer strategies aimed at improving flocculation and settling. The chief concern regarding this approach is the chemical and operating costs as well as the impact the process has on availability of suitable fibrous by-products.
- Alternative settling systems, i.e. decanting centrifuge, aeration/lime, and electro-coagulation were all evaluated as a means to achieve effective flocculation/settling but without the intensive chemical costs. Each of these has its own capital, operating and performance cost benefits and concerns.

- Below is a summary table (Table 7.9) of projected costs for each of the studied technologies. In some cases, additional scaled research is needed to further nail down real costs, but importantly, a matrix of potential technologies and their relative costs and capabilities is now available and summarized for potential commercial development and use. Notably, the aeration/lime treatment approach is particularly appealing in regard to its performance, cost reductions both from operating and capital sense, and integration to existing farm systems and a proposed integrated nutrient management system that combines P-treatment with N-treatment.

Table 7.9: Summary of capital and operating costs with performance capability for P-technologies

Approach	TS	TP	Dewatering	Chemical Input	Operating Cost		Estimated Capital Cost /cow
	Removal	Removal			Chemical	Electrical	
	%	%					
Settling Weir	20-30	20-30	Settling	-----	-----	-----	\$40-50
Aeration	25-40	45-55	Settling	-----	-----	9¢/m <sup>3</sup>	\$50-60
Aeration/Lime	45-70	70-80	Settling	Lime (1.0kg/m <sup>3</sup> )	8¢/m <sup>3</sup>	9¢/m <sup>3</sup>	\$60-70
E-coagulation	40-60	70-90	Settling	Sacrificial Cathode	20¢/m <sup>3</sup>	6¢/m <sup>3</sup>	\$100-120
Kemira	70-75	80-90	Belt Press	Poly (195 ml/m <sup>3</sup> ) Alum (1,250 ml/m <sup>3</sup> )	\$2.90/m <sup>3</sup>	7¢/m <sup>3</sup>	\$80-100
Centrifuge	45-55	50-60	Centrifuge	-----	-----	9¢/m <sup>3</sup>	\$60-80
Cent/Polymer	55-65	65-70	Centrifuge	Poly (195 ml/m <sup>3</sup> )	\$0.75/m <sup>3</sup>	9¢/m <sup>3</sup>	\$100-120
Struvite	5-10	45-55	Crystal	Mg, Alkali, etc.	\$1.58/m <sup>3</sup>	9¢/m <sup>3</sup>	\$100-150

In regard to climate impacts, P recovery technology and subsequent marketing of the phosphorous-rich solid product could have important implications, as replacement of inorganic-based P in the fertilizer industry would generate a global warming potential offset via reductions in climate emissions from P mining and production. Using the earlier assumptions regarding an assumed achievable 40 dairy AD installation operating under co-digestion scenarios, the following mitigation potential could be realized from just the sale of P recovered from an assumed aeration/lime/settling scenario capable of 80% recovery (Table 7.10).

Table 7.10: Greenhouse credits from 40 dairy AD assumption—Bio-phosphorous

	Phosphorus Product MT-P/yr <sup>a, b</sup>	GWP MT CO <sub>2</sub> e/MT P <sup>c</sup>	Total Offset MMT CO <sub>2</sub> e/yr
Bio-phosphorous	500	6.11	0.0031

<sup>a</sup> Assume 0.048 lbs P/cow day and 0.4 kg P/MT food waste (Frear et al., 2009) and an 80% P recovery

<sup>b</sup> MT = metric tons (1 MT = 1 Mg); MMT = million metric tons (1 MMT = 1 Tg)

<sup>c</sup> (Davis and Haglund, 1999)

### Key Project References Related to Chapter

The majority of the work presented in this chapter has been previously published as:

- Zhang, T., Bowers, K., Harrison, J., Chen, S., 2008. Impact of calcium on struvite precipitation from anaerobically digested dairy wastewater. *Preprints of Extended Abstracts presented at the ACS National Meeting, American Chemical Society, Division of Environmental Chemistry*, 48, 499.
- Zhang, T., Bowers, K.E., Harrison, J.H., Chen, S., Submitted. Releasing phosphorus from calcium for struvite fertilizer production from anaerobically digested dairy effluent. *Water Environment Research*.
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