

**STRUVITE RECOVERY FROM
DIGESTED DAIRY MANURE
AND
REGIONAL MANURE
ANAEROBIC DIGESTION STUDY**

**FINAL REPORT 06-10
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**NEW YORK STATE
ENERGY RESEARCH AND
DEVELOPMENT AUTHORITY**





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Prepared for the
**NEW YORK STATE
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ABSTRACT

This study investigated the reduction of phosphate in dairy manure through precipitation of struvite and the development of a regional manure anaerobic digester. These two investigations address different manure handling problems (nutrient removal and odor/pathogen reduction) and are not inherently related to each other. However, the study investigated the potential of precipitating struvite from the filtrate of an anaerobically digested dairy manure dewatering process. A successful struvite removal system could bring benefits to a regional digester as well as to a digester serving a single farm. The Team reviewed literature, visited full-size operating systems, performed lab-scale precipitation tests, and developed a regional manure digester model. Two series of bench-top precipitation tests were performed. The first series of tests attempted to clarify the filtrate using gravity clarification, vacuum filtering, pressure filtering, centrifugation and polymer addition, but none of these were successful. Testing proceeded using the filtrate. The first series of tests included varying magnesium addition rates, end-point pH levels, and magnesium sources (MgO vs. MgCl₂). Little difference in results was found between the two reagents and no trends could be discerned in the amount of phosphate versus the amount of magnesium added. The second series of bench-top tests were adjusted to focus on enhancing the environment for struvite crystal formation by increasing the mixing rate and adding galvanized washers and struvite crystals. None of these changes had significant effect on the level of phosphate removal. The phosphate removal level did not exceed 20% in any of the test cases, indicating that it is not feasible to precipitate struvite from dairy manure.

The second part of the study evaluated a regional manure anaerobic digester. A facility model, that includes collection of the manure, anaerobic treatment, return of treated manure to area farms, and use/sale of the digester gas is presented.

Keywords: regional anaerobic digester, struvite, dairy manure, manure, dairy manure dewatering

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SUMMARY

New York dairy farmers are faced with manure handling challenges including odor, nutrients, and pathogens. Over the years, dairy herds have been growing in size and residential housing has been built closer to the farms. These trends have resulted in larger amounts of manure, requiring handling and appropriate treatment, coupled with an increased concern about nutrient application to the land and odors in the area of the farm. Farms in Cayuga County, due to their location in several sensitive lake watersheds, need to be especially mindful of phosphorous loading. Farms that lack the land base to return the nutrients to the soil, or are limited in their land application due to close proximity of lakes, streams, or sensitive neighbors, would benefit tremendously from finding an affordable method for removing nutrients from their waste stream.

In a project funded in part by New York State Energy Research and Development Authority (NYSERDA), the Cayuga County Soil and Water Conservation District (District) and Wright-Pierce (the Team) investigated two possible solutions to the challenges that the Cayuga County dairy farmers face:

1. Phosphate reduction through precipitation of struvite (magnesium ammonium phosphate)
2. Odor/pathogen reduction and energy recovery through the development of a regional manure anaerobic digester

These two solutions address different problems (nutrient removal and odor/pathogen reduction) and are not inherently related to each other. However, the study investigated the potential of precipitating struvite from the filtrate of an anaerobically digested dairy manure dewatering process. A successful struvite removal system could bring benefits to a regional digester as well as to a digester serving a single farm. The Team reviewed literature, visited full-size operating systems, performed lab scale precipitation tests, and evaluated the applicability of the struvite precipitation technology to digested dairy manure. The District hoped to apply the struvite technology at Twin Birch Dairy, LLC, which has constructed an anaerobic digester to treat manure on its 1,200-cow dairy farm. This farm is located in two sensitive Finger Lakes watersheds and is adjacent to a golf course and homes. To address the second solution, the Team developed a model for a regional manure digester facility in Cayuga County to handle the manure from a number of small dairies. Anaerobic digestion is generally a cost prohibitive for small dairies, however, a regional facility benefits from economies of scale.

In reviewing both the struvite precipitation option and the regional anaerobic digester option, the Team visited full-scale facilities in Europe to gather information. Specifically, the Team visited the Mestverwerking Gelderland facility in Putten, Netherlands that operates a veal manure treatment facility

that precipitates struvite prior to discharging the treated wastewater. The Team also visited the Ribe Biogas Plant in Ribe, Denmark, which anaerobically digests manure and industrial organic waste to generate biogas. This biogas is used to power the town's central power and heat plant.

Struvite can be formed by the controlled addition of magnesium to a waste stream containing ammonia and phosphate (PO_4). Historically, much of the concern with struvite precipitation has been in determining how to avoid struvite scale from forming in the piping and equipment of wastewater treatment systems, particularly anaerobic digesters. More recently the focus has shifted to controlled precipitation of struvite with the goal of phosphorous removal. Full-scale struvite precipitation systems are in use overseas for phosphorous removal at municipal, industrial, and agricultural (i.e. manure) waste treatment systems. Struvite research in the U.S. has focused on swine manure.

Two series of bench-top precipitation tests were performed using the filtrate of anaerobically digested dairy manure dewatering process. With the first series of tests, attempts were made to clarify the filtrate. The Putten facility had found that solids concentration over 1,000 mg/l reduced the level of struvite precipitation achieved. Although gravity clarification, vacuum filtering, pressure filtering, centrifugation and polymer addition were tested, none of these were successful in generating a clarified sample. Testing proceeded using the whole filtrate at optimum struvite precipitation conditions reported in the literature. The first series of tests included varying magnesium addition rates, end point pH levels, and magnesium oxide (MgO) and magnesium chloride (MgCl_2). Little difference in results was found between the two reagents and no trends could be discerned in the amount of phosphate removed versus the amount of magnesium added. The phosphate removal level did not exceed 20% in any of the test cases.

The second series of bench-top tests were adjusted to focus on enhancing the environment for struvite crystal formation. Studies reported in the literature indicated the formation of the crystal was more difficult than growing a small crystal into a larger one and that crystals formed more readily on rough surfaces than smooth ones. Therefore, galvanized washers and struvite crystals were added to the test beakers to improve the likelihood of struvite precipitation. In addition, the mixing rate was increased since struvite precipitation has been found to occur where the mixing energy was greatest. None of these changes had significant effect on the level of phosphate removal and the Series 2 tests ranged from between 0% and 16% phosphate removal.

Overall, the struvite precipitation testing indicated that it is not feasible to precipitate struvite from dairy manure. It is possible that the solids level in the filtrate hindered struvite precipitation, however, struvite has been successfully precipitated from whole swine manure, which would have similarly high levels of solids. It may be that the phosphorous is associated with solids fraction either adsorbed onto the surface of the solids or incorporated in the solids in some manner as to be unavailable for precipitation.

The second part of the study elevated a regional manure anaerobic digester. Anaerobic digestion has become the benchmark method for treating manures, addressing both pathogen and odor issues and producing digester gas, that can be used to generate heat and electricity. However, anaerobic digestion can be technically complex and, particularly for smaller dairies, cost prohibitive. When each dairy has its own system, economies of scale are not available, not only in employee and equipment costs, but also in the ability to effectively use all of the digester gas that is generated. The regional manure digester facility model includes collection of the manure on the farms, anaerobic treatment of the manure at the facility, return of the treated manure to the dairy farms and area crop farms, and beneficial use/sale of the digester gas generated at the facility. In order to keep the farmer's cost low, the facility will be operated as a non-profit organization and will take in outside organic wastes. Assuming the grant funding is available to cover the entire capital cost of the project (estimated at \$4.2 million), a tipping fee will be charged for collection of manure and delivery of digested manure (approximately \$1.50 per ton of manure) and for treatment of other organic wastes (approximately \$32 per ton).

Section 1
INTRODUCTION

New York dairy farmers are faced with manure handling challenges including odor, nutrients, and pathogens. Over the years, dairy herds have been growing in size and residential housing has been built closer to the farms. These trends have resulted in larger amounts of manure requiring handling and appropriate treatment, coupled with an increase concern about nutrient application to the land and odors in the area of the farm. Farms in Cayuga County, due to their location in several sensitive lake watersheds, need to be especially mindful of phosphorous loading. Farms that lack the land base to return the nutrients to the soil or are limited in their land application due to close proximity of lakes, streams, or sensitive neighbors would benefit tremendously from finding an affordable method for removing nutrients from their waste stream.

Most methods for removing nutrients from manure are expensive. Some of these high-cost alternatives available include two-stage biological treatment, membrane technology and constructed wetlands. Trucking manure to remote locations and anaerobic treatment are both energy-intensive, membrane technology is expensive and constructed wetlands require a large area and have seasonal limitations. Addition of lime or ferric chloride is used in municipal wastewater treatment plants to precipitate phosphorous and may be applicable to manure treatment systems; however, these chemicals will also precipitate many other ions and tend to produce a large amount of additional solids, that must be handled. Removal of phosphorous by precipitation of struvite has been used in Europe and Asia for both animal manures and municipal wastewater. Struvite is a mineral formed from three specific components: magnesium, ammonium and phosphate. Struvite (magnesium ammonium phosphate) precipitates as a compact crystal. Therefore, a small amount of easily settleable solids is generated in a struvite precipitation process. In addition, struvite is easily transported and can be used as a slow-release fertilizer.

Anaerobic digestion has become the benchmark method for treating manures. Although anaerobic digestion does not remove the nutrients, it addresses both pathogen and odor issues and produces digester gas which can be used to generate heat and electricity. However, anaerobic digestion can be technically complex and, particularly for smaller dairies, cost prohibitive. When each dairy has its own system, economies of scale are not available, not only in equipment and employee costs, but also in the ability to effectively use all of the digester gas that is generated. Cayuga and Onondaga Counties in upstate New York have many farms that are too small to economically use anaerobic digestion to treat their manure. Regional anaerobic digester facilities can provide economies of scale by combining manure from many small dairies. Regional manure digestion facilities are used successfully in Europe to manage manure and to generate renewable power. In Denmark, over 20 regional facilities are in operation providing a significant amount of renewable power.

The District and the Team investigated phosphorous removal by struvite precipitation and development of a regional manure anaerobic digester in a project funded in part by NYSERDA. The Team reviewed literature, visited full-size operating systems, performed lab scale precipitation tests, and evaluated the applicability of the struvite precipitation technology to digested dairy manure. The District hoped to apply the struvite removal technology at Twin Birch Dairy, LLC. The dairy has constructed an anaerobic digester to treat manure on its 1,200-cow dairy farm. This farm is located in two sensitive Finger Lakes watersheds and is adjacent to a golf course and homes. The Team also developed a model for a regional manure digester facility in Cayuga County.

This report presents the findings of the Team's study and includes discussion of the relevant background information and a literature review of struvite (Section 2), visits to operating manure treatment plants that include struvite precipitation and regional manure treatment (Section 3), bench-top struvite precipitation tests (Section 4), a model for a regional manure anaerobic digestion facility (Section 5) and a discussion of the results of the study (Section 6). Section 7 present recommendations on where to proceed after this study.

Section 2

STRUVITE PRECIPITATION: BACKGROUND AND LITERATURE REVIEW

BACKGROUND

Struvite is a chemical compound, magnesium ammonium phosphate, which can be formed by the controlled addition of magnesium to a waste stream that contains nitrogen in the form of ammonia and phosphorous in the effluent from a manure treatment system allows reduced land application field area. Second, struvite has a commercial value, either as a pure high-phosphorous fertilizer, or as a supplement to compost or other fertilizers.

Historically, much of the literature and concern with struvite precipitation has been in determining how to avoid struvite scale from forming in the piping and equipment of wastewater treatment plants and agricultural waste systems. As concern grows over the management of nutrients (especially phosphorous) in wastewater and manure, research on and application of controlled struvite precipitation has increased around the world. The Netherlands, Australia and Japan are among the first countries where a significant amount of research on struvite precipitation has been completed. Proprietary struvite recovery processes for municipal and industrial wastewaters have been developed both in the Netherlands and Japan. A non-proprietary struvite recovery process is treating veal manure at a full-scale plant in the Netherlands. Work in the United States has been largely research on pilot studies using hog manure.

STRUVITE PRECIPITATION CHEMISTRY

The chemistry of struvite precipitation has been extensively studied due to the need to prevent struvite from forming on the walls of pipes and pumps in recirculation streams at municipal wastewater treatment plants and flushed agricultural operations. Struvite precipitation occurs naturally in waste streams with the right environmental conditions.

To precipitate phosphorous, the phosphorous must be available as soluble phosphate (also referred to as orthophosphate). Organically bound phosphorous can be converted to phosphate in anaerobic treatment processes as well as in other biological processes.

Once the phosphorous is in the form of phosphate, it will bind with available cations, typically calcium, magnesium and ammonium, potassium and ammonium, or potassium and magnesium. Addition of calcium to a phosphate solution will form calcium phosphate. Addition of magnesium or potassium provides the opportunity to remove both ammonium and phosphorous. Struvite is an ammonium phosphate precipitate with either magnesium or potassium. "Struvite" generally refers to magnesium ammonium phosphate

(MAP), whereas “potassium struvite” refers to potassium ammonium phosphate. More information is available in the literature about the magnesium form of struvite than the phosphate form.

Struvite is typically found as $MgNH_4PO_4 \cdot 6 H_2O$, although at higher temperatures it can be formed as $MgNH_4PO_4 \cdot 1 H_2O$. The pH affects the reaction by changing the fraction of ionization of each component (e.g., ammonia vs. ammonium ion and Mg^{++} vs. MgO^+). Magnesium is typically added as magnesium chloride ($MgCl_2$), magnesium oxide (MgO) or magnesium hydroxide ($Mg(OH)_2$). Both MgO and $Mg(OH)_2$ raise the pH and can come close to the ideal pH of 8 or 9 depending on the dosage. The use of $MgCl_2$ with a base (typically caustic soda ($NaOH$)), allows the pH to be raised to the ideal level without over- or under-dosing magnesium.

The ability to remove some nitrogen and the compact nature of the struvite crystals has prompted some researchers to focus on struvite and potassium struvite as opposed to the other phosphorous removal methods. A full-scale manure treatment system with potassium struvite precipitation is in operation in the Netherlands. This system uses biological nitrification and denitrification to treat manure first. Then potassium ammonium phosphate is precipitated from the clarified effluent before it is discharged to the municipal sewer system.

There has been some debate among researchers as to the effect of the solids and fiber content in the struvite process. Research in the Netherlands has indicated that the solids level over 1,000 mg/l total suspended solids (TSS) adversely impacts struvite precipitation. However, researchers at the University of Tennessee are successfully precipitating struvite from whole hog manure with TSS levels of over 10,000 mg/l. Further research will be necessary to determine the effect of solids and fiber on struvite precipitation.

DEFINITIONS

The following terms are pertinent to phosphorous recovery chemistry:

Compound	Chemical Formulation	Synonyms
Struvite:	$MgNH_4PO_4$	Magnesium Ammonium Phosphate, MAP
Potassium Struvite:	$K_2NH_4PO_4$	Potassium Ammonium Phosphate
KMP:	$KMgPO_4$	Potassium Magnesium Phosphate
Hydroxyapatite	$Ca_5(PO_4)_3OH$	
Phosphate Rock	Various Forms	Apatite
Calcium Phosphate	Various Forms: $Ca_3(PO_4)_2$	

REACTOR CONFIGURATIONS

There are several different conceptual designs for struvite reactors. These vary depending on the level of treatment required and the market for the product formed. Companies in the Netherlands and Japan have developed sophisticated reactors, designed to form a uniform, larger pellet that can be marketed to the fertilizer industry or even within food processing or feed industries. Simple reactors have been developed for the industrial wastewater and animal waste industries as a method for removing phosphorous with less regard to the quality of the product formed.

The more complicated reactors are generally a column with a cone bottom. These reactors are generally a fluidized bed using a seed material that allows the struvite to form as a pellet within the reactor and to be removed periodically. In these reactions, the magnesium salt is added just upstream of the reactor or directly into the reactor. The influent flow can be introduced into either the top or bottom of the reactor. Mixing is provided by sparging air into the base of the reactor or using the influent flow to fluidize the bed. The heavier, larger pellets move to the bottom of the reactor where they are removed periodically. The operating conditions of the fluidized bed can be set to remove crystals of a uniform size. Pellets removed from the reactor freely drain to a low moisture content.

The simpler systems do not use a seed material and result in much variability in the precipitate. In these simpler systems, the magnesium salt is typically added at the beginning of a rectangular reactor with a rapid mixing section (using either a nozzle or air) followed by a quiescent section to allow the material to settle out in the downstream end of the tank. Thus the same tank is used as a reactor and as a rectangular clarifier. Manually raking or shoveling the crystals out of the tank has accomplished removal of the crystals from the small systems developed to date.

STATUS OF STRUVITE PRECIPITATION OVERSEAS

Please refer to the attached summary tables. Table 2-1 presents project experience around the world and Table 2-2 presents commercially developed reactors.

There are full-scale operating systems in the Netherlands (Crystalactor, two installations) and in Japan (Unitika-Phosnix, four installations). These installations treat industrial and municipal wastewater. There is also one full-scale engineered system operating on manure in the Netherlands. Numerous researchers are approaching the topic as a result of a European Union push to develop the technology as a method of recycling phosphorous. Europe does not have reserves of phosphorous to mine and the EU expects an eventual shortage of phosphorous.

Table 2-1. Summary of Struvite Experience

Project Location	Waste Type	Influent P Conc. (Mg/l)	Effluent P Conc. (Mg/l)	Reactants	Status
Netherlands Netherlands Netherlands	Veal slurry clarified effluent of nitrification/denitrification Potato processing anaerobic digester effluent Municipal Wastewater	300	30	MgCl ₂ MgCl ₂	Full-scale Full-scale Full-scale (inactive)
Japan Japan	Wastewater (1 industrial, 3 municipal) Municipal Wastewater sludge sidestream	50 to 111	70% removal	MgCl ₂ Seawater	Full-scale Unknown
Australia	Municipal Wastewater	61	5	MgO	Pilot scale
North Carolina	Hog Manure				Bench scale
Tennessee	Hog Manure			MgCl ₂	Bench scale
Illinois	Hog Manure				Bench scale (unsuccessful)
Missouri	Hog Manure				Pilot scale
California	Domestic Wastewater				Bench scale
UK UK	Municipal Wastewater (3 separate projects) Municipal Wastewater (3 separate projects)	10.3	0.7		Proposed research Bench scale
Italy Italy	RIM-NUT, Municipal Wastewater Municipal Wastewater (belt press liquid)	160	1 to 2 20	Quartz (FBR)	Proposed research Bench scale
Sweden	Municipal Wastewater				Proposed research
Korea Korea	Industrial: hazardous Waste Wastewater Domestic/Industrial Wastewater		97% Removal 39% Removal		Bench scale Bench scale

Table 2-2.
Commercial Struvite Processes and Designs
 Proprietary, pilot and full-scale systems

Crystalactor	Netherlands	Fluidized bed precipitator designed by DHV originally for removal of calcium phosphate from domestic sewage. Two full-scale reactors have been constructed for struvite precipitation from food processing and municipal wastewater.
Unitika Phosnix	Japan	Fluidized crystallization reactor designed for struvite precipitation from secondary sewage digester effluent. The wastewater is introduced at the base of air-agitated reaction tower. Caustic soda and magnesium chloride are added to precipitate struvite. Full-scale systems have been applied to industrial and domestic wastewater. Struvite is sold at \$200/ton.
RIM-NUT Ion-Exchange	Italy	Ion exchange followed by struvite precipitation. Applied to a fraction of domestic sewage in West Bari to meet stringent effluent limitations.
Kurita Water Industries	Japan	Fluidized bed crystallization column packed with phosphate rock particles. Sewage that is conditioned with calcium chloride and caustic soda passes upward through column. Hydroxyapatite is precipitated.
OFMSW/BNR	Italy/Spain	Three-stage process integrating anaerobic digestion of the organic fraction of municipal solid waste, biological nutrient removal and phosphate crystallization as either struvite or hydroxyapatite. Demonstrated at laboratory scale.
Sydney Water Board	Australia	Crystallizes struvite in an air-agitated bed reactor. Applied to supernatant from dewatering anaerobically digested sludge. Laboratory scale.
CSIR Process	South Africa	Crystallizes in a fluidized bed column at laboratory scale at sewage treatment works. Struvite and hydroxyapatite are precipitated.

STATUS OF STRUVITE PRECIPITATION IN THE U.S.

There are researchers working on struvite precipitation in the U.S. These are primarily within the hog industry. The interest in the hog industry is a result of the awareness of struvite scaling problems and the need to limit phosphorous in irrigated effluent. Research includes the following:

- North Carolina State University - research on hog manure, bench scale, beginning design of pilot scale reactor
- University of Tennessee - research on hog manure and dairy manure, pilot-plant for hog manure
- University of Illinois - proposed research on hog manure following unsuccessful anaerobic sequencing batch reactor (SBR)
- Midwest hog operation - research on hog manure, operating a pilot plant

VALUE OF RECOVERED STRUVITE

In pure form, struvite crystals contain 5.7% elemental N, 12.6% elemental P and 0% elemental K. On an agricultural fertilizer basis, the struvite analysis is 5.7% N, 29% P₂O₅, and 0% K₂O. Although the value of a natural 6-29-0 product is expected to be high, struvite is not currently a common commercial product that has a well-defined market value. At one point in time, WR Grace, a fertilizer company, produced struvite from its individual components. However, this form of production was found to be too costly for the value of the product. Beal et al. has estimated a value of \$206 per dry ton of struvite based on the nutrient value.

Potential markets for struvite include the natural foods and organic industry and backyard gardeners interested in environmentally friendly products. Due to its lower solubility level, struvite is considered a slow release fertilizer. The largest potential bulk market for struvite is the turf industry. There are approximately two million acres of managed turf grass in New York State. Turf requires a tremendous amount of magnesium and supplemental zinc and copper in addition to nitrogen, phosphorous and potassium. The turf grass industry in New York State is concentrated primarily in the metropolitan areas with a lot of turf grown on sandy Long Island.

There are two approaches for a farmer or farm group to generate revenue from the recovery of struvite. The first is to produce a relatively pure crystal and sell it to a fertilizer company or as a stand-alone product. The second is to blend struvite with harvested solid material (e.g. compost) and reap the benefit in terms of a higher price for the blended product.

Section 3

VISITS TO STRUVITE AND REGIONAL DIGESTER FACILITIES

Struvite precipitation and regional anaerobic digesters are commonly used in the United States; however these types of facilities are in full scale operation in Europe and Asia. In order to see full-size facilities and to speak with the design and operating staff of these facilities, the project team visited two facilities in Europe: one, the Mesterwerking Gelderland calf manure treatment facility in Putten, Netherlands, which precipitates struvite from the treated manure; and two, the regional manure digester in Ribe, Denmark. These facilities and the treatment process used at each facility are summarized below. Trip reports for each of these visits are included in Appendix A.

STRUVITE RECOVERY SYSTEM: MESTVERWERKING GELDERLAND IN PUTTEN, NETHERLANDS

The Mestverwerking Gelderland is a foundation (i.e. a non-profit company) that operates four manure treatment plants servicing 900 veal farms in the Gelderland province of The Netherlands. The foundation was established in the early 1980s when new regulations in The Netherlands imposed strict limits on manure application to farmland. Most of the farms in this area are situated on sandy soil and have only a fraction of the land needed to dispose of the manure they generate. The foundation provides for treatment and disposal; the farmers contact separately for transportation to the treatment facilities.

In total, the four plants receive 660,000 cubic meters (175 million gallons) of veal calf manure from approximately a half million calves annually. All four plants have facilities for biological nitrification and denitrification, with discharge of the treated liquid to local municipal wastewater treatment plants. Three of the plants remove phosphorous by adding lime to the nitrification reactor to precipitate out calcium phosphate. The Putten plant removes phosphorous by precipitation of struvite by adding magnesium oxide to the denitrified clarified effluent.

The Putten plant is located about 50 km east of Amsterdam, in the northerly part of Gelderland province. The site covers about two acres, and is surrounded by a narrow wooded buffer. It receives about 150,000 cubic meters (40 million gallons) of manure per year. The plant converted to using magnesium oxide addition rather than lime addition for phosphorous control because the lime addition precipitates more than just calcium phosphate and the solids generated are more difficult to dewater than the struvite. It is estimated that the plant saves about 1 million guilders (approx \$400,000) in solids transport costs each year by precipitating struvite.

At the Putten plant, the influent manure is treated in a biological nitrification and denitrification system, including solids removal prior to the struvite precipitation. This treatment process is thought to convert nearly all of the organic phosphorous to orthophosphorous, the form needed for struvite precipitation. The influent to the struvite precipitation process is a clear liquid with a relatively low suspended solids level of 100 mg/1 total suspended solids. Struvite is precipitated in three struvite reaction tanks in series; although it is thought that a single tank would be sufficient. Magnesium oxide is mixed with the effluent in a small mix tank where a 5% slurry is made. The slurry is pumped to the first of three struvite reaction tanks. Each tank has a single mechanical mixer. The slurry does not dissolve completely when it is first added to the reactor but as struvite is formed, taking magnesium out of the solution, more magnesium is dissolved. Since the flow through the plant is nearly constant, the operators are able to set the MgO feed pump once per day at a level that results in a small excess Mg dose. No separate pH control is needed. From the struvite reaction tanks the wastewater flows to a conventional gravity clarifier. Struvite is concentrated in the underflow at about 4% solids; the overflow is the clarified treated manure water that is discharged to a local wastewater treatment plant. The underflow is directed to a storage tank where it is gravity thickened. The plant attains 15% to 20% solids by simple gravity draining. They expect that up to 40% solids could be obtained through mechanical dewatering, such as with a filter press or centrifuge. The plant finds that struvite settles and dewateres well and is free flowing and non-hygroscopic in the dry state. While the foundation could use its centrifuge to dewater the struvite to 40% solids, it is easier to handle at 15% to 20% solids.

The struvite recovery system removes >95% of the total phosphorous from 600mg/1 to less than 30mg/1.

REGIONAL MANURE DIGESTER IN RIBE, DENMARK

Denmark Background

Interest in developing biogas facilities started growing in Denmark in the 1970s with the energy crisis. More recently, the driving force for the Kyoto agreement was concern about the environment but this also brought attention to improving agricultural practices and handling of wastes. This is important in Denmark in particular, since in addition to the 4 million people in the country, there are 6 million pigs. Dairy and swine farms produce 40 million tons per year of manure slurry (roughly 1/3 dairy, 2/3 swine).

The Danish national approach to these issues coordinates environmental issues with energy and agricultural policies. It encourages the use of regional digester facilities for manure management and green energy production. One of the results of these policies is that many regional digester plants buy diesel fuel to heat their digester rather than using the biogas they are producing, because the biogas is more valuable as a green fuel to power plants.

Ribe Biogas Plant

The Ribe Biogas Plant, built in August of 1990, uses anaerobic digestion of manure and industrial organic waste to generate biogas that powers the town's central power and heat plant. The facility collects manure from its member farms in three trucks (one larger and two smaller). These trucks off-load the manure into feed tanks and then reload with digester effluent. The digester effluent is transported to storage tanks near the farm fields where it will be spread. In this way the transport trucks operate with a full load as much as possible. These trucks unload manure and reload digester effluent in a two-bay building. During unloading and reloading the doors of the building are closed.

Industrial and food wastes are also taken into the facility and transferred to a separate feed tank. These wastes include outdated foodstuffs, fish processing wastes, slaughterhouse wastes, etc. Long term contracts are set up with the industrial and food waste sources to ensure a constant feed composition to the anaerobic system.

Feed from the two inlet waste tanks is pumped into three parallel anaerobic digesters. The average feed has 7% dry matter while the effluent has approximately 4.5% dry matter. The plant has an overall capacity of 150,000 T/year with 120,000 T/yr coming from manures and the remaining 30,000 T/yr from other organic sources. The digesters are fed every two to four hours.

The digester effluent is stored in two in-ground covered tanks. These tanks are not aerated. Digester gas is pulled off these tanks as well as the digesters. The gas is stored in a balloon tank with a four-hour capacity. Ferric chloride is added to the process to reduce the sulfide content of the biogas. The biogas is continuously monitored for methane and sulfide content. Producing a consistently high quality digester gas is a high priority of the facility since this is the facility's main income. The feed to the digester is carefully controlled to maintain maximum efficiency of the biogas production.

The digester effluent is transported from the storage tanks at the plant to storage tanks located near the fields on which it will eventually be spread. These field storage tanks are standard pre-engineered open-topped tanks made of precast concrete panels and ribs. This style tank could be seen throughout Denmark and was clearly the standard cost-effective style tank. These tanks store nine-months worth of digester effluent. Danish law allows spreading digester effluent only during the growing season. It also requires a 10 to 15 cm thick floating layer at the top of the biosolids storage to prevent ammonia from volatilizing. The tank examined had a layer of lightweight expanded clay aggregate (LECA) pellets that served as a barrier for ammonia loss. Approximately 90% of the ammonia is retained in the biosolids. These tanks are owned by the Ribe Biogas Plant. The government provided approximately 40% of the construction costs for these tanks.

Biogas is transmitted via low pressure lines to a power plant 3 km from the Ribe Biogas Plant. This power plant provides to the grid and heat to the city of Ribe. The Ribe Commune (communes are similar to US counties) has approximately 17,000 people. The plant also uses natural gas as necessary but, due to government incentive, the plant first uses all of the approximately 15,000 m³/day of biogas generated at the Ribe biogas Plant. The power plant produces 2 MW of electricity and 1.8 MW of heat from the biogas. The hot water is pumped to town residences and businesses that use it for heating the buildings and for their hot water needs. The power plant is owned by a separate organization from the Ribe Biogas Plant. The power plant produces a total of 8 MW of electricity.

Ribe Biogas Plant is organized as a cooperative company or “Limited” company. The ownership of the plant is divided among member farms and other interests as follows:

Member farms:	40%
Fish processing	20%
“Green” investors	20%
Insurance companies	20%

The member farms consist of approximately 80 animal-producing farms and 40 “agri-farms” (farms growing produce but without animal production). Of the animal-producing farms, 70% are dairy farms and 30% are pig farms. The farms involved in the original project each put up \$2,500 at the start of the project for a total of \$100,000 from farms. The facility cost approximately \$5.5 million to build including the storage tanks at the farm fields.

The Ribe Biogas Plant derives income from gate fees (tipping fees) for the industrial waste it processes and from sale of the biogas to the power plant. It is responsible for the collection of raw manure and distribution of the effluent biosolids. The plant owns the biosolids storage tanks and rents them to crop farmers at approximately \$0.50 per cubic meter storage per year. Several farmers may share space in a single tank. The farmers are responsible for ensuring equitable distribution of the biosolids. The crop grower also pays for the biosolids at approximately half the price of commercial fertilizer on a pounds of N-P-K basis. The manure-producing farms do not pay for receiving biosolids and actually earn income for the difference in the manure they supplied and the biosolids they received (i.e. income from the excess biosolids which are sold to the crop farmers). There is a credit/fee calculation to adjust the compensation for the water content of the manure.

Danish Biomass Plants

There are twenty centralized biomass plants in operation in Denmark. Biogas plants in Denmark are all organized and operated somewhat differently. Some are more cooperative (farmer-owned) than others. The specific contracts between the entities set quantity and quality of feedstock and product, frequency of pickup, delivery and sampling etc. The main issues for a successful biogas plant are:

- Biomass Availability – either manures or food wastes, for a period of 10 to 20 years (i.e. the life of the plant); and
- Heat users in the area of the power plant. Not only seasonal residential users but year-round industrial users.

In addition, the need for farms to contribute significantly to the cost of any cooperation facility was emphasized. In Denmark, the biogas plants that require farmer contribution have worked better than those that have been provided by other funding. If the farmers do not feel they have an investment in the facility, they are less likely to treat the enterprise as a business and will not be invested in making the facility work.

Logistics are a large part of a successful biogas program. Optimizing the placement of tanks to minimize hauling distances, and coordinating manure pick-up trips with effluent delivery trips to minimize the time trucks travel with no load, are important to maximize profits of the plant. Trips must also be coordinated with farm needs to ensure a steady removal of manure and delivery of effluent.

In Denmark residential housing is kept close to village centers. Land use restrictions do not allow many free-standing homes in the country that are not related to farmsteads. This provides advantages over a more dispersed population such as exists in the United States. Odor and hauling manure over country roads are less likely to be issues. Small villages provide concentrated areas for heat distribution to residential housing.

Section 4

STRUVITE PRECIPITATION TESTING

Experimentation with dairy manure to precipitate struvite is presented in this section. Two series of laboratory tests were performed. Originally, the experimental design included collecting samples from two dairies using anaerobic digestion and performing the same tests on samples from both of the dairies. However, due to the results of the first set of tests, the experimental design was adjusted significantly for the second set of tests. For this reason, the two series of tests are presented separately below.

BACKGROUND AND THEORY

Much research has been done on the thermodynamics of struvite precipitation over the years due to the problem of struvite scale forming at wastewater treatment plants with anaerobic digestion systems and to the fact that kidney stones are largely made of struvite. As indicated in Section 2 of this report, struvite is made up of ammonium, phosphate, and magnesium ions in a 1:1:1 ratio. Struvite precipitates when the concentrations of the constituent ions become supersaturated in the solution. Supersaturation occurs when the point of solubility is exceeded. This point is defined by the solubility product constant as follows:



where $\{\}$ indicates the ion-activity concentration. The ion activity concentration equals the analytical concentration times the activity coefficient (a function of the ionic strength of the solution). For dilute solutions, the ionic strength correction is small enough to ignore, resulting in the following solubility equation:



where $[]$ indicates the concentration of the ion in the solution. Solubility products are generally reported as the negative log of the solubility product or pK_{sp}. Various values of pK_{sp} struvite have been reported in the literature, ranging from 12.6 to 13.26 (Ohlinger et.al, 1998) (Buchanan et. al.). Historically a pK_{sp} struvite of 12.6 has been used (reported by both Ohlinger et. al. 1998 and Buchanan et. al.) although this solubility factor ignores ionic strength corrections (Ohlinger et.al, 1998). Buchanan et. al. documents an apparently correct factor of 13.15 originally published by Taylor in 1963.

Rather than model the precipitation level based on solubility equations, many struvite precipitation researchers have taken the approach of basing experiments on the stoichiometric amount of magnesium added in relation to phosphorous. Burns et al. achieved a 91% phosphate reduction by adding magnesium at a rate to achieve a 1.6:1 magnesium-to-total-phosphate ratio and adjusting the pH to 9.0 s.u. Beal et al used a twice stoichiometric rate of magnesium to attain 88% phosphate removal with swine manure. Conversations with Dr. Olaf Schuiling (a consultant to the Mestverwerking Gelderland facility in Putten) recommended magnesium be added at a 110% of the stoichiometric amount. This study took the approach of using the stoichiometric ratio.

The pH level of the solution is an important factor in the level of struvite precipitation that occurs. Each of the ions that make up struvite will also form other complexes, both with each other and with hydrogen and hydroxide ions. For instance, phosphate can be in the form of PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- , or MgH_2PO_4 ; ammonia can be in the form of ammonia (NH_3) or ammonium (NH_4^+); and magnesium can form magnesium hydroxide (MgOH^+) and other forms with phosphate. The pH level of the solution impacts the amount of these parameters in the NH_4^+ , PO_4^{3-} , and Mg^{2+} forms needed to exceed the struvite solubility product and cause struvite to precipitate. The literature reports minimum struvite solubility (e.g. optimum struvite precipitation conditions) at pH levels of 9.0 (Olinger et al.) (Buchanan et al.) and 9.0 to 9.5 (Miles and Ellis).

This study focused on anaerobically digested dairy manure since treatment would convert more of the total phosphorous to the phosphate ion. Beal et al. also found anaerobically digested swine manure to have higher struvite precipitation rates than undigested manure. The study evaluated only magnesium chloride and magnesium oxide as magnesium sources because several sources indicated difficulty with the low solubility level of magnesium hydroxide. In addition, since the percentage of magnesium in dairy manure that is available is not known, a wider range of magnesium doses was investigated.

SERIES 1 BENCH TOP TESTS

Objectives

Bench scale trials conducted on anaerobically digested dairy manure to study phosphate removal by magnesium addition and subsequent struvite precipitation. Digested manure from Aman's Dairy was tested for the first series of tests. The primary objectives of the first series of bench top tests was to determine phosphate levels in separated and whole effluent, and what percentage of the phosphate can be recovered as struvite. In addition to reaching these primary goals, secondary objectives were set; these included the following:

- Evaluate phosphate removal using $MgCl_2$ and MgO addition to determine impacts of using different reagents;
- Evaluate effects of reagents and magnesium dosages on struvite precipitation;
- Determine level of phosphate removal that can be attained and the equivalent struvite precipitation rate;
- Determine the impact of not adjusting pH to simulate operations in which pH adjustments are neglected or unfeasible;
- Review effects of solids interference on precipitation of struvite;
- Determine settling rate of the struvite; and
- Determine struvite purity and NPK analysis.

Experimental Design

The experiment consists of three phases: Sample Collection and Handling; Sample Preparation; and Struvite Precipitation. Sample collection and handling involved collecting a several-gallon sample of manure from the dairy. The point of collection was the filtrate stream from a screw-press dewatering anaerobically digested manure. The sample was collected by a District employee, packed on ice and shipped overnight to the laboratory at Wright-Pierce. At Wright-Pierce, the sample was stored at 4°C until used.

Sample preparation entailed mixing the entire sample, preparing the sample for the bench tests, and taking triplicate samples for analysis of initial conditions. The original plan was to prepare the raw sample by composting the samples shipped (samples were shipped in several 1-gallon containers) and gravity settling (if feasible) or filtering to obtain samples with less than 700 mg/L TSS for use in the precipitation tests. To most closely simulate large-scale plant operations, gravity settling of the raw sample was preferred, if feasible, for obtaining adequate clarified sample volumes.

To determine the sample volumes needed to generate a sufficient clarified sample for the precipitation tests, to establish the most favorable clarification methods (gravity settling vs. filtration), and to firmly establish the techniques and feasibility of the procedural plan described below, a small sample (~ 1 gallon) was obtained and subjected to sample preparation procedures. This pre-testing sample was not analyzed for the concentration of any compounds. As is discussed below, these separation techniques did not produce a clarified sample and the decision was made to proceed with the precipitation tests with the whole sample.

The struvite precipitation tests included the addition of magnesium and pH adjustment to cause struvite to precipitate. Two reagents ($MgCl_2 \cdot 6(H_2O)$ and MgO) were used as magnesium sources to study the variation in phosphate removal as a function of magnesium concentration as well as

differences arising from the use of dissimilar reagents. The initial sample used in the testing was analyzed to provide baseline component measurements for comparison to post experiment levels and to verify that the phosphorous level was within the expected range for digester effluent (i.e. representative of typical operations). These parameters and their associated symbols or abbreviations are listed in Table 4-1.

Table 4-1. Compound Analysis

PARAMETER	SYMBOL
Orthophosphate	PO ₄
Total Phosphate	P
Calcium	Ca
Magnesium	Mg
Potassium	K
Ammonia-Nitrogen	NH ₃ -N
Total Kjeldahl Nitrogen	TKN
Total Suspended Solids	TSS
Conductivity	Cond
Alkalinity	Alk

The phosphate level in the sample used in the tests dictated the amount of additional magnesium needed for the experiment. Table 4-2 summarizes the testing conditions and parameter measurements planned for the first series of tests and those eliminated due to the difficulty with clarifying the sample. The initial pH, conductivity and temperature were recorded in each trial. The final pH, temperature, and volume of NaOH added in each precipitation trial were also recorded. Most of the trial runs were intended to study the relationship between magnesium concentration (via addition of MgCl₂ and MgO) and struvite precipitation, and were only analyzed for dissolved orthophosphate (PO₄²⁻-P) and conductivity to allow a smaller trial sample volume. Several 2-liter trials were planned to verify the optimum magnesium dosages and to allow post struvite precipitation analysis of all the parameters given in Table 4-1.

Table 4-2. Series 1 Sampling Plan

Trial No.	MgCl ₂ % Stoch	MgO % Stoch	pH Adjustment		Parameters										Settling Test			
			NaOH	None	Ortho P	Total P	Ca	Mg	K	NH ₃ -N	TKN	TSS	ORP	Alkalinity				
I	50%		pH = 9.0		X												X	
^a II	80%		pH = 9.0		X												X	
III	100%		pH = 9.0		X												X	
^a IV	115%		pH = 9.0		X												X	
V	130%		pH = 9.0		X												X	
VI		50%	pH = 9.0		X												X	
VII		100%	pH = 9.0		X												X	
VIII		130%	pH = 9.0		X												X	
^b IX	Slightly more solids	100%	pH = 9.0														X	
^b X	More solids	100%	pH = 9.0		2X												X	
^b XI	Increasing solids	100%	pH = 9.0		2X												X	
^b XII	Whole effluent	100%	pH = 9.0		2X												X	
XIII		100%		X	X												X	
XIV		130%		X	X												X	
^c XV	X		pH = 9.0		X												X	
^c XVI	X		pH = 9.0		X	X	X	X	X	X	X	X	X	X	X	X	X	X
^c XVII		X	pH = 9.0		X	X	X	X	X	X	X	X	X	X	X	X	X	X

^a The graduation of MgCl₂ samples were reduced to allow for more in-depth trials with MgO.

^b Unable to achieve clarification, the partial solid trials were substituted with additional MgO trials.

^c Because it was not possible to distinguish the optimum concentration, duplicates at the optimum magnesium addition (denoted by an “x”) could not be run.

Due to difficulties in clarifying the manure sample and in achieving any significant level of struvite precipitation, several of the tests included in the original experimental design were not performed. These tests are indicated with footnotes in Table 4-2 and are discussed below:

- Four trials (nos. IX, X, XI, and XII) were designed to study the effect of manure solids concentration on the level of struvite precipitation by combining clarified samples with increasing amounts of the solids previously separated by gravity settling/filtration. Due to the inability to clarify the initial sample from the farm, the sampling plan was modified to eliminate these trials.
- Trial nos. XVI and XVII were designed to be run using 2-liter trial volumes to test for an extended list of parameters as shown in Table 4-1 and listed in Table S-2. These trials were to be conducted at the conditions that produced the optimum level of struvite precipitation in the smaller tests. Comparison of these post-precipitation measurements with the same parameters measured prior to precipitation would reveal the effects of magnesium addition and struvite precipitation on the sample chemistry. These tests were submitted with the additional trial runs to verify the initial tests performed.
- The trials at 115% and 80% of the stoichiometric magnesium addition were eliminated to allow additional replications of individual trial runs.

Procedures

A detailed list of procedures is provided in Appendix B. Bench-top analysis was conducted in single-day batches, taking a total of three days to complete all the testing. The entire volume of samples for the days' testing was set out on the bench top to reach room temperature, around 22°C. The magnesium reagents were weighed out, sample was measured into beakers, and a titration station was set up. Equipment was calibrated and initial conditions were read on all the samples prior to starting the precipitation tests. Tests were performed according to the procedures and final conditions were recorded and samples gathered and analyzed.

Results and Discussion

This section discusses the results of both the sample clarification and the struvite precipitation tests and the impacts these results had on the testing as it progressed.

Sample Clarification. Prior to receiving the several-gallon sample needed for the bench top study, a pre-sample was collected to verify sample preparation methods. The primary goal of this phase of the project was to determine how best to clarify the digested dairy manure to obtain the clarified fraction for use in the struvite precipitation tests. As discussed above, the original plan was to gravity clarify or vacuum filter the whole sample to obtain a clarified fraction. The following methods were explored; however, none were completely successful.

- *Gravity Clarification.* A portion of mixed sample was transferred into a bottle and stored in the refrigerator overnight to gravity clarify the sample. The sample did not show any signs of settling after 12 hours.
- *Vacuum Filtering.* An attempt to vacuum filter through Whatman #40 paper was completely unsuccessful
- *Pressure Filtering and Centrifugation.* A portion of the sample was shipped to Maine Environmental Labs in Yarmouth, ME for pressure filtration beyond Wright-Pierce's in-house capabilities. Pressure of 75 to 90 psi yielded only several drops of clear liquid. With sample remaining, centrifugation was tried. After 15 minutes no observable phase separation was apparent with the exception of a few grit particles that appeared at the bottom of the tube.
- *Polymer Addition.* Polymers were added to the sample to encourage flocculation of the solids. The following polymers from Calgon were bench tested at the Wright-Pierce laboratory: CAT-FLOC, CAT-FLOC-L, POL-E-Z 652, and POL-E-Z 692. Approximately 1 ml of polymer was added to 500 ml of water, mixed thoroughly and allowed to stand for 30 minutes to allow activation. Polymer was added in doses from 1 to 100 ml per 500 ml of sample and observed for any visible coagulation after shaking vigorously. These tests did not reveal any visible coagulation. Unable to achieve separation in the Wright-Pierce laboratory, General Alum and Chemical (GAC), in Searsport, ME was contacted and sent a fresh five-gallon sample for them to determine the best polymer to use. GAC was unable to clarify the sample. They indicated that the high conductivity (14,000 ohms/cm) of the sample was significantly beyond the range for which polymer flocculation is effective on sludge. GAC did not try alum since it would remove phosphate from solution. GAC recommended further testing using a diluted sample, hoping a lower conductivity would enable some degree of flocculation. This suggestion was not tried as adding a large quantity of fresh water to the manure to decrease the conductivity level would not be feasible with a large scale system on a farm.
- *Dilution and Alum Addition.* Even though alum will remove phosphate, sample clarification by alum addition was tried. A dose of 5 ml of commercial alum to 100 ml of undiluted sample caused the entire sample to foam up. Smaller doses caused only a fraction of the sample to foam up. Similar results were achieved using alum chloride though the dose required for similar results were higher. A 200 ml dilution of 1 part sample to 3 parts water and a 5 ml alum dose similarly caused a foaming action while lifting the solids to the surface. Over a period of a few hours, the foam volume was condensed to 50 ml and clarified liquid appeared below the foam blanket (approx. 150 ml). It was also noted that a white precipitate had settled to the bottom of the beaker. The gas/air bubbles in the sludge foam were uniform and about 1/16 inch in diameter. The foaming action was attributed to the acidification of the sludge causing carbon dioxide to be driven out of solution. Since such a high dose of alum was added, it was assumed that a significant portion of the phosphate would be removed. Due to this high level of foam generated, this method of clarification was not pursued further.

Struvite Precipitation Tests. Being unable to achieve clarification, the struvite tests went forward using the whole digested manure effluent. The tests to determine the impact of different levels of solids in the solution were eliminated from the test series.

Initial Conditions. Three samples of the initial manure sample were taken and analyzed for the parameters listed in Table 4-1. Table 4-3 lists the results of these analyses and the typical levels found in dairy manure as outlined in the ASAE Standards. For all of the parameters, the variation among the three samples was well within expected analytical accuracy for a high solids sample. The phosphorous, calcium, magnesium and potassium levels of the manure samples are roughly

half the “typical” dairy manure concentrations indicating that the manure has been diluted by wash water. The total solids of the sample are significantly lower than the ASAE manure level and the ammonia-nitrogen level is higher than the ASAE manure level reflecting the anaerobic treatment of the manure.

Test Results. The primary objective of the precipitation tests was to determine the level of phosphate removed by the addition of magnesium. Figure 4-1 presents the phosphate removal rates in graphic format. See Appendix C for tabular listing of the results. As Figure 4-1 indicates, the removal rates of phosphate were not good and, in fact, the amount of phosphate appeared to be higher than the initial starting point in roughly a third of the tests. In addition, multiple tests done at the same conditions did not give the same results. Because of the poor results in meeting the primary objectives of the test, almost none of the secondary objectives could be evaluated.

Duplicate analyses of the same trial run indicated that the phosphate analytical testing was reproducible.

Table 4-3. Series 1 – Initial Conditions

Parameter		Initial Manure Sample			Dairy Manure ¹
		Sample A	1B	1C	
PO ₄ ⁻ P	mg/l	406	408	401	709
Tot P	mg/l	505	505	505	1,093
Ca	mg/l	865	904	904	1,860
Mg	mg/l	363	385	388	826
K	mg/l	1,475	1,519	1,534	3,372
NH ₃ ⁻ N	mg/l	2,870	2,716	2,828	919
TKN	mg/l	4,998	4,970	5,026	5,233
TS	mg/l	48,430	46,750	46,790	139,535
TSS	mg/l	20,000	21,000	18,333	-
pH	s.u.	8	8	8	7
Cond	umhos	98,500	94,700	97,700	-

¹From Manure Production Standards listed in ASAE Standards
Converted to Concentrated using total manure mass values.

Magnesium Dosage. Samples were dosed at different stoichiometric ratios in a large range. Dosing at different concentrations would theoretically show a wide range of removal, and provide insight to the best dosage for maximum phosphate removal. Magnesium chloride was added at concentrations of 50, 100, and 130% of the stoichiometric magnesium level, based on the initial phosphate concentration. Likewise a range was used with the magnesium oxide addition, but broadened to span 50 to 200% the stoichiometric magnesium amount.

Figure 4-1 presents a graph of the end-point phosphate concentration versus the percent stoichiometric magnesium added. The test results indicated little difference between the two magnesium reagents, and that higher magnesium dosage did not appear to increase phosphate removal. No trend could be seen, and repeat-tests conditions (reagents and doses) produced different removal rates. It was not possible to identify an optimum level of removal, or to really quantify that struvite precipitation occurred. It is possible that the range of magnesium addition was not high enough to show any removal or that too much of the phosphorous was in an unavailable state, making the dosage level inconsequential. The phosphorous removal rate did not exceed 20% for any of these cases. At this rate of phosphorous reduction, the impact on farm manure handling options would be minor.

While the optimum conditions as reported in literature for the precipitation of struvite were recreated in the laboratory with the manure from the Aman Dairy, it was difficult to definitively state why there was no apparent removal of phosphate. The inconclusive evidence from the first round of bench-top experimentation prompted a re-evaluation of the laboratory tests.

PH Effects. After reagent was added and allowed to mix with the sample, the pH was rebalanced, to reach 9.0, the optimum level for struvite precipitation recorded in literature. The amount of NaOH used to return the sample to 9.0 was recorded so that an estimate could be made of the amount of chemical that would be required if operating on a full-scale basis. The pH dipped about 0.3 standard units after magnesium was fully mixed into the sample.

Two magnesium oxide samples were run without changing the pH. The final pH level of the sample was 8.4 and 8.3 standard units. At magnesium doses of 100% and 130% the phosphate removal was 5% and 11% respectively, while the same concentrations with pH adjustments had 13% and 18% removal, indicating that the pH adjustments would be beneficial when using magnesium, oxide as a precipitation reagent.

SERIES 2 BENCH TOP TESTS

The first round of bench-top testing produced unsatisfactory results. It was thought that the level of solids in the sample may have impacted these results. The team explored a new method of solids removal using a Jannanco membrane process. A sample was shipped to Jannanco, LLC for testing, but they were unable to clarify without adding polymers that removed the phosphorous. The second round of testing proceeded using the whole effluent.

Objectives

The goals for the second round of bench top testing focused on precipitating struvite at some significant level. Due to the results of the first round of tests, no testing was aimed at subtle changes in dosage or methods.

Experimental Design

Based on the outcome of Series 1 testing, refinements to the procedure were made to enhance the environment for crystal formation. Based on further review of literature and crystal formation theory, several changes to the experimental procedures were made. Formation of crystals can be broken into two stages: crystal formation (or nucleation) and crystal growth. Modifications were made to the precipitation tests to improve both of these stages of crystallization. Specifically the following changes were made:

- Addition of struvite to the initial mixture. Ohlinger et. al. (1999) reports that struvite formation is the rate limiting step, and that crystal growth typically occurs at greater rates than formation. One method to improve crystallization is to seed the solution with a surface upon which the crystals can grow. Several techniques have been successfully used with struvite, including addition of sand or struvite to the solution to provide a base for crystal growth. Struvite crystals were added to the initial mixture in each test of seeded crystallization.
- Addition of a galvanized steel washer. Ohlinger et. al. (1999) also found that struvite crystals form more readily on rough surfaces than on smooth ones. To increase the chance of struvite formation, a galvanized washer was added to the beakers used in the precipitation tests. Galvanized steel provides a rougher surface than the glass beaker used in the tests.
- Increase in mixing rate. Much of the early struvite literature focuses on how to prevent struvite precipitation in anaerobic digester equipment and piping. Struvite precipitation was found to occur to the greatest extent where the mixing energy was the greatest, such as at the discharge of pumps and at pipe bends. Crystal growth can be limited by the inability of the constituent ions to be in contact with one another. High mixing energies bring the constituent ions into close contact and provides energy for precipitation to occur. High mixing rates were used during the precipitation tests.

The second round of testing used the same two reagents ($\text{MgCl}_2 \cdot 6(\text{H}_2\text{O})$ and MgO) for the magnesium source as the first round of tests. The test used a magnesium dose of 200% of stoichiometric amount to ensure that adequate magnesium was available. Also remaining the same from the Series 1 bench top study design were the pH adjustment, mixing, choice of magnesium reagent, and settling activities. The volume of each individual test was tripled from 200 ml to 600 ml. This allowed sufficient volume to allow settling

after the mixing period. At the end of the test run, the mixture was allowed to settle and samples were drawn from two locations for analysis, one sample from the top fourth of the beaker and one from the bottom fourth of the beaker.

Procedures

The procedures used in the second round of testing was nearly identical to the first round of testing. The sample was collected in the same manner with the exception that the sample was taken from the filtrate of Twin Birch Dairy’s anaerobic digester effluent dewatering process. This sample was used directly in the precipitation tests. The basic test procedures are provided in Appendix B.

Results and Discussion

As with the Series 1 tests, the initial sample for the Series 2 tests was analyzed for a variety of parameters. The Series 2 tests used filtrate from the Twin Birch Dairy anaerobic digester dewatering process. Table 4-4 summarizes the initial condition of the filtrate. The phosphate levels were within the expected range.

Table 4-5 lists the test conditions and parameters measured in the Series 2 tests and Table 4-6 summarizes the results of the Series 2 tests. Trail 5 which tested inclusion of only struvite crystals and a metal object addition showed no real change from initial conditions to final conditions nor any gradation between top or bottom sample locations. This indicated that the struvite did not dissolve, adding phosphate to the solution, nor did the struvite or the metal object provide a surface for struvite precipitation without the driving force of addition magnesium. Therefore, the addition of struvite and a metal object had no impact on the solution but may have acted as a catalyst with the addition of magnesium.

Table 4-4. Series 2 – Initial Conditions

Parameter	Initial Manure Sample			Dairy Manure ¹	
	Sample A	1B	1C		
PO ₄ ⁻ P	mg/l	299	275	299	709
Tot P	mg/l	460	460	1,237	1,093
Ca	mg/l	1,326			1,860
Mg	mg/l	800			826
K	mg/l	3,130			3,372
NH ₃ ⁻ N	mg/l	284			919
TKN	mg/l	1,753			5,233
TS	mg/l	47,360			139,535

¹From Manure Production Standards listed in ASAE Standards
 Converted to Concentration using total manure mass values.

Table 4-5. Series 2 Sampling Plan

Trial No.	MgCl ₂ % Stioch	MgO % Stioch	Struvite Crystals	Metal Object	pH Adjustment		Parameters			
					NaOH	None	Ortho P	TS	ORP	Alkalinity
1	200%		X	X	pH = 9		X	X	X	X
2		200%	X	X	pH = 9		X	X	X	X
3	200%				pH = 9		X	X	X	X
4		200%			pH = 9		X	X	X	X
5			X	X	pH = 9		X	X	X	X

Table 4-6. Series 2 Test Results

Trial Number	Final pH s.u.	Sample Location	Phosphate Concentrations		
			initial mg/L	final mg/L	removal %
1	8.97	Top	291	293	-1%
		Bottom	291	251	14%
2	9.01	Top	291	254	13%
		Bottom	291	254	13%
3	8.95	Top	291	263	10%
		Bottom	291	263	10%
4	9.03	Top	291	263	10%
		Bottom	291	245	16%
5	9.01	Top	291	293	-1%
		Bottom	291	293	-1%

Phosphate removal for the four tests involving magnesium addition ranged between 0% and 16%. There was no trend between top and bottom samples. Data to support whether struvite had been created and allowed to settle to the bottom were inconclusive based on this method. Assuming struvite was formed, a 16% reduction in phosphate (and thus a lower percent removal of the total phosphorous) is likely not significant enough to warrant addition of struvite removal equipment at a dairy farm.

CONCLUSIONS

The testing that was performed in the Wright-Pierce laboratory indicates that it is not feasible to precipitate struvite under these testing conditions. Most likely the largest hindrance to crystal formation was the use of whole effluent. Work with veal manure in Europe has found that solids levels impact the struvite precipitation process. However, work in the U.S. with whole swine manure has successfully precipitated struvite. It may also be that the phosphate is associated with the solids fraction either adsorbed onto the surface of the solids or incorporated in the solids in some manner as to be unavailable for precipitation.

The precipitation testing also found that it is very difficult to clarify the filtrate from anaerobically digested dewatered dairy manure. The solids levels and ion levels in the manure contributed to a conductivity too high for many polymers to have any effect on clarification. The unsuccessful use of gravity settling indicates that the solids material has a specific weight almost identical to that of the liquid. This also hindered centrifugation from being successful. Likewise, the attempts to filter the sample, even under pressure, were not practical even at a bench-top scale because filters plugged instantly due to the mass-to-liquid-volume ratio. The clarification focus in the second round of testing with Jannanco involved the use of their membrane filters. While Jannanco tried a bench-top gravity filter through their filters, it took too long to get even 100 ml of clarified sample.

Section 5
REGIONAL MANURE ANAEROBIC DIGESTER

A regional manure anaerobic digester can provide economies of scale by combining the manure from many small farms. In addition, some dairy farms may not have the land available to apply all of their manure at agronomic rates. A regional manure digester facility can help regional dairy farms comply with the Concentrated Animal Feeding Operations (CAFO) regulations by acting as a “manure bank,” providing the ability to find alternate application sites for excess nutrients, whether with cash croppers or other dairy farms. Regional manure digestion facilities are used successfully in Europe to manage manure and to generate renewable power. The regional digester facility proposed below follows the basic model used in Denmark with modifications to fit the situation in Cayuga County.

FACILITY MODEL

The Regional Manure Anaerobic Digester Facility Model includes collection of the manure from the farms, anaerobic treatment of the manure at the facility, return of treated manure to the dairy farms and area crop farms, and beneficial use/sale of the digester gas generated at the facility. The exact split of farmer responsibility versus digester facility responsibility will ultimately be negotiated between these entities, but for this model we have assumed the farm will be responsible for storage of the manure and will own the treated effluent lagoons at the farm sites. The regional facility will be responsible for the transportation of manure and treated effluent, manure treatment system and biogas use systems.

There are many types of digester systems available, ranging in degree of initial capital expenditure and operational complexity and cost. In terms of manure digesters, there are three conventional established and proven designs including covered lagoon digesters, complex mix digesters and plug-flow digesters. Lagoon digesters are not well suited to the cold weather found in New York State and are typically found only in warmer states. At a preliminary design level, an evaluation of plug-flow digesters versus complete mix or other systems should be done, comparing system capital and operating costs including the level of biogas produced.

Biogas can be used essentially anywhere natural gas can be used. The broad categories included electricity generation, heat generation, and combined power and heat generation. In order for a regional facility to be economical, the biogas must generate income. This can be accomplished by sale of biogas directly or by the generation and sale of power and/or heat. Electricity and heat could be sold to either a neighboring facility or to the power grid. The laws of New York State allow sale of power from small distributed power generators to the grid, but currently such sales are not always economical for the small generator. Location next to a large power- or heat-using industry will likely be essential to obtain higher prices for power and

heat. A neighboring facility could pay more for energy and still see greater overall cost savings than a utility firm would pay for small amounts of power.

REGULATORY REVIEW

A regional manure digester crosses many regulatory areas, including agricultural regulations (manure management), environmental regulations (solid waste facility, air discharge), power generation, and sale and transmission regulations. New York State's agricultural regulations apply to activities occurring on or associated with an individual farm. Since the regional manure digester is associated with many farms and is under the control of no individual farm, many of the agricultural regulations do not apply. The most significant applicable agricultural regulation is that manures and treated manures may not be discharged directly to water bodies but must be land applied in an appropriate manner. For the regional manure digester facility, this means that the treated manure will have to be returned to either the original dairies or to nearby crop farms for land application.

Once manure is removed from individual farms, handling/treatment facilities are no longer considered "agricultural" but would be regulated by the solid waste management regulations (6 NYCRR Subpart 360) and air regulations (6 NYCRR Part 201). Both of these regulations require permits/registrations before the construction of the facility. The type of air permit required depends on the level of air emissions from the facility and would be determined during the preliminary design of a regional facility.

The local utility buying electricity generated by the manure digester will have its own regulations and requirements for interconnection to its transmission system, as well as applicable tariffs. In Cayuga County, the local utility is currently New York State Electric and Gas (NYSEG). For NYSEG, tariffs and interconnection requirements are stipulated in P.S.C. No. 115. Specifically, service classifications 10 and 11 may apply to any small generators, such as the proposed regional digester facility.

Small generators desiring to sell electricity to NYSEG must apply to the utility for approval to interconnect to the grid. According to the New York State Energy Research and Development Authority (NYSERDA), which has developed and funded several manure digestion facilities, utility safety interconnection requirements have been a significant hurdle in the development process. Therefore, interconnection requirements and utility approval should be pursued during the preliminary design phase early in the development of the project.

New York State has enacted legislation that allows for "net metering" and effectively sets the price of electricity sales to the grid from qualifying farm waste electric generators at the retail market rate to the extent that the power generated can cover the costs of electricity and electricity demand on the farm operation. In essence, a small electrical generator can supply power to the grid and use power from the grid

as the needs arise. While the net metering law may be useful for a small generator that may draw power from the grid, it is not as beneficial for generators that endeavor to sell most electricity to the utility. Utilities have set their tariff structures such that at the end of the year, if more energy was measured going to the grid than passing to the generator, the generator will be paid for the surplus at the utilities' average "wholesale" avoided-cost rate.

While steps have been made in New York State Legislature to improve the economics of agricultural digesters with the passage of the net metering law, there is a need for improved acceptance of the power generation from the technology within the utility industry. Whether through beginning a dialog with utilities or by lobbying the legislature, the following additional changes to state law and utility regulations would greatly improve the economic viability of any agricultural digester facility seeking to actively market power:

- Increase the allowable size of a small generator from 400 kW to 1000 kW
- Allow the sale of electricity credits awarded by utilities for net metering to other entities
- Classify power generated from biogas as "green power"

ORGANIZATIONAL STRUCTURE AND OWNERSHIP APPROACHES

While many ownership and organizational structures for the regional manure digester are possible, a focus on minimizing the farmer's costs quickly leads to a non-profit type organizational structure. Critical factors in organization's structure include the following:

- **Buy-in by the farmers** – By having a financial commitment to the regional digester, the farmers are more likely to treat the enterprise as a business and they will be invested in making the facility work. This link was seen at facilities in Denmark, which has over 20 regional manure digesters. They have found that the regional digesters that require farmer contributions have worked better than those that have used other funding.
- **Long-term commitment on feed sources and treated manure users** – The consistent availability of feedstock and users of the treated manure for the life of the facility (approx. 10 – 20 years) are important to its success. Long-term contracts will stabilize the finances of the operation. In addition, contacts with both the feed sources and the treated manure users need to clearly define the quantity and quality of feedstock and product, frequency of pickup and delivery, etc.
- **Long-term commitment from heat and electricity users** – While electricity can be sold to the grid from any location, the heat produced in generating the electricity cannot be transported far distances. Proximity to stable heat users and premium electricity users is important. Long-term contracts with the heat and electricity users will stabilize the finances of the operation.
- **Logistics of transportation** – Transportation costs are a major portion of the annual operating costs. Locating the facility in proximity to feed sources and treated manure users will help minimize these costs. In addition, having central locations for treated manure storage coordinated with the feed source locations will minimize the costs of transportation.

There are several structures under which a non-profit regional digester business could work. Some of these include a farmers' cooperative, an independent non-profit entity and a non-profit entity established under Soil and Water Conservation District auspices. Each of these is discussed below:

- **Farmers Cooperative** – The farmers interested in using the facility to treat manure and the farmers wanting to use the treated manure would form a cooperative. Each member would contribute funds to cover the capital costs and startup costs of the facility beyond what is obtained via grants and loans. The buy-in costs could be prorated for each farm based on the amount of the manure it will send to the facility each year or the amount of treated manure it wants to receive each year. The cooperative would then have contracts with each farm defining the quality and quantity of the manure feedstock and treated manure.
- **Independent Non-Profit Entity** – An independent non-profit organization could be formed, which would be run by a board of directors. The regional facility organization would be responsible for obtaining necessary grants and loans to cover the capital costs and startup costs of the facility. Buy-in by the farmers may include a user fee in addition to the tipping fee. The user fee could be based on the yearly tons of manure sent to the facility and would be returnable to the farmer at the end of the contract.
- **Non-Profit Entity Under Soil and Water Conservation District** – A non-profit organization under Soil and Water Conservation District would be similar to the Independent Non-Profit except that the District would take the lead in managing the regional facility. Employees of the regional facility could be district employees receiving benefits under the District plan. As a county organization the District may have access to grants and loans that a private non-profit would not.

The specific structure would depend on the needs of the people interested in the regional digesters and would have to be developed as the project progresses.

ECONOMIC MODEL

An economic model of a regional anaerobic manure digester was developed. It is based on a plug-flow digester sized to treat a herd of 2,800 mature animals (approximately 28% of the animals in the study area) and 21,000 tons of high-strength wastes such as outdated food or food processing wastes. This herd size corresponds to a daily manure production rate of 56,000 gallons for an overall facility treated volume of 70,000 gallons per day. When treated by the digester, this daily volume will produce an estimated 280,600 cubic feet per day of biogas. The model is based on generating electricity and waste heat by burning the biogas in an engine generator set. The economic model assumes the following:

- Non-profit organization
- Approximately 30% of the electricity being sold to local users at a higher rate of \$0.08 per kW-hr with the remainder being sold to the local utility at a lower rate of \$0.04 per kW-hr
- Waste heat can be sold for approximately half the year
- All digested manure is distributed to participating farmers
- A tipping fee will be charged to the farmer for collection of manure and delivery of digested manure (approximately \$1.50 per ton)
- A tipping fee for other organic wastes will be charged (approximately \$32 per ton)
- Grant funding will be available to cover the entire capital cost of the project

Table 5-1 summarizes the base economic model for the regional manure anaerobic digester. In order to be economical for the farmer, the model assumes that all of the capital cost for the project can be covered by grant funding. Even with this assumption, and the income generated by the sale of electricity and heat, the cost of the facility will need to be shared by the participating farmers. The model assumes this cost sharing will be achieved through a tipping fee for the manure.

Table 5-1. Summary of Base Economic Model

Item	Cost/Income (\$)
Equipment Costs	1,793,000
Direct Installation Costs	50,000
Site Preparation, Building & Tanks	1,084,100
Total Direct Costs	2,927,100
Indirect Installation Costs	1,229,400
Total Capital Investment	4,156,500
Grant Funding	4,156,500
Investors Capital Cost	0
Direct Annual Expenses	755,500
Indirect Expenses	337,300
Equipment Replacement Sinking Fund	184,000
Capital Recovery	0
Total Expenses	1,276,800
Direct Annual Income*	1,277,200
Total Annual Profit	400

* Based on tipping fee of \$1.47 per ton for manure, and \$32.00 per ton for food wastes.

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APPENDIX A
TRIP REPORTS

Memorandum

To: File
From: M.D. Giggey
Date: 14 December 2001
Project No.: 10036A
Subject: Cayuga County Struvite Recovery Project
12 December 2001 Visit to Putten Facility

Melissa Hamkins and I visited the manure treatment facility in Putten, Holland on Wednesday 12 December 2001. We were accompanied by Jim Hotaling and Kate Parsons of the Cayuga County Soil and Water Conservation District, and by Kim Scamman of the New York Watershed Agricultural Council. We met with Ms. J. A. Verhoek of the Mestverwerking Gelderland and with Dr. Olaf Schuiling of Utrecht University.

The facility in Putten is one of four manure treatment plants owned and operated by this "foundation" (a non-profit company). In total, the four plants receive 660,000 cubic meters of veal calf manure annually. All four plants have facilities for biological nitrification and denitrification, with discharge of the treated liquid to local municipal wastewater treatment plants. Three of the plants add lime to the nitrification reactor to precipitate out calcium phosphate. The Putten plant removes phosphorous by precipitation of Struvite by adding magnesium oxide to the denitrified effluent. It receives about 150,000 cubic meters of manure per year.

The four plants serve about 900 veal farms, all located in Gelderland province. At any one time, there are approximately 250,000 calves at these farms, so the average farm size is about 280 animals. According to Olaf, the farms range from 100 to 1000 animals. He said that the animals are approximately 100 pounds when purchased, and about 700 pounds when slaughtered. Ms. Verhoek estimated that the average annual manure production is 2.5 to 3.0 cubic meters per slot at about 2% dry solids. It takes 6 months to grow out the calves, so the annual production is about 0.5 million calves.

The foundation was established in the early 1980s when new regulations imposed strict limits on manure application to farmland. Most of the farms in this area are situated on sandy soil and have only a fraction of the land needed to dispose of the manure they generate. The foundation is a non-profit organization, and not a cooperative. The foundation provides for treatment and disposal; the farmers separately contract for transportation to the treatment facilities. There is additional demand for 150,000 cubic meters of annual disposal volume, beyond what the foundation is now able to handle, so the foundation is planning to expand two of its plants.

The Putten plant is located about 50 km east of Amsterdam, in the northerly part of Gelderland province. The site covers about 2 acres, and is surrounded by a narrow wooded buffer. There are a number of small farms nearby, the closest about 1000 feet

away. There were noticeable odors on the site itself, but apparently not beyond the site boundaries. Odor control consists of ducting the air from the influent holding tank and screening equipment to the intake to the nitrification blowers.

The fresh manure goes through the following treatment steps:

- Truck scale
- Open discharge area
- Sampling
- In-line screening (two parallel systems)
- Storage (2,500 cubic meters, or about 7 days detention in a 6-meter deep covered tank with mechanical mixing)
- Denitrification in two circular activated sludge basins (8,000 to 9,000 cubic meters each)
- Settling (?)
- Nitrification in two circular activated sludge basins (7,500 cubic meters each) each with 20 dome-type fine bubble diffusers and operated at about 7,000 mg/l MLSS
- Settling
- Struvite reactors (three tall circular tanks in series)
- Struvite settling
- Struvite storage
- Discharge of liquid effluent to the municipal sewer

The settled activated sludge (at about 4% solids) is stored in a concrete tank, then polymer conditioned and fed to an Alfa Laval centrifuge. The resulting 12% cake is mixed with undewatered solids to produce an 8% mixture that is hauled away in tanker trucks. Ms. Verhoek said that one truckload of solids is produced for each 6 truckloads of fresh manure. The solids are land spread in northern Holland. Olaf estimated that the farmland sites are about 60 to 100 km away.

Magnesium oxide is imported from China and obtained in 1000-kg sacks. A screw conveyor lifts the MgO into a mix tank where a 5% slurry is made. The slurry is pumped to the first of three Struvite reaction tanks. Each tank has a single mechanical mixer. Olaf told us that the slurry does not dissolve completely when it is first added to the reactor. As Struvite is formed and takes Mg out of solution, more Mg dissolves. He said that the second and third reactors have turned out not to be needed; a single tank of 2-hour detention time should be adequate. Since the flow through the plant is nearly constant, the operators are able to set the MgO feed pump once per day at a level that results in a small excess Mg dose. No separate pH control is needed. We noticed some Struvite had formed on the walls of the reactor and a downstream wetwell. Olaf said that scaling is not a major problem. The tanks and equipment are periodically cleaned with high pressure hoses.

The foundation buys MgO for 300 to 350 guilders per ton. Olaf said that this price is “below market” by 50 to 100 guilders.

The Struvite is concentrated in a conventional clarifier that is larger than necessary. The underflow is at about 4% solids(?). It is thickened in storage to about 15% dry matter. The foundation has been unable to develop a market for the struvite, and is trucking it to Germany where it is used agriculturally. Olaf told us that it is easy to attain 15% to 20% solids by simply gravity draining. He expects that up to 40% solids can be obtained through mechanical dewatering, such as with a filter press.

Olaf said that Struvite is a better way to remove phosphorous than calcium phosphate precipitation because there is significantly less volume produced. Apparently the lime addition removes more solids than does MgO, and the solids do not dewater as well. Olaf estimates that the foundation saves about 1.0 million guilders in transport costs per year by using MgO. When the other plants are upgraded, they will shift to struvite precipitation. The reduction in sludge volume is the primary force behind the conversion to struvite production.

The fresh manure received at Putten contains about 2,500 mg/l total nitrogen (2,000 mg/l ammonia) and 600 mg/l total phosphorous. The effluent from the nitrification/denitrification system contains about 100 mg/l total nitrogen (less than 10 mg/l ammonia) and about 250 to 300 mg/l orthophosphorous. Olaf believes that the 14-day detention time in the nitrification/denitrification system converts virtually all of the organic phosphorous to phosphate. The struvite recovery system removes total phosphorous to less than 30 mg/l. The biological system effluent generally has 100 mg/l TSS, although peak TSS sometimes reaches 300 mg/l. Olaf believes that the struvite reaction will be adversely affected by TSS over about 1000 mg/l. The plant effluent is limited to no more than 50 mg/l BOD, 150 mg/l nitrogen, and 30 mg/l phosphorous. The sewer bill is not on a volume basis, so the plant strives for the lowest possible N, P and BOD.

Olaf told us that the biological effluent contains much less Mg than is needed to precipitate struvite and that the potassium is in excess. Since the effluent is nearly completely nitrified, the struvite that is formed is almost entirely "potassium struvite", or potassium magnesium phosphate. For the situation where molar concentrations of ammonia and potassium are equal, Olaf predicts that "ammonium struvite" would predominate over potassium struvite due to solubility issues.

Ms. Verhoek told us that the manure comes in at about 40 degrees C in the summer and 20 degrees C in the winter. Unlike municipal nitrification/denitrification facilities, the concern is excessive temperature in the summer. She believes that some inhibition of the nitrification reaction occurs in the summer due to high temperature.

The foundation charges 20 guilders per cubic meter for treatment and disposal of effluent and solids. The farmers pay separately for transportation to the facility; about 5 guilders per cubic meter haul distances less than 10 kilometers. Since each calf produces about 1.5 cubic meters of manure over its 6-month life, the cost of manure transport and treatment is about 40 guilders per calf. It costs about 300 guilders to buy a calf for veal production.

Farmers pay the transport costs and the 20 guilders-per-cubic-meter treatment fee on an on-going basis. To join the foundation, the farmer must pay an up-front fee of 10 guilders per cubic meter, based on one year of manure production. Thus, a farmer with 300 slots would pay about 9000 guilders to join and 18,000 guilders per year for treatment plus transport. The up-front fee is returned to the farmer if he discontinues use of the facility.

The foundation is required to sample each load of manure that is received. Assuming 38-cubic-meter trucks that translate to about 20,000 samples per year. Ms. Verhoek said that this frequency is dictated by the government and not by the foundation.

We met with Dr. Schuiling at our hotel on Thursday morning 13 December and continued our discussion.

Olaf said that the struvite settles and dewateres well and is free flowing and non-hygroscopic in the dry state. While the foundation could use its centrifuge to dewater the struvite to 40% solids, it is easier to handle at 15% to 20% solids.

Struvite crystals are long and thin, with a diameter of 5 to 15 microns and a length of 50 to 100 microns. X-ray diffraction should be used to confirm that a given precipitate is struvite. (If magnesium chloride is used, the precipitate may also include magnesium phosphate.)

Olaf favors MgO as the Mg source over magnesium chloride due to cost and built-in pH adjustment. He recommends about a 10% overdose of Mg.

Olaf is working on a project with a potato processor to recover struvite from the wastewater. They are considering CO₂ stripping for pH adjustment. Magnesium chloride did not work well on this waste.

We discussed the concept of adding phosphorous to a high N waste to maximize the nitrogen removal. Olaf does not support this approach due to the high cost of phosphorous.

During the lab tests for the Putten project, it took 3 hours for the struvite to precipitate, although pilot tests were successful at 0.5 hours.

Olaf said that the literature presented conflicting reports on the impacts of temperature on solubility. For practical purposes, it may not be important.

Biosecurity is not an issue at the farm served by the foundation, since manure does not return to the farm.

We gave Olaf our proposed letter agreement, which he found acceptable and signed.

Memorandum

To: File

From: Melissa Hamkins

Date: 14 December 2001

Project No.: 10036A

Subject: Cayuga County Struvite Recovery Project
Site Visit to Ribe Biogas Plant

Jens Bo Holm-Nielsen, head of the Bioenergy Department at the University of Southern Denmark, met us at the hotel in Ribe. The group included Melissa Hamkins and Mike Giggy of Wright-Pierce, Jim Hotaling and Kate Parsons of the Cayuga County Soil and Water Conservation District, and Kim Scamman and Bob LaDue representing themselves. As we were a large group, we used several cars. Mike Giggy rode with Jens during the tour. We drove out to the Ribe Biogas Plant for a tour and then visited a distributed digested sludge tank and a member pig farm. We continued on to the Lintrup Biogas Plant where Jens had to leave us. At Lintrup, we met with Teodorita Al Seadi for a discussion of Denmark's legislation and the organization of biogas plants in Denmark. This discussion was followed with a tour by one of the operators. There was much discussion during the course of the day, which is organized and summarized below.

Denmark Background

Interest in developing biogas facilities started growing in Denmark in the 1970s with the energy crisis. More recently, the driving force for the Kyoto agreement was concern about the environment, but this also brought attention to improving agricultural practices and handling wastes. This is important in Denmark in particular since although there are 4 million people in the country, there are 6 million pigs. Dairy and swine farms produce 40 million tons per year of manure slurry (roughly 1/3 dairy, 2/3 swine).

A driving force toward better handling of manure wastes in Denmark has been the groundwater legislation with respect to nitrogen level in the groundwater. There have been two statuses passes on nitrogen levels in the groundwater. The legislation has not until recently been focused on phosphorous levels in the groundwater although there is currently a statute being discussed.

The Danish national approach to these issues coordinates environmental issues with energy and agricultural policies. It encourages the use of regional digester facilities for manure management and green energy production. One of the results of these policies is that many regional digester plants buy diesel to heat their digester rather than using the biogas they are producing, because the biogas is more valuable as a green fuel to power plants.

The Danish regulations pay a lot of attention to time, temperature, covers, and methods of application etc. to attain the maximum environmental benefit with respect to greenhouse gases. Farmers are allowed to apply nitrogen at 70% efficiency (i.e. 70% of the total applied should be taken up by plants). Farmers are not allowed to spread manure or biosolids in the fall for the next year's crops, thus manure and biosolids must be stored for up to nine months before applying to the land. In addition, the farmers must incorporate the applied biosolids within a short time after application (12 to 24 hours?).

Draft legislation in Denmark is proposing that, starting next year, feedstock for the digesters will require sterilization or pasteurization before being treated. Depending on the class of the feedstock, the level of pretreatment varies. For instance, category 1 (includes dead animals, etc.) will be excluded from digester feed; category 2 (pig slurry and dairy manure) will require high-pressure pasteurization; and category 3 (food waste) will require pasteurization at 70°C for 1 hour. There is some concern about the extent of these requirements.

In Denmark, landfilling organic wastes is not allowed. Animal bedding varies in Denmark, however, no sand or woodchips are used. Some farms use straw, some use nothing.

Teodorita reported a technology currently getting some attention is Bioscan's decanter centrifuge. After digesting the manures, the effluent is dewatered to 30% solids. This technique can move up to 25% of the nitrogen and 75 – 80% of the phosphorous. We did not have the opportunity to explore this technology further.

Ribe Biogas Plant

The Ribe Biogas Plant, built in August of 1990, uses anaerobic digestion of manure and industrial waste to generate biogas which powers the town's central power and heat plant. The facility collects manure from its member farms in three trucks (one larger and two smaller). These trucks off-load the manure into feed tanks and then reload with digester effluent. The digester effluent is transported to storage tanks near the farms fields where it will be spread. In this way the transport trucks operate with a full load as much as possible. These trucks unload manure and reload digester effluent in a two-bay building. During unloading and reloading the doors of the building are closed.

Industrial and food wastes are also taken into the facility and transferred to a separate feed tank. These wastes include outdated food wastes, fish processing wastes, slaughterhouse wastes, etc. Long term contracts are set up with the industrial and food waste sources to ensure a constant feed composition to the anaerobic system. These wastes are unloaded outside by opening a large cover (approx. 1.5 m by 4 m (visual est.)) and pumping the truck contents into the tank. We observed this occurring as we left the site. There was significant odor associated with unloading. Jens commented that in newer plants, the industrial waste unloading is done in an enclosed area.

Feed from the two tanks is pumped into three parallel anaerobic digesters. The average feed has 7% dry matter while the effluent has approximately 4.5% dry matter. The plant has an overall capacity of 150,000 tons/year with 120,000 T/yr coming from manures and the remaining 30,000 T/yr from other organic sources. The digesters are fed every 2-4 hours.

The digesters are operated at 50°C (thermophillic). The digester influent (?) is ground and then is preheated in exchange with the effluent with five spiral heat exchangers in series (3 in series and 2 in series??). The operators need to clean struvite out of these heat exchangers approximately once a week. Additional heat is provided by oil, not biogas. It is more cost efficient to buy fuel oil and sell more biogas than to use the biogas in the facility.

The digester effluent is stored in two in-ground covered tanks. These tanks are not aerated. Digester gas is pulled off of these tanks as well as the digesters. The gas is stored in a balloon tank with four-hour capacity. Ferric chloride is added to the process to reduce the sulfide content of the biogas. The biogas is continuously monitored for methane and sulfide content. Producing a consistently high quality digester gas is a priority of the facility since this is the main income of the facility. As discussed above, the feed to the digesters is carefully controlled to maintain maximum efficiency of the biogas production.

The entire site is approximately 100 m by 100 m. There is an earthen berm built around the entire site. The nearest home is about 300 meters away.

The digester effluent is transported from the storage tanks at the plant to storage tanks located near the fields on which it will eventually be spread. These field storage tanks are standard pre-engineered open-topped tanks made of pre-cast concrete panels and ribs. This style tank could be seen throughout Denmark and was clearly the standard cost-effective style tank. These tanks store 9 months worth of digester effluent. Danish law only allows spreading digester effluent during the growing season. It also requires a 10-15 cm thick floating layer at the top of the biosolids storage to prevent ammonia from volatilizing. The tank we saw had a layer of leca pellets that served as the barrier for ammonia loss. Approximately 90% of the ammonia is retained in the biosolids. These tanks are owned by the Ribe Biogas Plant. The government provided approximately 40% of the construction costs for these tanks.

Biogas is transmitted via low pressure lines to a power plant 3 km from the Ribe Biogas Plant. This power plant provides power to the grid and heat to the city of Ribe. The Ribe Commune (communes are similar to U.S. counties) has approximately 17,000 people. The plant also uses natural gas as necessary, but due to government incentives, the plant first uses all of the approximately 15,000 m³/day of biogas generated at the Ribe Biogas Plant. The government originally paid 0.60 DKK/kw for energy from biogas. This value will be reduced in the future. The power plant produces 2 MW of electricity and 1.8 MW of heat from the biogas. The hot water is pumped to town

residencies and businesses that use this hot water for heating both the buildings and for their hot water needs.

The power plant is a separate organization from the Ribe Biogas Plant. The power plant produces a total of 8 MW of electricity. Two 20-cylinder gas engines are dedicated to using biogas fuel. Three converted diesel engines operate on natural gas. The two biogas engines have recently been replaced. Earlier, two Caterpillar engines were used for 40,000 hours each before they were overhauled. They worked very well. They were replaced with a different brand due to higher efficiency available with the new engines.

Ribe Biogas Plant is organized as a cooperative company or “Limited” company. The ownership of the plant is divided among member farms and other interests as follows:

Member farms:	40%
Fish Processing	20%
“Green” investors	20%
Insurance companies	20%

The member farms consist of approximately 80 animal producing farms and 40 “agri-farms” (farms growing produce but without animal production). Of the animal producing farms, 70% are dairy farms and 30% are pig farms. The farms involved in the original project each put up \$2,500 at the start of the project for a total of \$100,000 from farms. The facility cost approximately \$5.5 million to build including the storage tanks at the farm fields.

The Ribe Biogas Plant derives income from gate fees (tipping fees) for the industrial waste it processes and from sale of the biogas to the power plant. It is responsible for the collection of raw manure and distribution of the effluent biosolids. The plant owns the biosolids storage tanks and rents them to crop farmers at approximately \$0.50 per cubic meter storage per year. Several farmers may share space in a single tank. The farmers are responsible for ensuring equitable distribution of the biosolids. The crop growers also pay for the biosolids at approximately half the price of commercial fertilizer on a pound of N-P-K basis. The manure producing farms do not pay for receiving biosolids and actually earn income for the difference in the manure they supplied and the biosolids they received (i.e. income from the excess biosolids which are sold to the crop farmers). There is a credit/fee calculation to adjust the compensation for the water content of the manure.

Danish Biogas Plants

There are twenty centralized biomass plants in operation in Denmark. Biogas plants in Denmark are all organized and operated somewhat differently. Some are more cooperative (farmer owned) and others are not. The specific contracts between the entities set quantity and quality of feedstock and product, frequency of pickup, delivery and sampling etc. The main issues for a successful biogas plant are:

- Biomass Availability – either manures or food wastes, for a period of 10 to 20 years (i.e. the life of the plant); and
- Heat users in the area of the power plant. Not only seasonal residential users but year-round industrial users

In addition, Jens emphasized the need for farms to contribute significantly to the cost of any cooperation facility was emphasized. In Denmark, the biogas plants which require farmer contribution have worked better than those which have been provided by other funding. If the farmers do not feel they have an investment in the facility, they are less likely to treat the enterprise as a business and will not be invested in making the facility work.

Jens also emphasized that logistics is a large part of a successful biogas program. Optimizing the placement of tanks to minimize hauling distances and coordinating manure pick-up trips with effluent delivery trips to minimize the time trucks travel with no load are important to maximize profits of the plant. Trips must also be coordinated with farm needs to ensure a steady removal of manure and delivery of effluent.

In Denmark residential housing is kept close to village centers. Land use restrictions do not allow many free standing homes in the country that are not related to farmsteads. This provides advantages over a more dispersed population such as exists in the United States. Odor and hauling manure over country roads are less likely to be issues. Small villages provide concentrated areas for heat distribution to residential housing.

We received the following documents from Jens and Teodorita:

1. “Status and Perspective for an Accelerated Development of Biogas” by Andreeas Andreassen, Chairman of Danish Biogas Plants.
2. “The Impact of the Legislative Framework on the Implementation and Development of Manure Based, Centralized Co-Digestion Systems in Denmark. By T Al Seadi, K Hjort-Gregersen and J.B. Holm-Nielsen.
3. Biogas Production – agriculture, environment and energy
4. Joint Biogas Plant – Agricultural Advantages – circulation of N, P and K. Report made for the Danish Energy Agency 2. Edition August 1997.
5. Good Practice in Quality Management of AD Residues from Biogas Production.
6. Danish Centralized Biogas Plants – Plant Descriptions. Bioenergy Department, University of Southern Denmark, 2000.

APPENDIX B
LAB PROCEDURES

STRUVITE PRECIPITATION TEST PROCEDURE

A. Sample Collection and Handling

1. Collect digested manure sample from the post-digester solid separator liquid effluent in 5 gallon container to be used for transport; ensure pH and temperature.
2. Ship container to laboratory in cooler packed with ice.
3. At the lab, measure pH, and store container in 4°C refrigerator prior to use.
4. Conduct trials as soon as practical once the lab returns sample analysis.

B. Sample Preparation

1. Mix contents well. Take 3 samples for analyte analysis of initial conditions listed in Table 2.
2. Reserve a 1-liter portion of well-mixed raw sample for analyte/parameter measurement and for the “whole effluent” trial
3. Analyze raw sample for analytes/parameters. Orthophosphate concentration should be analyzed immediately to determine the amount of magnesium reagent to be added to the trial volumes in the prescribed stoichiometric ratios.
4. Sample not to be used on the same day should be stored at 4°C until used.

C. Struvite Precipitation

1. Add sample volume to beaker:
 - (a) For 200 mL samples: Mix entire sample thoroughly and collect individual sample in a 400 mL beaker.
 - (b) Add 2 L to a 2 L beaker for trials requiring total parameter/analyte analysis.
2. Allow sample volume to reach room temperature and record the temperature.
3. Measure magnesium reagent ($\text{MgCl}_2 \cdot 6(\text{H}_2\text{O})$ or MgO) in stoichiometric proportion to the concentration of orthophosphate analyzed previously. Add reagent to beaker.
4. Place beaker under a paddle stirring rack and mix the solution for at least 30 minutes.
5. Measure solution pH after initial mixing and titrate with 0.1 M NaOH as necessary to raise pH to 9.0. Titrate with 0.1 M HCl if pH must be lowered from initial level to 9.0. For the two non-pH-adjusted trials, no addition of NaOH is to be made.
6. Mix for 1 hour then measure pH and conductivity
7. Stop mixing
8. Allow sample to settle quiescently
 - (a) Record observations of struvite/solids settling if visible

9. Measure sample for pH and conductivity and analyze for required analyte parameter per Table 1.
10. In 2 L trials, retain precipitate and dry at 105°C for 1 hour or prepare as necessary for x-ray diffraction analysis to confirm presence of struvite

Samples will be collected by district employees and shipped to Wright-Pierce's laboratory in Topsham, ME. An attempt will be made to coordinate sample collection at the Aman Dairy with the samples taken by Peter Wright (Cornell University) under a different preparation and bench top tests. Samples for chemical analysis will be submitted to the Wright-Pierce laboratory for analysis.

APPENDIX C
BENCH-TOP TEST DATA

Table C-1
Series 1 Test Results

Trial Number	Sample Volume	Temp °C	pH s.u.	cond. umhos	NaOH added	Final mL	Stioch %	initial Mg/L	final Mg/L	removal %
1	200	21.3	7.91	143,000	2.52	9.0	50 MgCl2	367	349	5%
2					dup analysis of trial No. 1			367	349	5%
3	200	21.5	7.95	157,800	3.25	9.1	100 MgCl2	367	325	11%
4	200	22.4	7.90	162,600	3.47	9.1	130 MgCl2	367	325	11%
5	200	24.1	7.83	124,300	2.10	9.0		405	583	-44%
6					dup analysis of trial No. 5			405	583	-44%
7	200	23.8	7.88	128,900	2.12	9.0	50 MgO	405	571	-41%
8	200	20.8	7.85	165,300	2.28	9.0	80 MgO	460	460	0%
9	200	23.8	7.88	129,600	1.95	9.0	80 MgO	405	583	-44%
10	200	22.4	7.93	164,300	none	8.3	100 MgO	367	349	5%
11	200	20.0	7.83	156,500	2.27	9.0	100 MgO	460	401	13%
12	200	23.5	7.85	133,800	1.95	9.0	100 MgO	405	553	-37%
13	200	23.4	7.85	132,800	1.72	9.0	115 MgO	405	511	-26%
14	200	22.7	7.93	164,000	none	8.4	130 MgO	367	325	11%
15	200	21.9	7.86	169,300	1.9	9.0	130 MgO	460	377	18%
16	200	21.6	7.85	168,800	1.85	9.0	130 MgO	460	389	15%
17	2,000	21.9	7.87	173,000	20.95	9.0	130 MgO	460	460	0%
18	200	23.5	7.87	134,000	1.43	9.0	200 MgO	405	493	-22%
19	200	24.1	7.89	170,600	1.45	9.0	200 MgO	460	431	6%
20	200	23.9	7.91	172,300	0.95	9.0	300 MgO	460	460	0%

(1) Samples were taken of the initial phosphorous level at the beginning of each day of testing.

**Table C-2
Series 2 Test Results**

Trial Number	Initial Conditions			NaOH Addition		Mg Stoch %	Final Conditions			Sample Location	Phosphorous Concentrations			Total Solids	
	Sample Volume	Temp °C	pH s.u.	NaOH added	Final mL		temp °C	pH s.u.	cond. umhos		initial mg/L	final mg/L	removal %	final mg/L	difference mg/L
1	600	20.0	7.71	10.95	9.0	200 MgCl ₂	22.6	8.97	350,000	Top	291	293	-1%	56,870	2,490
										Bottom	291	251	14%	59,360	
2	600	19.8	7.75	7.75	9.0	200 MgO	22.0	9.01	1,310,000	Top	291	245	16%	54,440	3,120
										Bottom	291	263	10%	57,560	
2-dup	600	19.8	7.75	7.75	9.0	200 MgO	22.0	9.01	1,310,000	Top	291	263	10%	54,780	2,530
										Bottom	291	245	16%	57,310	
3	600	19.8	7.77	10.8	9.0	200 MgCl ₂	22.2	8.95	17,400,000	Top	291	263	10%	52,360	3,120
										Bottom	291	263	10%	55,480	
4	600	20.4	7.65	8.6	9.0	200 MgO	22.2	9.03	16,800,000	Top	291	263	10%	51,690	2,820
										Bottom	291	245	16%	54,510	
5	600	20.8	7.67	10.0	9.0	none	21.9	9.01	17,800,000	Top	291	293	-1%	53,660	4,960
										Bottom	291	293	-1%	58,620	

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**STRUVITE RECOVERY FROM DIGESTED DAIRY MANURE
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