REIN And ASSOCIATES
Environmental Engineers and Operators

Phase III of "Converting Thin Stillage into Renewable Energy, Renewable Fertilizer and Recyclable Water"

Final Report

Phase III - Struvite Pilot Demonstration and the Struvite/Digester Process

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January 22, 2008

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- ✓ Nalco Company, Jason S. Van't Hul and Philip Randklev, for jar testing and dosage adjustment for solids separation.
- ✓ Freemont Industries, Inc., Jeff Nicholls, for jar testing and consultation for solids separation.

CERTIFICATION

I hereby certify that this plan, specification, or report was prepared by me or under my direct supervision, and that I am a duly Registered Professional Engineer under the laws of the State of Minnesota.

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Date: January 22, 2008

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1 EXECUTIVE SUMMARY

1.1 Background

Since September 2006, Rein & Associates has been investigating the potential for extracting additional energy from stillage produced at corn-based ethanol production facilities. It was first demonstrated, on a bench scale, that "thick stillage" was an ideal feedstock for biologically producing methane gas (a green replacement for natural gas). Based on the early bench scale success, funding for additional full-scale and pilot-scale work was sought, and provided, by the Agricultural Utilization and Research Institute (AURI), the Minnesota Corn Growers Association, Otter Tail Power and the City of Fergus Falls. This funding was provided in three funding packages, Phase I, Phase II and Phase III.

<u>Phase I</u> was a full-scale digestion demonstration conducted at the Fergus Falls Wastewater Treatment Plant using thick stillage as an additional bio-feed stock for the City's anaerobic digesters. This project successfully demonstrated that thick stillage could be used in an existing anaerobic digester to produce sufficient additional biogas to completely satisfy the natural gas demand at the Fergus Falls Wastewater Treatment Plant.

<u>Phase II</u> was a pilot scale digestion demonstration conducted at the Fergus Falls Wastewater Treatment Plant using thin stillage as the bio-feed stock for a 10,000 gallon pilot plant. This phase of the project demonstrated that thin stillage could successfully be digested at a loading rate of 3 Kg COD/m^3/day, and produce up to 3,000,000 ft^3/day of methane. In addition, bench-scale testing demonstrated that large quantities of struvite, a renewable, slow-release fertilizer, could be generated as a process by-product. Struvite generation resulted in high percentages of dissolved magnesium and phosphorus removal from the thin stillage (up to 98%).

1.2 Struvite Pilot Demonstration

<u>Phase III</u>, the "Struvite Pilot Demonstration", was conducted at the Fergus Falls Wastewater Treatment Plant using a skid-mounted struvite production pilot plant. Its purpose was to demonstrate the feasibility of producing a relatively pure struvite in conjunction with biogas at an ethanol-production facility. This phase of the project confirmed that large quantities of struvite could be efficiently recovered from thin stillage prior to digestion. The pilot plan achieved average phosphate, ammonia, and magnesium removals of 74%, 65% and 89%, respectively.

Overall, the struvite product recovered from the pilot unit was consistently of good size and hardness. This product contained somewhat lower concentrations of magnesium, ammonia and phosphate than is typically produced when using Ostara's process to treat municipal wastewater. This indicates that the purity of the struvite product was lower than normal. The main impurities, however, appear to be potassium, calcium, sulfur and sodium, with significant amounts of iron and manganese. All of these compounds are either plant nutrients, or are innocuous.   This product should be able to be marketed as a slow release 5-27-1 fertilizer with micronutrients.

It should be noted that the harvesting of struvite prior to the digester not only produces a marketable byproduct, but also reduces the potential negative impacts of having the struvite precipitate in the digester. These impacts include equipment scaling and loss of useful digester volume.

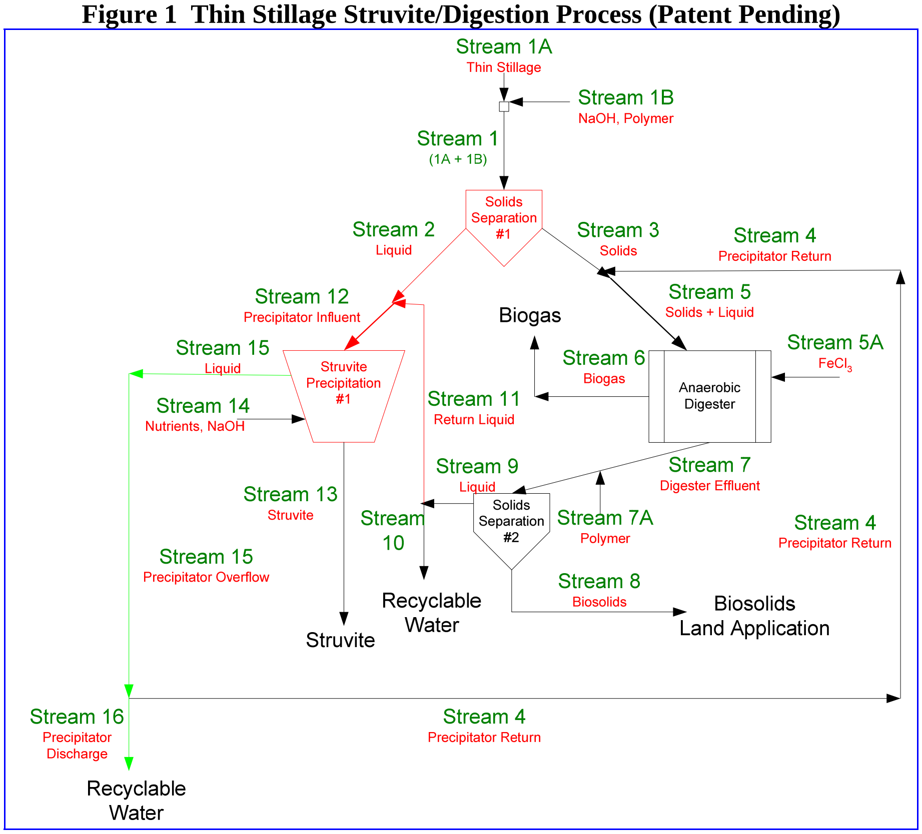
A final benefit from struvite harvesting would be if the biosolids were disposed of through land application. Struvite harvesting would prevent the over-application of phosphorus to crop land when applying biosolids at agronomic rates based on nitrogen.

1.3 Struvite/Digestion Process

Figure 1 is a conceptual flow diagram for the struvite/digestion process that incorporates the findings of Phases I, II, and III of this project. There are four potential by-product streams shown in Figure 1: biogas, struvite, biosolids, and effluent water.

Based on mass balance calculations for the Otter Tail Ag Ethanol Facility, it is estimated that this process could produce approximately 3,000,000 ft^3/day of methane gas; 9 to 10 tons/day of struvite fertilizer; 20 to 25 tons/day of biosolids (dry basis); and up to 570,000 gpd of recyclable process water.

Figure 1 Thin Stillage Struvite/Digestion Process (Patent Pending)



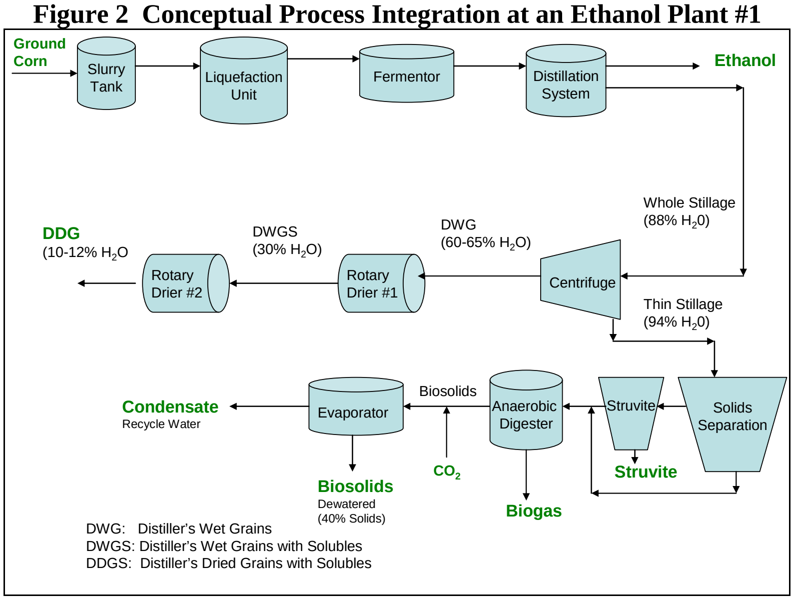
1.4 *Integration at the Ethanol Plant*

In our opinion, the process shown in Figure 2 shows the easiest means of incorporating the struvite /biogas process into an ethanol facility. In this figure, the ethanol plant would continue to operate its evaporators; however, the feed for the evaporators would be digester effluent instead of thin stillage. As shown, products from this process include condensate, biosolids, biogas, and struvite.

The benefits achieved by continuing to operate the evaporators are:

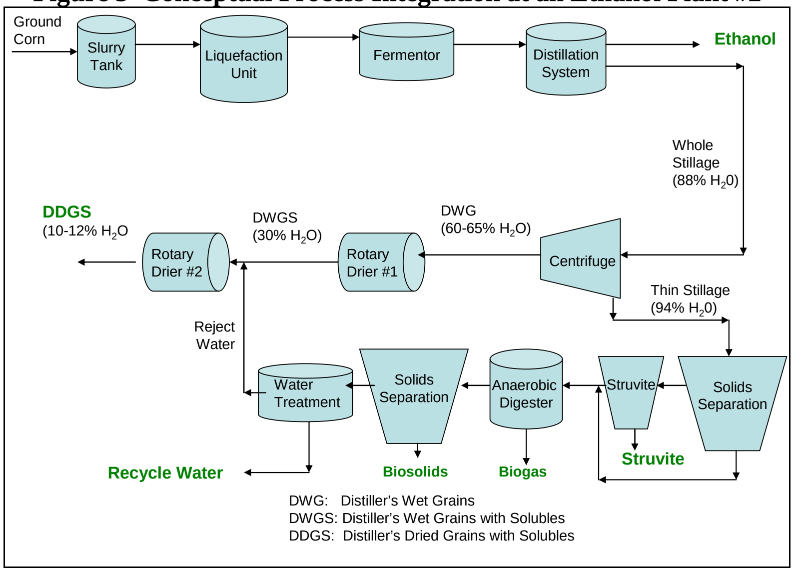
- ✓ Capital expenditures for additional water treatment, such as MBRs and ROs, are eliminated because condensate from the evaporators will still be generated and reused.
- ✓ Elimination of the need for Solids Separator #2.
- ✓ Biosolids are thickened from 2% to 40% solids prior to land application, or some other processing step, such as making the biosolids into pellets.

Figure 2 Conceptual Process Integration at an Ethanol Plant #1



Another option for integration is shown in Figure 3. This option includes treatment of process effluent from Solids Separator #2 (see Figure 1) to produce recyclable water and biosolids.

Figure 3 Conceptual Process Integration at an Ethanol Plant #2



1.4.1 Estimated Full Scale Operating Income

A budget estimate for the operation for a 538,000 gpd plant using Scenario 2A (without Solids Separator #2) and the flow scheme shown in Figure 2 is shown below. (Note, this estimate does not consider capital recovery).

1. **Revenues*:**

Struvite	9.6 tons/day @ $1,500/ton = $14,400/day
Methane	3,153,400 scf/day @ $8/1,000 CF = $25,226 /day

Total Revenues = $39,626/day

2. **Chemical Expenses**:

NaOH	17.87 tons/day @ $350/ton = $6,256/day
NH_3	0.463 tons/day @ 325/ton = $150/day
Na_3PO_4	2.94 tons/day @ $180/ton = $529/day
Polymer*	285 gpd @ $7/gal = $1,995/day
$FeCl_3$	1.57 tons/day @ $350/ton = $550/day

(*Solids Separator #1 Only)

Total Chemical Expenses = $9,480/day

3. **Electrical Expenses @ $0.055/kWh)**

Item	**Hp**
Pumps	20
Mixers	1,500
Biogas	300
Belt Press	100
Ostara	400
Total (say)	**2,500 or $1,500/day**

4. **Labor**

Total	**$400/day**

5. **Maintenance**

Total	**$300/day**

6. **Total Expenses**

Total	**$11,700/day**

7. **Net Income**

Total	**$28,000/day or $10,000,000 per year**

*Possible additional revenue from carbon credits.

1.5 Conclusions and Recommendations

The conclusions and recommendations are as follows:

1. Thin stillage can be digested to produce large quantities of methane gas. Up to 3,000,000 CF/day are projected for the Otter Tail Ag facility.

2. It is unlikely, however, that a digestion process could be sustained without struvite precipitation ahead of the digester. The buildup of struvite within the digester associated appurtenances would cause long-term operation and maintenance (O/M) problems.

3. The combined struvite/digestion process described in this report will not only substantially reduce O/M problems but has the potential to produce large quantities of struvite, methane gas, biosolids and recyclable water.

4. Based on mass balance calculations, the combined struvite /digestion process would yield net operating income of $28,000 per day.

5. A preliminary budget estimate for a 180,000 gpd demonstration plant is:

Capital Costs:	
Biogas Digester	$6 million
Struvite Precipitator	$5.0 million
Press	$1.5 million
Gas scrubber	$0.7 million
Total	$13.2 million
Operating (Revenues – Expenses)	$3,400,000/year

6. Further development of this concept through a preliminary engineering cost estimate and a 180,000 gpd demonstration project is strongly recommended.

2 INTRODUCTION

2.1 Background

Ostara Nutrient Recovery Technologies Inc. carried out preliminary jar testing to demonstrate that struvite fertilizer could effectively be recovered from thin stillage during Phase II of this project. The results were sufficiently promising to recommend proceeding to pilot testing in order to demonstrate that Ostara's process could be operated under continuous conditions treating thin stillage. The jar testing showed that up to 98% of magnesium and phosphate present in the thin stillage liquor could be removed; and that more than 85% of the precipitate formed was struvite fertilizer, which Ostara markets as Crystal Green™. Based on these findings, a pilot struvite demonstration (Phase III) was undertaken at the City of Fergus Falls WWTP.

2.2 Purpose/Objectives

Struvite production is critical in the conversion of "Thin Stillage into Renewable Energy, Renewable Fertilizer and Recyclable Water". It produces a value added by-product (a renewable fertilizer) and reduces the scaling potential inside the methane reactor (the anaerobic digester).

The goal for the struvite pilot study was to demonstrate the feasibility of producing a relatively pure struvite that was not commingled with thin stillage solids or organic solids. The primary objective was to prove, on a pilot scale, the feasibility of producing struvite from thin stillage. A secondary objective was to begin optimizing process conditions for struvite formation.

3 MATERIALS AND METHODS

Two separate steps were used to prepare the thin stillage for the struvite precipitator, Solids Separation #1 (see Figure 1), and a separate pH adjustment step (see Figure 1). Solids Separation #1 was performed on the City of Fergus Falls' gravity belt. The separate pH adjustment step, with subsequent gravity settling, was used to remove oils and fats from the filtrate of Solids Separator #1. Struvite precipitation was done with the Ostara pilot precipitator.

3.1 Solids Separation #1

Liquid/Solids separation was accomplished using the full-scale gravity-belt filter press at the Fergus Falls Wastewater Treatment Plant. The thin stillage was stored in a sludge day tank, treated with a polymer, and run across the gravity belt sludge dewatering equipment for solids liquid separation. The liquid stream from the gravity belt was then stored in another day tank until used for struvite formation.

Prior to full-scale operations, jar tests were conducted to determine which flocculants and flocculent doses might produce good solids separation on the belt filter. The tests were conducted by Jason S Van't Hul and Philip Randklev of the Nalco Company. The thin stillage was flocculated and clarified in jars using Nalco 7767 at 500 ppm. No pH adjustment was needed for good flocculation.

Nalco 7767 was again used to treat the thin stillage when solids separation was done on the full-scale gravity belt. The dosage used varied from 750 to 850 ppm. The polymer was fed at 110 ml/min into a carrier water flow of approximately 5 gpm. The thin stillage flow to the belt was estimated at 45 to 50 gpm. The belt-filter surface area was 60 ft^2 (12 ft x 5 ft). The belt speed was set at 80 to 90% of full speed. When the belt was run at slower speeds, the filtrate appeared to contain higher than desired levels of particulate matter.

Samples of the solids coming off the belt, filtrate water coming off the belt, the thin stillage (plus polymer and carrier water) going onto the belt, the thin stillage, and wash water were sent to the laboratory for analysis (see Appendix 7.2).

Figures 4 through 10 show the various streams going onto and coming off the belt press. Figure 4 shows the jar testing of Nalco 7767 on thin stillage prior to using the belt. The dosages from right to left were; 150 ppm, 200 ppm, 300 ppm and 750 ppm.

Figure 4 Jar Testing Nalco 7767

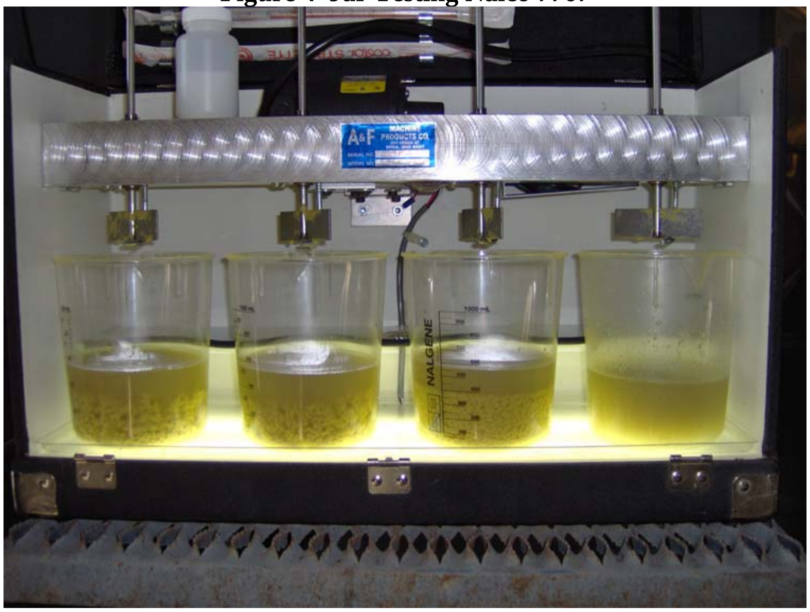


Figure 5 shows the two jars dosed at 300 and 750 ppm. Going to 750 ppm caused the solids to both float and settle.

Figure 5 Jar Testing, 300 and 750 ppm

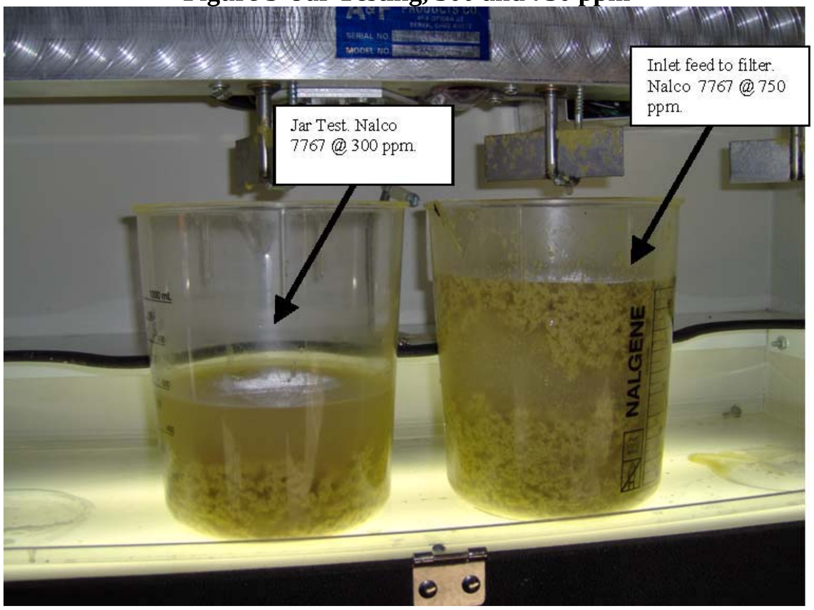


Figure 6 shows the thin stillage, plus carrier water and polymer, dropping from the influent distribution tray onto the dewatering belt.

Figure 6 Thin Stillage, Carrier Water and Polymer Going onto Filter

Figure 7 shows the thin stillage, carrier water, and polymer mixture just after the mixture has been deposited onto the belt.

Figure 7 Thin Stillage, Carrier Water and Polymer Mixture on the Belt

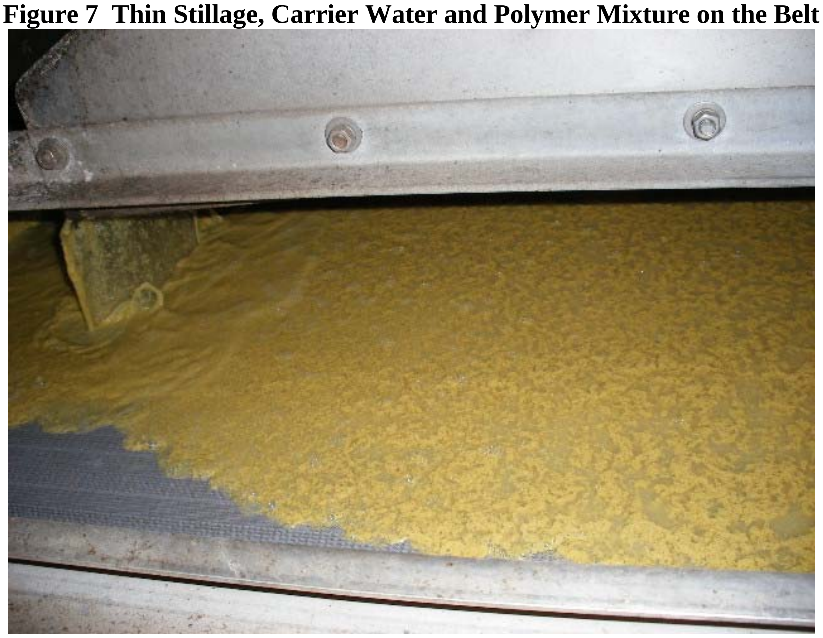


Figure 8 shows the dewatered solids as they are coming off the belt.

Figure 8 Solids Coming Off Belt

Figure 9 is another picture of the solids coming off the belt.

Figure 9 Solids on Belt

Figure 10 shows the thin stillage liquid stream flowing into the storage tank after the solids have been removed by the belt.

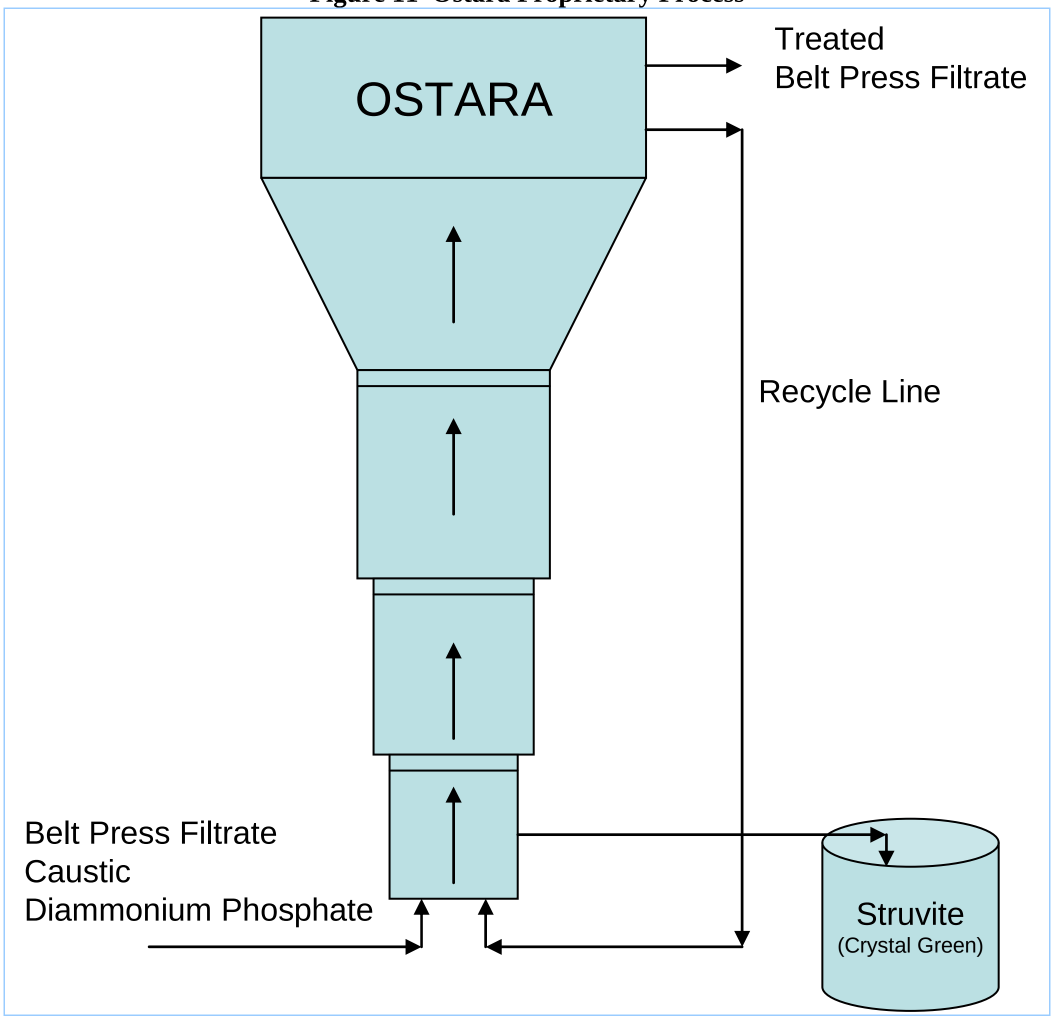
Figure 10 Thin Stillage Filtrate

The belt dewatering process removed approximately 97% of the TSS from the thin stillage prior to the gunk removal process.

3.2 Struvite Pilot Plant

A schematic of the struvite precipitator used in this project is shown in Figure 11.

Figure 11 Ostara Proprietary Process



3.3 pH Adjustment of Belt Press Filtrate

Soon after beginning operation of the pilot plant, it became apparent that it was necessary to remove oil and fats from the belt press filtrate to reduce fouling in the reactor. The oil and fats were precipitated in the pH range of 5.8 to 6.6. The best oil and fat removal occurred at higher pH values. Unfortunately, magnesium is better retained in solution and available to be precipitated later as struvite at lower pH values. Table 1 shows the effect of pH adjustment on the dissolved magnesium concentration.

3.3.1 Effects of pH Adjustment

The pH-adjustment procedure was reasonably effective in removing oil and fats, as the Ostara precipitator was able to operate without excessive fouling after the procedure was instituted. Some fouling of the Ostara precipitator was noted when the Ostara reactor was operated at higher pH values, e.g., 8.0.

As indicated in Table 1, a tension exists between oil and fats removal and retention of magnesium. At higher pH values, oil and fats removals appear to improve, but so do removals of magnesium. The magnesium so removed is not available to the Ostara reactor; and, thus, the yield of struvite product is reduced.

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Table 1 Effects of pH Adjustment

	pH	Mg
Belt Press Filtrate	**4.5**	400
pH Adjusted Filtrate	**5**	410
pH Adjusted Filtrate	**5.75**	390
pH Adjusted Filtrate	**6.2**	340

4 STRUVITE PILOT PLANT OPERATIONS

The struvite recovery pilot plant was operated in four distinct operating modes:

1. without pre-adjustment of the stillage pH,
2. pH adjustment with high ammonia and phosphate dosing,
3. pH adjustment with low ammonia and phosphate dosing, and
4. pH adjustment with no ammonia and phosphate dosing.

The struvite recovery plant was initially started treating stillage without pre-adjustment of the stillage pH. Under these conditions the struvite recovery reactor was found to foul within hours with a greasy gray sludge material, later identified as fats and oils from the stillage.

To reduce the fouling, a pH adjustment step was inserted upstream of the struvite recovery reactor to separate the oils and fats from the liquid portion of the thin stillage. This was done using two tanks, one for pH adjustment and oil and fat removal by settling, and the other for storing the pH-adjusted stillage. In a permanent installation, this pH adjustment step would likely be carried out in conjunction with the solids separation step to allow the fats to be separated along with thin stillage solids. Both would then be sent directly to the digestion process in one step.

Substantial amounts of soluble phosphate and magnesium were removed by the pH-adjustment process. However, for the first 16 days of operation, the effects of the pH-adjustment step on the soluble constituents were not known. The dosing levels used assumed no removals and thus, were higher than needed. Lab results revealed that a substantial amount of soluble phosphate and magnesium was removed in the pH-adjustment step and that the remaining ammonia, magnesium and phosphate levels were nearly ideal for struvite formation, without additional chemical addition.

Once this overdosing was discovered, the reactor was operated for two additional four-day periods; one with a low dose of ammonia and phosphate, and one with no supplemental ammonia or phosphate dosing.

It should be noted that high magnesium removal (a treatment goal) requires the molar ratios of ammonia to magnesium and orthophosphate to magnesium both be at least 1.0. Lower ratios result in incomplete magnesium removals. Higher ratios result in improved magnesium removals. Any change of the molar ratios prior to the Ostara process affects the potential removal.

4.1 High Ammonia and Phosphate Dose

During this phase, the ammonia and phosphate solution was dosed to the struvite recovery process influent at levels higher than required for struvite formation (as discussed above). This resulted in relatively high residual ammonia and phosphate concentrations in the struvite reactor effluent, with no additional benefit in terms of magnesium removal (see Table 2). It should be noted that these dosing levels were the result of a lack of data on the influent composition to the struvite reactor caused by long laboratory turnaround times. These chemical dosing levels would not have been used had the impact of the pH adjustment step been known in advance. For this reason, no further discussion of these results is presented.

Table 2 High Ammonia and Phosphate Dose

	PO_4-P mg/L	NH_3-N mg/L	Mg mg/L
Struvite Reactor Influent	453	181	328
Added by Dosing	170	230	-
Struvite Reactor Effluent	274	275	37
% Removal	**58**	**33**	**89**

4.2 Low Ammonia and Phosphate Dose

Once the composition of the pH adjusted thin stillage was known, revised chemical dosing rates were developed to ensure there was a slight excess of ammonia and phosphate in the reactor effluent to allow uninhibited magnesium removal (see Table 3). Under these conditions, it was possible to achieve over 80% magnesium removal, while maintaining 70% phosphate removal and 55% ammonia removal. This represented an improvement from the previous conditions; however, it was also determined that the economics of the process could be further improved by stopping ammonia and phosphate dosing altogether, without harming magnesium removal.

Table 3 Low Ammonia and Phosphate Dose

	PO_4-P mg/L	NH_3-N mg/L	Mg mg/L
Struvite Reactor Influent	366	211	300
Dosing	25	37	-
Struvite Reactor Effluent	117	109	50
% Removal	**70**	**55**	**84**

4.3 No Ammonia or Phosphate Addition

Table 4 shows the results of the final phase of pilot operation during which no ammonia or phosphate was supplemented to the struvite recovery process. This option showed the best overall results in terms of removal of magnesium, ammonia and phosphate. This option also has the lowest potential operating costs at large scale. The reaction was not nutrient limited during this period; that is, the phosphorus to magnesium and the ammonium to magnesium molar ratios were both above 1.0. It is possible to operate in the no-nutrient-supplementation mode as long as the nutrient to magnesium molar ratio remains at 1.0 or above. However, it seems likely that the struvite precipitation process will be ammonium- or phosphate-deficient (or both) during some portion of its operating life. Therefore, it is prudent to provide ammonium- and phosphate-addition facilities.

Table 4 No Ammonia and Phosphate Addition

	PO_4-P mg/L	NH_3-N mg/L	Mg mg/L
Struvite Reactor Influent	444	254	335
Dosing	None	None	None
Struvite Reactor Effluent	106	69	20
% Removal	**78**	**75**	**94**

4.4 Summary

During the last two phases of the pilot study, removals of Mg, NH3-N, and ortho-P averaged 89%, 65%, and 74%, respectively (see Tables 2 and 3). Removals were highly variable; that is, standard deviations were high percentages of the means. There seemed to be little correlation between percentage removals of these components and pH (see the charts on the spreadsheet). The apparent increase in ammonia is most likely not real, as there was some difficulty measuring ammonia during the pilot study.

Ca, Al, and Fe removals averaged 51.1, 82.0, and 71.5 % respectively. Removals of these components are significantly less variable; and, therefore, are more predictable than removals of Ma, NH3-N, and ortho-P.

Removing Mg in the preliminary pH-adjustment step hurts Ostara’s economics. A very high percentage of the Mg in thin stillage must be available to the Ostara reactor for it to be profitable on its own. The jar tests indicate we would have to operate at about pH of 5 to minimize Mg removal in the preliminary pH-adjustment step. Oil and fat removal at pH 5 might be inadequate. There is still a lot of uncertainty in this step.

Removing Ca, Al, and Fe in the preliminary pH-adjustment step helps to enhance the purity of struvite product precipitated in the downstream reactor.

4.5 Struvite Quality

One of the principal objectives of the pilot scale struvite recovery project was to demonstrate that the Ostara process was capable of recovering struvite pellets of adequate size, hardness and purity from thin stillage for direct sale into the slow release fertilizer market.

Overall, the struvite product recovered from the pilot unit was consistently of good size and hardness, despite occasional difficulties related to the accumulation of residual oils and fats on the surface of the crystals. These substances caused the crystals to stick together in the reactor.

Table 5 on page 17 shows the composition of seven samples of Crystal Green product produced during the pilot demonstration. Overall, this product contains somewhat lower concentrations of magnesium, ammonia and phosphate than is typically produced using Ostara's process when treating municipal wastewater. This indicates that the purity of the struvite product is lower than normal. The main impurities, however, appear to be potassium, calcium, sulfur and sodium, with significant amounts of iron and manganese. As all these compounds are either plant nutrients, or are innocuous, this product should be able to be marketed as a slow release 5-27-1 fertilizer with micronutrients.

The presence of 1 % potassium and the lower phosphate levels than Ostara's usual 5-28-0 Crystal Green product would require that this product be marketed under a separate brand (such as Crystal Green Plus) due to the different fertilizer analysis. This product may actually be more attractive than normal Crystal Green to certain users if its composition proves to be consistent. Ostara would need to complete further market assessment, field trials, and release rate testing to confirm the value of this product.

It should also be noted that due to the relatively short duration of the pilot study, it was not possible to evaluate the variability of the product characteristics. A longer duration trial at pilot (or demonstration) scale would be required to confirm this. It is, however, anticipated that with operating experience it would be possible to produce a consistent product.

Table 5 Crystal Green Chemical Analyses

Sample ID	1	2	3	4	5	6	7			% Deviation	Pure
Description	Oct 3 2007	Oct 5 2007	Oct 8 2007	Oct 10 2007	Oct 26 2007	Oct 28 2007	Oct 31 2007	Average	SD	From Pure Struvite	Struvite
Total Nigtrogen - %	5	4.9	5.1	5	5.2	5	4.9	5.01	0.11	-12%	5.71
Ammonia Nitrogen - %											
Available P - %	12.5	12.2	12	12.1	12.2	11.8	11.4	12.03	0.35		
Available P_2O_5 - %	28.5	27.9	27.4	27.7	27.8	26.9	26	27.46	0.81	-5%	28.92
Soluble K_2O - %	1.52	1.39	1.19	1	0.94	1.36	1.47	1.27	0.23		
Soluble K - %	1.27	1.15	0.99	0.83	0.78	1.13	1.22	1.05	0.19		
Calcium - %	<0.41	<0.43	<0.37	<0.38	0.49	<0.42	0.41	0.45	0.06		
Magnesium -%	9.64	9.52	9.29	9.13	9.33	9.48	9.39	9.40	0.17	-5%	9.90
Zinc - ppm	<103	<108	<92.3	<94.4	<110	<105	<99.4				
Copper - ppm	<309	<324	<277	<283	<331	<314	<298				
Manganese - ppm	51.7	89.5	106	118	135	141	152	113.31	34.57		
Iron - ppm	<463	814	927	1050	1060	985	1130	994.33	112.21		
Boron - ppm	0.57	4.24	1.95	2.42	2.43	2.34	0.69	2.09	1.24		
Molybdenum - mg/kg	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5			
Total Sulfur - %	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.10			
Sodium - %	0.13	0.14	0.14	0.1	0.12	0.14	0.26	0.15	0.05		

4.6 Preliminary Design for Demonstration Project

Based on the stillage composition measured during Phases II and III of this project and a comprehensive mass balance on the complete struvite recovery/digestion system (see Section 5 of this report) an estimate of expected struvite reactor influent characteristics was developed. A preliminary design sizing for a demonstration scale struvite recovery facility was then developed for treating a thin stillage flow of 180,000 GPD according to the mass balance composition. Table 6 below shows the expected concentrations of magnesium, ammonia and phosphate at key points in the struvite recovery system.

Table 6 Expected Struvite Recovery System Performance

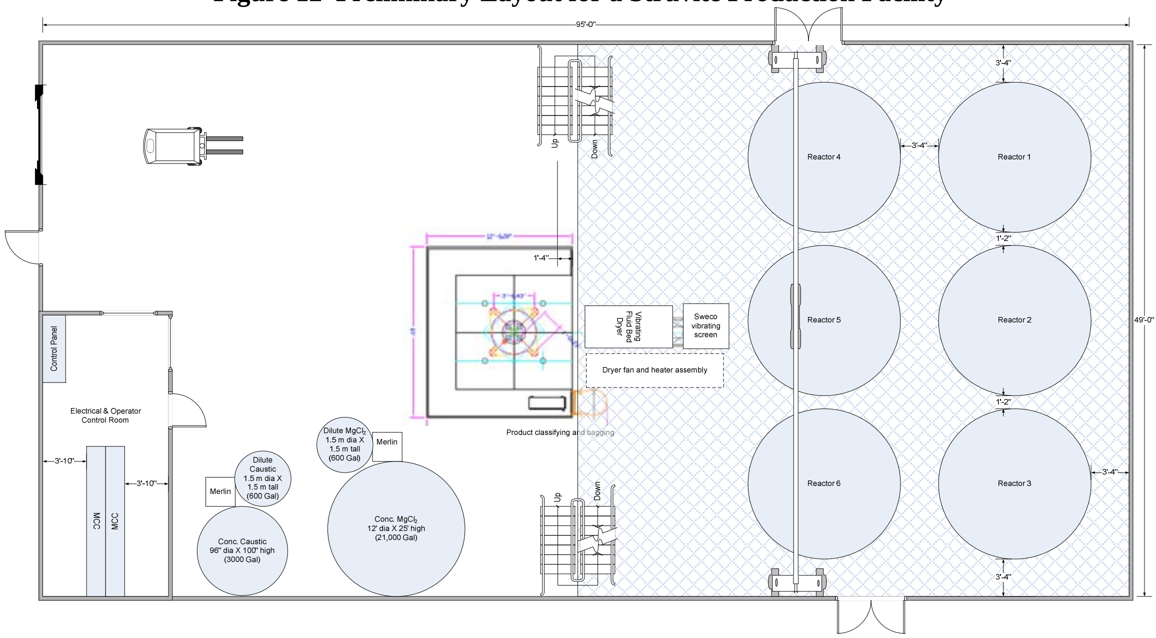
Parameter (mg/L)	Pre-treated Thin Stillage	After Chemical Addition	After Struvite Reactor
Dissolved Mg	529	529	61
Ammonia	94	305	35
Ortho-Phosphate	441	674	77

Under these conditions, approximately 8,000 mg/L of caustic soda are required for pH adjustment (assumed to be provided as a 6,000 mg/L in the pH adjustment/dewatering step and 2000 mg/L in the Ostara reactors. When required, ammonia would be supplemented as anhydrous ammonia gas, while tri-sodium phosphate would be used to supplement the phosphate concentration when required. Both these chemicals are alkaline and would reduce the requirement for caustic to a certain extent when used. Digester effluent could be used as an alternative source of ammonia for the struvite reactor. This would result in a larger flow rate through the digester and struvite recovery system, but would not significantly impact the process sizing for the struvite recovery facility.

The struvite recovery facility (see Figure 12) would consist of six of Ostara's 32" diameter reactor columns, each capable of treating approximately 30,000 gallons per day of pH-adjusted, thin stillage filtrate (economics of scale could reduce these costs). This facility would require a building footprint of approximately 5,000 square feet, including space for product storage and shipping (as shown in Figure 12).

This facility would have a production capacity of 6,300 lbs per day (1,150 tons/year) of struvite product when operating under conditions predicted by the process mass balance. A preliminary budgetary cost for the struvite recovery facility on a turnkey basis (including design, equipment, installation, and commissioning) would be $5 million, plus the cost of the 5,000 ft^2 building to house the facility. Based on an estimated industrial building cost of $75/$ft^2$, the building cost would be an estimated $375,000.

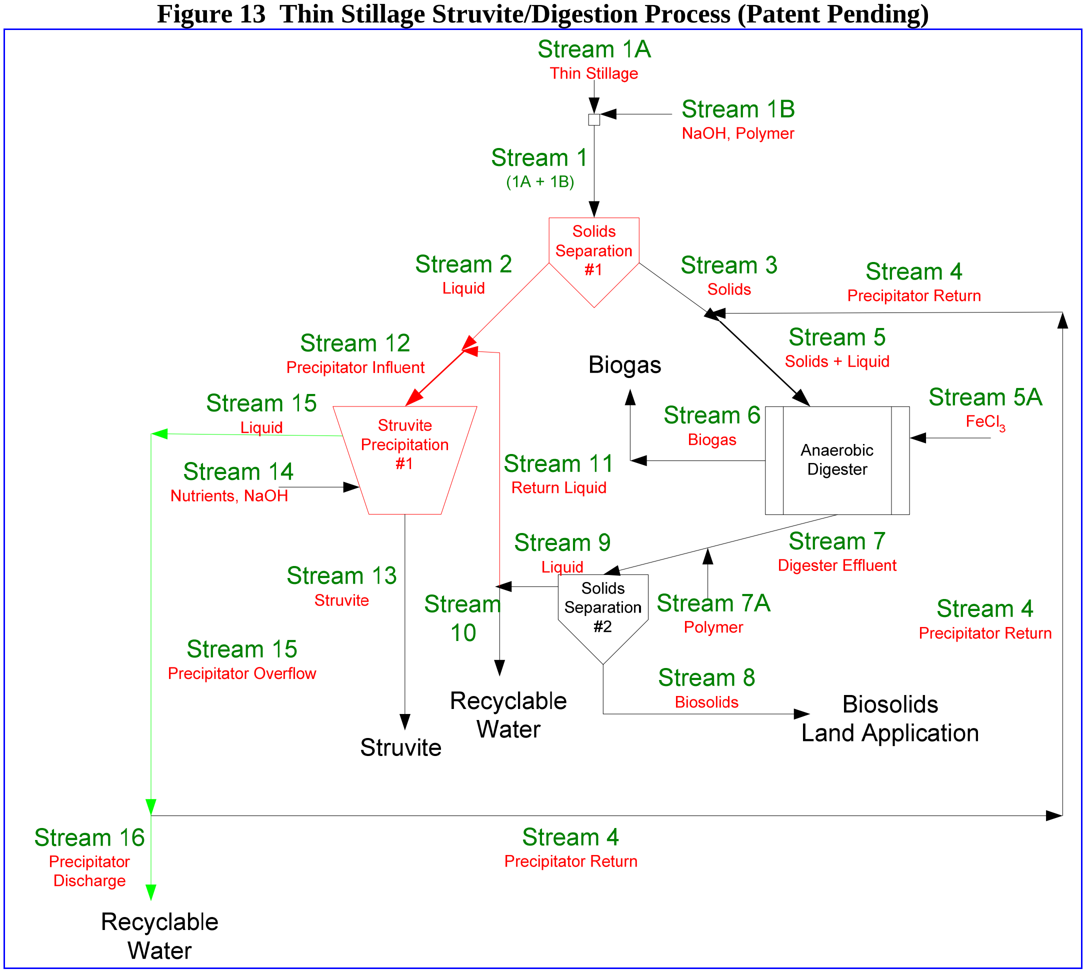
Figure 12 Preliminary Layout for a Struvite Production Facility



5 MASS BALANCE, DIGESTION/STRUVITE PRECIPITATION PROCESS

A mass balance model has been developed based on the findings from Phases I, II, and Phase III of this study. This model has been used to predict results from the struvite/digestion process (as shown in Figure 13) if implemented at the Otter Tail Ag Ethanol Facility.

Figure 13 Thin Stillage Struvite/Digestion Process (Patent Pending)



The mass balance model predicts mass flow rates and concentrations of selected components for all process streams, treatment chemical requirements, and solids production. The model to date has been used to evaluate five scenarios for Otter Tail Ag, as listed below. The first scenario is the least complex and easiest to implement. Subsequent scenarios are more complex and build on the previous ones. Thus, the effects of the changes can be readily seen.

- Scenario 1: Digestion of thin stillage for methane production.
- Scenario 1A: Same as Scenario 1, but $FeCl_3$ is added to the digesters to eliminate struvite scaling therein. Phosphorus preferentially reacts with the iron, forming ferrous phosphate, a more tractable solid than struvite. Insufficient phosphorus remains to form struvite.
- Scenario 2: Thin stillage digestion for methane production, plus struvite precipitation for fertilizer production by the Ostara process.
- Scenario 2A: Same as Scenario 2, but $FeCl_3$ is added to the digesters to control struvite precipitation and scaling therein.
- Scenario 3: Same as Scenario 2A, but high-ammonia filtrate is recycled from Liquid/Solids Separator 2 to the Ostara unit to eliminate Ostara's commercial ammonia supplement.

5.1 Feed Water Flow and Composition

All treatment scenarios are supplied with the same feed water so that process results can be compared directly.

- The influent flow is 538,000 gallons per day.
- Table 7 describes the composition of a typical process influent. Note that magnesium is present in a high concentration and is predominantly in the dissolved form. Thus, most of the magnesium can be diverted from the influent stream by an efficient solids/liquid separation device.
- The molar ratio of magnesium/ammonium/orthophosphate = 1.0/0.24/0.74. The water is ammonia and orthophosphate deficient. Ammonia and orthophosphate supplements will be needed to provide high magnesium removals.

Table 7 Influent Thin Stillage Chemical Analysis

Item	Total	Dissolved
COD, mg/L	138,000	70,000
Conductance, umhos/cm	7,164	--
TDS, mg/L	--	28,110
Total solids, mg/L	65,000	--
Total volatile solids, mg/L	61,000	--
pH	3.4	--
Magnesium		
mg/L	730	720
mmol/L	30.0	29.6
Ortho-P		
mg/L	714	679
mmol/L	23.0	21.9
Total P		
mg/L	1,303	1,108
mmol/L	42.0	35.7
Ammonium, as N		
mg/L	--	101
mmol/L	--	7.2
TKN		
mg/L	1,802	1,064
mmol/L	128.7	--
Na, mg/L	100	100
Aluminum		
mg/L	12.0	8.5
mmol/L	0.4	0.3
Iron		
mg/L	26	7.8
mmol/L	0.5	0.1

5.2 Analysis of Unit Operations

Table 8 provides a unit-by-unit analysis of full-scale operations.

Table 8 Full Scale Mass Balance Calculations

Item	Scenario				
	1	1A	2	2A	3
Overall removals, %					
COD	97	97	97	97	98
TSS	93	94	95	95	96
VSS	97	97	97	97	98
TKN	12	13	16	15	27
Total P	55	54	60	60	67
Mg	61	9	88	82	88
Liquid/Solids separator #1					
% solids capture	N/A	N/A	98	98	98
% cake solids	N/A	N/A	35	35	35
NaOH, lb/day, pure basis	0	0	26,936	27,036	27,036
Polymer, gpd, pure basis	0	0	269	270	270
Digester operations					
COD destruction, %	90	90	90	90	90
VSS destruction, %	77	77	77	77	77
Methane production, 1,000 scf/day	3,129	3,129	3,111	3,153	3,111
Digester flow, gpd	537,106	539,503	579,489	579,838	894,153
Na concentration, mg/L	100	100	4,799	4,796	4,708
$FeCl_{3,}$ lb/day, pure basis	0	21,514	0	3,144	4,474
Struvite precipitation, lb/day	22,151	0	2,292	0	0
Ostara process					
Feed rate, gpd	N/A	N/A	528,134	528,134	842,968
Chemical consumption, lb/day, pure basis					
NH3-N (gaseous)	0	0	930	930	0
Na_3PO_4	0	0	5,885	5,885	6,295
NaOH	0	0	8,814	8,814	8,814
Struvite production, lb/day	0	0	19,066	19,066	20,393
Liquid/Solids Separator #2					
% solids capture	85	85	85	85	85
% cake solids	15	15	15	15	15
Polymer, lb/day, pure basis	282	283	304	304	468

A discussion of the results shown in Table 8 follows:

- Component removals. Overall COD, TSS, and VSS removals are similar for all five scenarios. Not surprisingly, magnesium removals are highest for the scenarios involving the Ostara process. TKN and P removals are moderately higher for the scenarios involving the Ostara process.

- Liquid/Solids Separator #1.

    - A key to successful operation is separation of most of the magnesium from the thin stillage stream. A high degree of separation prevents struvite scaling and accumulation in the digesters while maximizing the struvite yields in the Ostara process. A plate-and-frame filter press has been selected for Solids Separator #1. This unit is capable of separating more water from a liquid stream than any other dewatering device and producing the most solids-free filtrate. We have assumed the press can squeeze out enough water to produce a 35% solids filter cake and that it will capture 98% of the influent solids. This assumption must be tested in the next phase of development.

    - The initial pH adjustment consumes large quantities of sodium hydroxide (caustic).

    - In the pilot study, an average of 28% of the dissolved Mg in thin stillage was precipitated in the pH-adjustment process step at the pilot plant. The precipitated magnesium was thus not available to the Ostara process, which meant a 28% reduction in struvite production. This step was operated around pH 6.0. We have assumed a lesser loss (21%) in the mass balance calculations on the assumption that the procedure can be improved. Even better results (i.e., lesser dissolved Mg removals) may be able to be obtained by reducing the pH in this step to near 5.0.

- Digester Operations.

    - Methane production is similar for all five scenarios.

    - Digester flow increases significantly (54 %) when filtrate from Liquid/Solids Separator #2 is recycled to eliminate the need for ammonia supplementing (Scenario 5). Scenario 5 requires a 54% larger digester than the other scenarios to maintain residence time and performance.

    - Caustic dosing required for the Ostara process raise digester sodium concentrations to levels that may inhibit digester operation.

- Ostara Process.

    - The Ostara process feed rate increases significantly (54 %) when filtrate from Liquid/Solids Separator #2 is recycled to eliminate the need for ammonia supplementing (Scenario 5). However, Ostara unit performance relates to constituent mass loadings, which increase much less (i.e., the magnesium loading increases only 7%). Therefore, Ostara system performance (unlike digester performance) is relatively insensitive to variations in feed flow rate.

  - Significant amounts of caustic are needed for the Ostara process.

- Struvite Production (quantity and location).

  - Large quantities of struvite are generated in the digester in Scenario 1. It has the potential to accumulate within the digester, reducing its useful volume, and to scale equipment surfaces. A significant amount of struvite precipitation was observed in the pilot digester tanks during Phase II of this study.

  - Struvite precipitation can be forestalled by adding a large amount of ferric chloride to the digesters (Scenario 1A).

  - Incorporation of the Ostara process (without ferric chloride addition) to the digesters (Scenario 2) allows production of a large amount of useful struvite product. However, struvite scaling is still possible within the digesters.

  - Addition of a relatively small amount of ferric chloride to the digesters (Scenario 2A) eliminates struvite scaling in the digester, while maintaining the Ostara process' struvite production rate.

  - Recycling of filtrate from Solids Separator #2 to eliminate Ostara's supplemental ammonia requirement (Scenario 3) increases Ostara's struvite production moderately (7%) while raising ferric chloride requirements significantly (42%).

- Liquid/Solids Separator #2. Liquid/Solids Separator #2 dewaters the digester effluent to produce dewater biosolids. A solids capture of 85% and a cake solids concentration of 15% have been specified for this unit. A belt filter press can likely satisfy these requirements. Another option would be to use the existing atonal plant evaporator to produce the dewatered bio-solids and condensate water.

5.3 Characteristics of Discharged Liquid Streams

Streams 10 and 8 are discharged externally. Table 9 describes their flows and compositions.

- Recyclable Water Stream (Stream 10). Stream 10 has relatively high pollutant concentrations and may have to be further treated if it is to be reused in the ethanol plant. The water from Scenario 5 is less contaminated than the water from other scenarios. If the existing evaporator were used a high quality recyclable water would be produced

- <u>Biosolids (Stream 8).</u> Stream 8 composition information can be used to estimate allowable loading rates to agricultural land.

- <u>Precipitator discharge (Stream 16).</u> Stream 16 could, in theory, be sent to the ethanol plant for use. This scheme would not be practical, in our opinion, because Stream 16 contains high concentrations of COD. Sending it to the ethanol plant or anyplace else, would result in lost methane production in our process. Therefore, we have set Stream 16 flow at zero in all our calculations.

Table 9 Flow and Composition of Process Liquid Discharges

	Scenario				
Item	1	1A	2	2A	3
Recyclable water (Stream 10)					
Flow, gpd	515,213	521,947	570,579	571,290	584,689
Composition, mg/L					
COD	4,933	4,892	4,496	4,493	2,941
TSS	2,576	2,320	1,898	1,878	1,250
VSS	1,166	1,151	1,046	1,045	673
TKN	1,653	1,620	1,426	1,447	1,213
Total P	605	616	492	492	389
Mg	297	684	83	121	81
Na	95	95	4,851	4,589	4,460
Fe	13	764	3	53	33
Biosolids (Stream 8)					
Flow, gpd	48,749	44,481	37,884	38,144	39,337
Composition, mg/L					
COD	98,847	108,002	125,692	124,854	120,877
TSS	154,285	154,297	161,998	161,993	161,999
VSS	69,839	76,540	89,310	88,701	87,214
TKN	2,381	2,738	3,413	3,071	2,823
Total P	7,957	8,512	6,666	7,024	7,139
Mg	4,901	789	3,167	2,582	2,622
Na	96	97	4,567	4,564	4,480
Fe	720	51,472	284	4,498	4,298

6 ECONOMICS

Table 10 sets forth estimates of process revenues and chemical costs for a 538,000 gpd processing plant. In summary Table 10 shows:

- Product revenues exceed chemical expenses by a wide margin. Net revenues for the most likely scenario (Scenario 2A) are on the order of $24,000/day ($9.21 million per year).
- Methane production provides about 60% of total revenue.
- Caustic and polymer are the most costly chemicals.
- Caustic costs could come down. The ethanol plant acidifies thin stillage to prevent scaling in the plant's evaporators. If thin stillage was diverted to the digestion/precipitation process tested by this project, acidification would not be needed and the digestion/precipitation process' caustic requirements would drop accordingly. A caustic reduction of up to 15% might be possible.

Table 10 Partial Economic Analysis (538,000 gpd of Thin Stillage)

	Scenario				
Item	1	1A	2	2A	3
Chemical costs, $/day					
NaOH	N/A	N/A	6,256	6,274	6,274
NH3-N (gaseous)	N/A	N/A	151	151	0
Na_3PO_4	N/A	N/A	530	530	567
Polymer	1,974	1,983	4,013	4,021	5,166
$FeCl_3$	0	3,765	0	550	783
Sum	1,974	5,748	10,950	12,304	12,789
Revenues					
Struvite	0	0	14,300	14,300	15,295
Methane	25,035	25,035	24,891	25,226	24,891
Sum	23,877	23,877	39,327	39,526	40,411
- Net revenue	- 22,523	- 18,258	- 28,396	- 27,222	27,443

Chemical prices, bulk, pure basis	
NaOH, $/ton	350
NH3-N, $/ton	325
Na_3PO_4, $/ton	180
Polymer, $/gal	7
$FeCl_3$, $/ton	350
Estimated product prices	
Struvite, $/ton	1,500
Methane, $/1,000 scf	8

A budget estimate for the operation for a 538,000 gpd plant using Scenario 2A and the flow scheme shown in Figure 2 is shown below.

- ***Revenues****

    - Struvite 9.6 tons/day @ $1,500/ton = $14,400/day
    - Methane 3,153,400 scf/day @ $8/1,000 CF = $25,226 /day

- **Total Revenues** = $39,626/day

- ***Expenses***

- **Chemical Expenses**:
    - NaOH 17.87 tons/day @ $350/ton = $6,256/day
    - NH_3 0.463 tons/day @ 325/ton = $150/day
    - Na_3PO_4 2.94 tons/day @ $180/ton = $529/day
    - Polymer* 285 gpd @ $7/gal = $1,995/day
    - $FeCl_3$ 1.57 tons/day @ $350/ton = $550/day
- (*Solids Separator #1 Only)

- **Total Chemical Expenses = $9,480/day**

- **Electrical Expenses @ $0.055/kWh)**

Item	**Hp**
Pumps	20
Mixers	1,500
Biogas	300
Belt Press	100
Ostara	400
Total (say)	**2,500 or $1,500/day**

- **Labor**
    - **Total** **$400/day**

- **Maintenance**
    - **Total** **$300/day**
- ***Total Expenses***
    - **Total** **$11,700/day**
- ***Net Income***
    - **Total** **$28,000/day or $10,000,000 per year**

*Possible additional revenue from carbon credits.

7 CONCLUSIONS AND RECOMMENDATIONS

The conclusions and recommendations are as follows:

1. Thin stillage can be digested to produce large quantities of methane gas. Up to 3,000,000 CF/day are projected for the Otter Tail Ag facility.

2. It is unlikely, however, that a digestion process could be sustained without struvite precipitation ahead of the digester. The buildup of struvite within the digester associated appurtenances would cause long-term operation and maintenance (O/M) problems.

3. The combined struvite/digestion process described in this report will not only substantially reduce O/M problems but has the potential to produce large quantities of struvite, methane gas, biosolids and recyclable water.

4. Based on mass balance calculations, the combined struvite /digestion process would yield net operating income of $28,000 per day.

5. A preliminary budget estimate for a 180,000 gpd demonstration plant is:

Capital Costs:		
	Biogas Digester	$6 million
	Struvite Precipitator	$5.0 million
	Press	$1.5 million
	Gas scrubber	$0.7 million
	Total	$13.2 million
Operating (Revenues – Expenses)		$3,400,000/year

6. Further development of this concept through a preliminary engineering cost estimate and a 180,000 gpd demonstration project is strongly recommended.

8 APPENDICES

8.1 Identification of Solids in Preliminary pH-Adjustment Step

1. Calculations with MINTEQA2 suggest the following saturation indices for a water with average thin-stillage concentrations of the spreadsheet (Mg = 446 mg/L, NH_3-N = 200 mg/L, etc.), a pH of 6.0 and an Eh of -400 mv (the latter typifies anaerobic conditions). A negative saturation index for a compound indicates the solution is under saturated with respect to that compound and it is, therefore, unlikely to precipitate. A positive index indicates precipitation of that compound is possible. However, it does not confirm that that compound is present.

8.1.1.1

Compound	Saturation Index
$MgNH_4PO_4.6H_2O$	-1.196
$Ca_3(PO_4)_2$	-1.048
$MgHPO_4$	-0.303
$Mg_3(PO_4)_2$	-1.208
$Al(OH)_3$ amorphous	1.686
$Mg(OH)_2$	-7.191
$Ca_5(PO_4)_3OH$	6.652
$Fe_3(PO_4)_2$	4.151
$AlPO_4$	

These calculations indicate that $Ca_5(PO_4)_3OH$ and $Fe_3(PO_4)_2$ and $Al(OH)_3$ precipitation are possible under these conditions. But what is removing Mg? Possibly $MgHPO_4$. Its saturation index is fairly close to being positive. Considering the data scatter and that MINTEQA2 calculations are just that (calculations and not proof positive) it seems possible that $MgHPO_4$ might be present. MINTEQA2 doesn't seem to spit out anything about $AlPO_4$. However, our experience indicates $ALPO_4$ forms in sewage systems before $Al(OH)_3$ does; therefore, AlPO4 is a good candidate.

2. Another way to look at this problem is to add up all the P associated with an assumed set of solids and compare it with P actually removed. If the sum of P associated with the solids is reasonably close to the P actually removed, then the assumption was valid. Assume solids are $MgHPO_4$, $Ca_5(PO_4)_3OH$, $Fe_3(PO_4)_2$, and $AlPO_4$.
    i. <u>Situation 1</u>. Calculate metals removals by subtracting average pH-adjusted thin stillage metal concentrations from average thin stillage metals concentrations.
        1. P associated with solids (calculated) = 202 mg/L
        2. Measured P removal = 155 mg/L

        This is a reasonable comparison.

ii. Situation 2. Data of Oct. 10, 2007. Possibly the most believable Mg and P data. Very high Mg and P removals, so analytical error small compared to removals. Calculate metals removals by subtracting Oct. 10 pH-adjusted thin stillage metals concentrations from Oct. 10 thin stillage metals concentrations.
   1. P associated with solids (calculated) = 414 mg/L
   2. Measured P removal = 372 mg/L

   A better comparison

8.2 Nalco Analyses of pH Adjustment Components

Nalco Analytical Resources

Cations/Metals	Parameter	Pre Settling	Post Settling	Reactor Effluent	Gray sludge
	Aluminum	11	4.8	3.8	
	Calcium (CaO)				6%
	Calcium	110	78	61	
	Iron	35	22	13	
	Magnesium (MgO				7%
	Magnesium	390	330	240	
	Phosphorus (P2O5)				24%
	Phosphorus (P)	660	580	500	
	Phosphorus (PO4)	2000	1800	1500	
	Potassium	990	990	720	
	Sodium	160	2700	2100	
	Calcium	290	190	150	
	Magnesium	1600	1300	970	
	Sodium	350	5900	4600	
	Calculated Hardness (CaCO3)	1900	1500	1100	
	Phosphate (PO4) Total	1800	1600	1500	
	Phosphate (PO4) Ortho & Poly	1600		1500	
	Phosphate (PO$)Ortho	1400		1400	
	Phosphate (PO4) Poly	200		100	
	Phosphate (PO$) Organic	200		0	
Anions	Bromide				
	Chloride	180	170	140	
	Sulfate (SO4)	1700	1300	1200	
	Chloride (CaCO3)	250	230	200	
	Nitrate (CaCO3)				
	Sulfate (CaCO3)	1800	1400	1300	
	Alkalinity				
	Bicarbonate		4900	4300	
Others	pH	4.1	5.8	6.5	
	Concuctivity	6000	11000	11000	
	Acidity free mineral (CaCO3)	460			
	Acidity Total (CaCO3)	6100			