DOE FINAL REPORT

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MASADA OXYNOL INC.

**CO-PRODUCT ENHANCEMENT AND DEVELOPMENT FOR THE MASADA
OXYNOL PROCESS™ PROCESS**

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1. Executive Summary:

The focus of this project was an overall process improvement through the enhancement of the co-product streams. The enhancement of the process operations and co-products will increase both ethanol production and the value of other process outputs and reduces the amount of waste byproducts. This leads to a more economical and environmentally sound alternative to landfill disposal of MSW. These enhancements can greatly increase the commercial potential for the production of ethanol from MSW by the Masada CES OxyNol™ process (Masada). Both technological and economical issues were considered for steps throughout the conversion process.

The research efforts of this project are varied but synergistic. The project investigated many of the operations involved in the Masada process with the overall goal of process improvements. The general goal of the testing was to improve co-product quality, improve conversions efficiencies, minimize process losses, increase energy efficiency, and mitigate process and commercialization risks.

The project was divided into 16 subtasks as described in general terms below. All these tasks are interrelated but not necessarily interdependent.

2. Project goals & objectives and accomplishments:

The focus of this project was the overall process improvement through enhancement of the co-product streams.

This project is divided into 16 subtasks and outcomes for each sub-tasks as follows:

Task 1: Develop Detailed Test Protocol: A test protocol was developed for several of the project tasks. These protocols were continually refined as testing proceeded, and as process improvements were identified and integrated into the overall process design.

Task 2: Design Hydrolysis System: A test system for the hydrolysis process was developed with TVA based on the Masada process. Additional systems were developed for portions of the hydrolysis and ethanol production process.

Task 3: Equipment Procurement/Installation: In March, 2007, Masada won a bid to purchase TVA's biomass pilot plant facilities and equipment for \$300,000. The decommissioning and relocating the TVA biomass to fuels pilot plant facilities and equipment in Muscle Shoals, Alabama to Auburn University's E.V. Smith research campus in Tallasee, Alabama is pending. Masada has donated the TVA pilot plant facilities and equipment. Auburn University is responsible for decommissioning and moving the equipment in the pilot facilities to Auburn, to date the decommissioning and

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relocation has not been completed. In addition, Masada has paid Auburn \$500,000 under a sponsored research commitment to support Masada's waste-to-ethanol technology research in biofuels.

Task 4: Raw Material Procurement: Masada procured raw MSW and waste water treatment Biosolids from several facilities with similar operational parameters to the Masada process design. Arrangements were made for the procurement of MSW from several appropriate sort facilities. Biosolids materials were procured for Task 5 testing from several facilities where sludge characteristics were typical of the material to be processed in the Masada facility.

Several vendors of commercial equipment were identified for preprocessing and moisture reduction in the feedstock. Technology evaluation was based on cost, energy efficiency and operability within the Masada process constraints. A testing protocol was developed to evaluate drying. A preferred vendor of equipment for MSW feed drying and preparation was identified. Feed drying facilities were reviewed and are suitable for the Masada process testing. The vendor's experience with similar applications was also reviewed to ensure a suitable level of relevant experience.

Task 5: Biosolids Processing: A preliminary evaluation of biosolids processing options was developed. This analysis suggested several minor modifications to the biosolids processing that will result in a more fuel-efficient process with the generated residue having higher value fuel than previous modeling suggested.

A scope for testing process modifications was developed. Preliminary testing was completed, including the analytical characterization of several sludge materials. Sludge characterization included the following physical and chemical characterization.

- Proximate analysis
- Ultimate analysis
- Btu value
- Bulk density
- Moisture content

This analysis was performed by a suitable third-party laboratory and as part of vendor testing.

TVA completed a laboratory bench scale evaluation of process alternatives. This testing involved processing under several conditions and analysis of the feed, processed biosolids, condensate, and off gases generated with varying process conditions. Several different temperature and acidification level combinations were tested at TVA using laboratory scale glass equipment.

Process testing was conducted under the supervision of Harris Group Inc., Masada's process engineer, and completed at the pilot scale at the Koline-Sanderson (KS) test

facility in High Bridge New Jersey and at Syangro Technologies, Inc. in Waterbury, Connecticut. The KS was identified as having suitable equipment for the Masada process and having a pilot-sized unit that can be used to test and optimize the process. The KS tested real sludge received from multiple locations with potential to provide sludge to the commercial facility. This sludge came from a variety of different waste treatment processes representing the range of expected sludge materials for a commercial Masada facility. Testing by KS included evaluation of equipment sizing based on design material flow and heat transfer characteristics of the sludge. During this testing multiple off-gas, sludge feed and products samples were collected and analyzed, allowing the more complete characterization of the process.

Masada was able to

- Determine material handling characteristics of blended sludge and of cooked and dried acidified biosolids.
- Verify that the vendor equipment is suitable for processing sludge without plugging and/or fouling.
- Determine heat transfer characteristics of acidified biosolids at various levels of moisture content.
- Confirm changes in sludge characteristics with addition of acid and heating.
- Develop additional fuel analysis for various blends of acidified biosolids.
- Dispel concerns with potential fouling of the dryer by sludge from the Zimpro process.

Critical improvements in the biosolids process portion of the Masada process was integrated into the commercial design of the Masada facility. These changes resulted in reductions in both capital and operating costs while providing a higher value biosolid fuel production.

Pilot testing has verified the suitability and performance of the vendor equipment. Harris Group Inc. oversaw the development of the selection of the vendor, the test protocol and the analysis of the test run data. The trip report filed by Harris Group, Inc. with Masada Resource Group, LLC is attached as Appendix A.

Task 6: Hydrolysis: A protocol for hydrolysis testing was developed. Earlier tests had focused on determining the minimum batch size that can be effectively processed in the TVA facility to optimize the use of available sample material. Several hydrolysis tests were completed at TVA and hydrolysis sample analysis was completed, allowing conversion to be determined. In addition to completing experimental sample analysis TVA also generated several numerical tools/programs used to evaluate conversion and trends in glucose yield as a function of hydrolysis parameters.

Additional process optimization included testing the conversion as a function of reaction time, and as a function of the amount of dilution water added during the hydrolysis reaction.

Harris Group, Inc., Masada Resource Groups process engineers evaluated the hydrolysis testing that was conducted at the Tennessee Valley Authority Pilot plant in 2000 and 2001. A project memorandum from Harris Group Inc. is included as Appendix B

Task 7: Filtration/Lignin Production: Additional testing was completed to assess and optimize the lignin filtration, particularly for the hydrolysis material generated in Tasks 6 and 12. These tests further defined filtration parameters, provided material for downstream process testing, confirmed and or rejected operational design assumptions, and analyze the lignin-biosolid fuel.

Task 8: Acid/Sugar Separation: Testing under Task 8 was defined. The preferred vendor for this process Osmonics, Inc. (n.k.a. GE Osmonics) provided the testing services and equipment. Osmonics provided sample size requirements for various test alternatives and provided their insight into the commercial impact of process enhancements affecting this separation process. Two levels of testing were evaluated; chromatic pulse testing, and pilot testing.

Because indications in the design of Masada's New York project indicated that the evaporation system for dilute acid was potentially compromised by remnant sugars (trace amounts <1% by wt.) in the eluted permeate from the chromatographic separation unit. Evaporation of acid has important and significant economic and environmental benefits for the Masada process through acid recycling and reduction of fresh acid purchase and delivery.

The nominal composition of the acid-sugar mixture entering the Osmonics process testing system was: Sulfuric Acid 8%; Glucose 0.6%; Xylose 0.1%, Mannose 0.1%.

Performance targets for the system was nominally: Minimum acid-sugar ratio 20:1; Optimized acid-sugar ratio 25:1; Increase in sugar concentration of 7 to 8 X input values; Working pressure through put of 440 GPM.

Results showed that the Osmonics spiral-wound membrane systems retained sugar at targeted values while allowing acid to pass through the filtration membranes. The Hytrec II® is a 5 µ nominal pore size and is nest able within stainless steel housing that achieved acceptable flow rates at pressures of 30-bar and above as similarly deployed in industrial settings.

Liquid Chromatographic analysis performed by Osmonics, Inc. for Masada Resource Group are included as Appendix C.

Task 9: Neutralization/Gypsum Production: Several alternative technologies were identified for this aspect of the process. Vendors for the various technologies were identified and preliminary testing was done to evaluate these technologies. These preliminary assessments were used by Seattle University in developing their evaluation

protocols for the technologies they assessed (see Appendix H). A general analysis of technology alternatives was conducted based on previous test results, and anticipated commercial performance specifications provided by the vendors. Testing on critical process issues identified was conducted and led to operational and performance criteria for the selection of a preferred vendor for the Masada process.

A preferred technology has been tentatively selected based on technical and economical feasibility, based on modeling for the Masada process. Other technologies evaluated had technical drawbacks or required further development and were not considered as viable for commercialization at this time.

Further evaluation of the Masada neutralization process had taken place. Testing of this new process concept indicates better process performance as defined by cake dryness and loss of sugar in the cake.

A cost estimate based on the testing results was completed to compare the new concept to the existing neutralization and gypsum removal process. This analysis indicates that a capital cost savings of over \$4.5 million dollars could be realized by implementation of the new process concept. The new process will reduce the annual operating costs and the process will take up less space, a key consideration for the Masada process at some locations.

Two phases of process testing have been completed. This testing utilized a simulation solution designed to mimic the actual Masada process solution. The simulation solution is based on analytical data produced in previous testing programs. Samples from both phases of neutralization were tested by TVA for pH, ion content, and sugar concentration. TVA also analyzed the moisture content of the precipitate gypsum cake.

TVA also completed calcium sulfate solubility versus temperature studies with hydrolyzate and stillage. This testing was completed as part of an overall evaluation of neutralization and its impacts on other processes within the Masada design.

All the process enhancements have been incorporated into the Masada process design. Test results on Acid Neutralization and Gypsum Dewatering conducted for Kvaerner Process on behalf of Masada Resource Group by EMICO Baker Hughes are attached as Appendix D.

Task 10: Sugar Concentration:

The solubility issues that impact neutralization were evaluated. This testing studied the solubility of key chemical species in the feed and product solutions from sugar concentration.

Testing under this task was primarily to take place at Auburn University to provide samples for fermentation testing.

An alternative technology proposed by a vendor was also evaluated. The process details are given in Quarterly Report for the Co-Product Enhancement and Development for the Masada OxyNol Process Project, Second Quarter of 2003.

Testing by a proposed vendor, [REDACTED] was conducted in early 2003 and the report by [REDACTED] as Appendix E.

Task 11: Acid Concentration: Bench scale testing on the acid concentration process has been successfully completed on two separate dilute acid solutions.

A suitable vendor with both laboratory and pilot plant capacities was identified for testing and evaluation of the acid concentration process.

The bench scale test results confirmed that the material can be evaporated to the specific concentration.

The pilot testing was completed, processing approximately 500 gallons of dilute acid into concentrated acid. The testing provided an indication of the impact of changing the final acid concentration on the processing. The pilot process is a triple effect evaporator. The first stage of processing was completed with pre-concentration of the dilute material to an intermediate concentration. All the dilute material was successfully processed. Final concentration was completed. Several processing runs were completed with various concentration targeted. Final concentrations were achieved that both met and exceeded the process specifications.

Two vendors systems were evaluated by Masada for applicability to the OxyNol process. This evaluation included a visit by Masada personnel and contracted process engineers to the [REDACTED]. However, no detailed process data were released [REDACTED] to Masada or its process engineers in accordance with commercial agreements with [REDACTED]. TVA also completed preliminary tests conducted with acid product to evaluate process for destroying organics than can otherwise cause fouling in the acid re-concentration process.

Masada identified a process enhancement that significantly reduces the amount of residual sugar in the acid product prior to acid concentration for recycle within the hydrolysis process. This improvement reduces the level of residual contamination of the acid catalysts, significantly improving the potential performance characteristics of the acid evaporative concentration unit. For the implementation of this enhancement, several vendors have been identified and with suitable technologies for the evaporative re-concentration process. Testing on synthetic samples designed to mimic the commercial solution have been performed by several vendors.

Task 12: Hydrolysis with Re-concentrated Acid: A phase one scope of work for this testing was developed and defined. TVA conducted this testing using both small scale and larger scale laboratory reactors to complete the hydrolysis reaction. This testing was continued at Auburn University.

This testing included side-by-side tests with re-concentrated and fresh acid to confirm previous experiments that indicated that hydrolysis yields are not adversely effected by the use of recycled acid.

Task 13: Fermentation: Several aspects of fermentation have been tested. A small test was performed to evaluate dried yeast addition rates. Evaluation of these tests included determination of glucose conversion and counting viability yeast cells. The results of these preliminary tests were used for preparation of the inoculum for 16-liter fermentation tests and defined the yeast usage for future testing.

TVA performed several flask fermentations to evaluate ammonium neutralized hydrolyzate as an alternative option to lime neutralization.

Studies included larger scale fermentations to confirm the ability of standard yeast to convert the Masada hydrolyzate and allowed the collection of CO₂ fermentation off-gas for complete analytical characterization. The primary focus of these tests was to collect CO₂ for analysis. During these tests TVA collected several CO₂ samples that were analyzed by a third-party. The CO₂ from both sets of testing was analyzed for non-condensable gases, volatile hydrocarbons, volatile sulfur compounds, volatile oxygenates and benzene, oxides or nitrogen, and others.

Two reports are included as Appendices F and G.

Task 14: Distillation/Wastewater Production: Samples from the preliminary fermentation process testing were collected. These samples were derived from flask scale fermentation testing and were distilled at TVA using a Roto-Vap setup. Samples were analyzed by TVA and provided to Seattle University for characterization in preparation for treatment studies on larger samples.

Latter, TVA completed stillage preparation using the fermentation broth. TVA processed five batches and added water to produce a representative sample of stillage from a fermentation process. TVA also completed a full and detailed analysis of the beer, ethanol, and stillage streams.

Task 15: Wastewater Treatment: The following is a chronological order of activities involved in this task:

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A general scope of work at Seattle University was developed. Participation of commercial process technology vendors was incorporated in this task with the vendors supplying technical support and materials.

The Seattle University team designed a fill-and-draw treatment system based on specifications provided by a commercial waste treatment technology vendor. The University team procured equipment for the treatment test system and developed a testing protocol. Seattle University completed system assembly and began shakedown testing using a simulated wastewater. The commercial system vendor also supplied a sample of its commercial activated sludge for use in the treatment testing.

Experimental reactors were constructed. A total of six reactors were built. Initially all six reactors were operated in the same manner. Ultimately, three of the reactors were used to test Masada wastewater and three acted as experimental controls using synthetic feed.

Reactors were started with the addition of methanogenic bacteria granules to a growth medium. The medium contained and latter provided sufficient nutrients. Each reactor was operated at a hydraulic residence time of 15 days. During this period, the test setup was taken through a shakedown phase. Initial reactor related problems were identified and solved. Methane gas production was consistently within 15 percent of theoretical range, indicating that the system operated properly using the synthetic feed.

Testing of the initial stillage sample from Masada was performed. The parameters that were analyzed included pH, alkalinity, five-day biochemical oxygen demand (BOD₅), chemical oxygen demand (COD), volatile solids, total suspended solids, and dissolved sulfate. Problems were encountered with the spectrophotometer that will be utilized to assess total kjeldahl nitrogen and total phosphorous concentrations and results were thus inconclusive with regards to total kjeldahl nitrogen concentrations.

A selected vendor supplied a scope of parameters to be tested and budget for non-biological treatment alternatives. The scope included lab scale processing, material characterization, and sample analysis.

Seattle University team completed its study of the wastewater digestion process. Testing showed that a suitable system for anaerobic digestion can be developed and deployed that properly controls pH in the digester.

Vendor testing was also completed using a non-biological treatment alternative. Testing successfully demonstrated the process, which will greatly enhance the recycling of the water within the Masada process and eliminate much of the facility waste water discharge and reduce water consumption and further minimize the environmental footprint of the Masada process.

Samples of the vendor process streams were provided to TVA and a third-party laboratory. Analysis showed the suitability of the water produced for use within the

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Masada process and that the byproduct stream characteristics make it a suitable fuel material for the production of process steam and/or electrical energy.

Seattle Universities Report *Co-Product Enhancement and Development for the Masada OxyNol Process*, June 2002b is attached as Appendix H.

Task 16: Evaluation: Analysis of the samples produced and testing results were used to evaluate the impact of processing alternatives and optimization of the economics and technical performance of the Masada process.

TVA has completed the analysis on a set of 14 samples. Analytical methods used include ICP, IC, TOM, conductivity, and HPLC. The analysis was utilized to evaluate process performance.

Masada Resource Group, LLC continues to work with Auburn University on further refinements to the Masada OxyNol Process and for new markets for commercial application of the Masada OxyNol Process, such as the development of a modified process to address paper sludge disposal for the paper manufacturing market.

No additional patents were developed as a direct result of the research efforts conducted under this award.

Appendix A

Komline Trip Report June 2002

June 12, 2002

TRIP REPORT 42006/02

Trip Date: June 4-6, 2002

Location: Location 1 Komline-Sanderson Test Lab
High Bridge, New Jersey

Location 2 Synagro
Waterbury, Connecticut

Contacts: Doug Grunwald, Komline-Sanderson (Location 1)
Kerry Kovacs, Komline-Sanderson (Locations 1 and 2)
Tim Judge, Masada Resource Group (Location 1)
Randy Tyrrell, Synagro, Operations Supervisor (Location 2)

Purpose: Location 1 Observe and monitor sludge cooking and drying testing
Location 2 See sludge drying operation

**KOMLINE-SANDERSON TEST LAB
(Location 1)**

Following are observations from testing. Komline-Sanderson (KS) will produce a report describing test procedures and results.

1. Sludges from Middletown, New York; Poughkeepsie, New York; and Passaic, New Jersey were tested. Both KS and Atlantic Labs did a thorough job of documenting tests and labeling samples. Samples of the "as received," blended, cooked, and dried material were taken and will be sent to Hazen labs for testing. Condensate samples were also collected for analysis. Atlantic labs received "grab" samples of gas from each test run and will do the gas analysis.

- [REDACTED]
2. KS also received samples from various locations on the dryer for equipment sizing purposes. In addition to the tests outlined in the HGI test matrix, KS did some additional testing. For example, KS attempted to dry Passaic (Zimpro) sludge without blending with the other high-moisture sludges.
 3. Sludge solids from Middletown and Poughkeepsie were measured at 17% and 23%, respectively. The Passaic (Zimpro treated) sludge was measured at 54% solids.
 4. The two non-Zimpro sludges are softer and appear to be quite pumpable. The Zimpro sludge is significantly firmer. The material may not be pumpable. [REDACTED]
[REDACTED]
 5. [REDACTED]
[REDACTED] This will enable them to reduce the number of dryers. [REDACTED]
[REDACTED] Sludge will come out of the cooker at 212°F.
 6. Cooked sludge has significantly different appearance and material handling properties than it does prior to cooking. It is significantly more flowable as it comes off the dryer hot. KS says cooked sludge becomes very difficult to pump after it has cooled.
 7. With the Zimpro and non-Zimpro sludge blend, product from the cooker looked and acted drier than the non-Zimpro blend but still had a gelatinous flowable character.
 8. KS had negative experience with drying Zimpro sludge in the past - poor heat transfer and significant fouling in the dryer. KS did not observe any fouling at any stage of the testing with Zimpro sludges blended with non-Zimpro.
 9. The dried product from the feed blended with Zimpro had a fluffy/powdery character, while the non-Zimpro blend was more granular. KS attributes this, not to differences in the feed, but rather to differences in the final moisture of the product. KS says that because the feed rate was constant for both feeds, and the Zimpro blend was drier, its final moisture was also drier. Regardless, both dried materials should be easily handled with typical bulk solids handling equipment.
 10. Zimpro sludge has significantly less odor than non-Zimpro sludge
 11. Dried material has significantly less odor than non-Zimpro sludge. However, if it is rewetted, the odor level increases.

- [REDACTED]
12. General Observation – The cooked acidified biosolids has a fairly fluid characteristic when hot. Komline-Sanderson doesn't think this material can be conveyed or metered with conveyors to the dryers. It will flow through a screw conveyor. Accurate metering to the dryers can be achieved by utilizing PD pumps for acidified biosolids. This is important because the plan is to have multiple dryers and we will want even distribution of the flow to each for optimization.

See the attached photographs.

SYNAGRO (Location 2)

Synagro has operations in 35 states around the U.S. that process sludge. They apparently both compost and incinerate sludge at their various locations. The Waterbury facility incinerates sludge for volume reduction. Some details and observations regarding the operation follow:

1. Location 2 processes about 300 wet tons per day of sludge [REDACTED]
[REDACTED]
[REDACTED] This plant would likely be a direct competitor to Masada.
2. Average moisture of received sludge is 20%.
3. Sludge is received via self-dumping trucks and roll-offs (containers) on tipping trucks. [REDACTED]
Smaller producers tend to store sludge and not ship on weekends. Larger facilities tend to ship sludge seven days per week. [REDACTED]
[REDACTED]
[REDACTED]
4. In the winter, sludge is sometimes frozen at the edge of the containers. Worst in this respect is sludge coming from the [REDACTED]
[REDACTED] [REDACTED]
5. Synagro appears to wash the containers after dumping.
6. The facility receives primarily digested sludge, but also receives undigested sludge. The undigested sludge has a heat transfer coefficient of about half that of digested sludge. (We should verify with Masada that we aren't going to get undigested sludge.)

- [REDACTED]
7. Sludge is dumped from trucks directly into a pit – roughly 30 x 25 x 20 ft deep. A clamshell crane loads sludge into a hopper feeding a series of three screw conveyors. The first two are at a 45-degree angle up and the last one is horizontal and feeds the dryer.
 8. The dried (24% solids) sludge exits the Konline-Sanderson Dryer Model 13W2000 (2000 sq ft).
 9. Synagro pumps the hot sludge using four Seepex pumps. The pumps have 4-in. discharge lines that combine to a single 12-in. line which then feeds a Dorr Oliver fluid bed incinerator. The 12-in. line is about 40 ft long with a flow rate of about 12 gpm and a pressure drop of 30 psig. Synagro says the pressure drop would be over 100 psig if the material was cold.
 10. When Synagro wants to shut down the dryer, the steam is shut off and the system is filled with undried sludge to enable the dryer and pumps to be started more easily.
 11. Synagro has problems with tramp material – rocks, metal – in the sludge and has continuing problems with damage to the Seepex pump stators as a result. Synagro is looking for a way to screen the tramp material out. Also, Synagro has to get “rags” that build up in the pump suction area out. It sounds like fibrous material coming in with the sludge forms rags in the pumps and other rotating equipment. KS doesn’t think they get any rag formation in the dryer. Rags don’t cause damage, but they do inhibit pumping. Synagro say a spare in-line pump would be helpful.
 12. Hot flue gas from the sludge incinerator is utilized to heat combustion air via heat exchangers. Flue gases are cleaned with an ESP and scrubber.
 13. A 500-hp package boiler supplies steam for the dryer. The overall system is a net heat user.
 14. The sludge process is largely a manual operation; i.e., no level or flow controls. The operator decides whether to load more sludge into the dryer feed conveyors by looking in the dryer door about once per hour.
 15. Some facility history:
 - The incinerator has been in operation for three years. [REDACTED]
[REDACTED]
[REDACTED]
 - Originally the plant had only a [REDACTED] dryer and material was dried to 90% using a recycle approach. Synagro has had a KS dryer since 1995 and used both dryers in series for several years with the [REDACTED] being used as a scalping dryer. The [REDACTED] dryer was wearing out and when the incinerator was put into service it

[REDACTED]

was abandoned in place and only the KS dryer was being used to dry the sludge to about 24%.

- [REDACTED]
- The stainless steel unit went in 1997 and has shown no signs of corrosion.

See the attached photographs.

JCL/mlm
Attachments

cc: Robert Hsu, Kvaerner (e-mail)
Thanh Trinh, Kvaerner (e-mail)
Susan Walther, Kvaerner (e-mail)
Carol Babb, HGI (e-mail)
Shari Laird, HGI (e-mail)
John Lukas, HGI (e-mail)
Lynn Montague, HGI (e-mail)
Danielle Sexton, HGI (e-mail)
Andrea Slayton, HGI (e-mail)
Jeff Ranney, HGI (e-mail)
File .0409

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Visit to Synagro Waterbury, Connecticut

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Appendix B

Kvaerner Hydrolysis Conversion Range Memo

May 6th, 2002

May 6, 2002

PROJECT MEMORANDUM 42010/04
MASADA HYDROLYSIS CONVERSION RANGE ANALYSIS

1. SUMMARY

Revisiting the statistical predictions from the conversion data from the 2000/01 pilot plant operations at TVA, we can make the following estimations and test hypotheses related to the conversion to glucose (referred to simply as conversion). We are primarily concerned with estimating what the "true" value of the mean of the conversion is for the hydrolysis of cellulose.

Based on the pilot testing and analysis of the results, the lower limit for conversion should be set at 69.1%.

From a predictive standpoint, one can estimate that the lower confidence limit (LCL) for the glucose conversion at a given confidence level. Kvaerner has indicated that it prefers a 99% confidence level for the estimation of this parameter. Based on pilot testing, at the 99% confidence level, the estimated LCL for the cellulose conversion to glucose is 69.13%. At the 90% confidence level, the LCL is 70.42%. What this indicates is that one can be 99% confident that the actual mean value for conversion is above 69.13%.

Hypothesis testing supports any hypothesis that the conversion is greater than 70% and rejects a hypothesis that the conversion is less than 70% at the 90% confidence level. One cannot statistically reject any hypothesis that suggests that the mean value of the conversion is greater than any hypothesized value as long as the hypothesized value is less than the observed mean for the sample set. Conversely, if one hypothesized that the true mean conversion is less than 70%, this hypothesis can be rejected at both the 90% and 95% levels.

These conclusions assume that the pilot data is representative of the entire population of conversion during hydrolysis and that pilot operations are representative of commercial operations. The analysis also assumes that the data is

sampled from a parameter (conversion) that has a normal distribution about a mean (average) value. While the data set used to estimate the conversion is limited, the methods and statistics account for the limited data set in predicting values and testing hypotheses.

As a secondary concern, one might ask what the probability is that during commercial operations testing, one might observe an average for a data set that is significantly below the true mean for conversion. As Ted Berglund pointed out previously, the data set for performance testing is expected to be quite large and therefore are expect to result with a high level of confidence in a value very close to the true population average.

2. DATA SET

Table 1 shows the conversion from the pilot runs at TVA during the 2000/01 pilot testing program. These runs were processed in the pilot plant using the hydrolysis mixing and cooking protocols developed during previous testing at TVA.

Table 1

Pilot Batch	RDF Source	Glucose Yield
1	95 RDF	
2	95 RDF	
4+5	Chicago	
6+7	Chicago	
8+9	Chicago	
11	Chicago	
12	Chicago	
13+14	Chicago	
15+16	Chicago	
17+18	Chicago	
19+20	Chicago	
Chicago RDF only		
Average		
Standard deviation		
Both RDF sources		
Average		
Standard deviation		

Previously, analysis of the expected conversion included data from only the Chicago RDF source. During the pilot operations, the initial two runs used MSW from preliminary runs acquired during 1995 testing of the Masada process. If these data

points are included, one can see that the AVE and STDEV change from the 71.88 and 3.40 without including this data to 71.69 and 3.07. The complete data set including Runs 1 and 2 are used. The impacts of including the new data are minimal. While the mean is lower, this effect is counteracted by a smaller standard deviation.

3. CONFIDENCE INTERVAL

Previously, a confidence interval for the average glucose yield (or conversion) was calculated based on the pilot plant processing data taken during test runs at TVA during 2000 and 2001. This data was limited to the test runs using the MSW from the Chicago sort facility. Here the more complete data set is used. Normally (and as done previously), one would calculate a confidence interval (CI) as

$$X \pm T(\alpha/2)S/\sqrt{N}$$

where X is the mean or average of the data, N is the number of data points, S is the standard deviation, and T(α/2) is the test statistic. The value of T is defined by α, which is 1 minus the confidence level (at 90% CI, α=0.1), and by the number of data points used to determine X and S (T gets smaller as N gets larger). We use the T statistic in place of the Z statistic as a more conservative statistic appropriate when our data set is limited. However, because our concern is not to bound the confidence interval but only the lower confidence limit (LCL), the appropriate estimator becomes

$$X \pm T(\alpha)S/\sqrt{N}$$

In other words, T(α/2) becomes T(α) because only a lower bound is considered (a higher than predicted value is not a concern for this case). Table 2 presents the values for the LCL at several CI for the data set.

Table 2

Average		
Standard deviation		
Number		
Confidence level	T(α)	LCL
90.0%		
95.0%		
97.5%		
99.0%		

[REDACTED]

As can be seen, the LCL for conversion at the 90% confidence level is 70.42 and 69.13 at the 99% confidence level.

One should point out that, although the average and standard deviation are based on a limited data set (number of pilot runs), this statistical method adjusts according to sample size. Both the test statistic T and the confidence value are functions of sample size and therefore account for samples size in an appropriate manner. For instance, if only two data points were available with a standard deviation of 5.35 (the actual deviation for the last two data points) and an average of [REDACTED]

[REDACTED]

In other-words, the number of samples is considered in the development of the statistic and method.

4. HYPOTHESIS TESTING

This test provides a method for testing a hypothesis. There are two types of hypotheses we might decide to test. In the first case, someone could hypothesize (Ho) that the average conversion is greater than or equal to some value. The alternative (Ha) would be that the true average conversion is less than the hypothesized value. For this test, the statistic is again $T(\alpha)$. For instance, if we hypothesize (Ho) that the conversion is greater than or equal to 70% the test looks like

$$H_o: \mu \geq 70$$

$$H_a: \mu < 70$$

The test fails if

$$(X - \mu) / S / \sqrt{N} < -T(\alpha)$$

Here μ is the actual or "true" average conversion and X is the observed average from the data. In this case we will always fail to reject the hypothesis no matter what the confidence level is. This happens because the null hypothesis is that the average conversion is less than what we have experimentally observed and we will therefore never fall below the negative value of $T(\alpha)$. No matter what value I hypothesize that the actual average (μ) is above, as long as it is below the observed average value, one cannot reject my hypothesis.

While there is a potential that one could fail to reject H_o when H_o is false (a Type 2 error), determining this probability is difficult and, as an alternative, we can test the

[REDACTED]

pessimistic hypothesis that μ is below some minimum. This is the second type of test. Here I choose H_0 as 69.99 and not 70.0 because the equality follows H_0 .

$H_0: \mu \leq 69.99$

$H_a: \mu > 69.99$

The test fails if

$$(X - \mu) / (S / \sqrt{N}) > T(\alpha)$$

At the 90% confidence level, $T(\alpha) = 1.372$. The value of $(X - \mu) / (S / \sqrt{N})$ is 1.83. Therefore there is sufficient evidence to reject the hypothesis H_0 . In fact, at the 95% level, one can also reject H_0 . This hypothesis test indicates that sufficient evidence exists to reject a hypothesis that the average conversion is less than or equal to 69.99%.

As one might imagine, the break-even point (the value of H_0 where one changes from pass to fail) is exactly the value of the LCL calculated at the same confidence level. In other words, at the 90% confidence level, any hypothesis that the mean is less than 70.42 will fail. This means that at the 99% confidence level, one can reject a hypothesis that the conversion is less than the LCL of 69.13%.

5. REFERENCE

For more details on these estimation and hypothesis testing methods, refer to *Probability and Statistics for Engineers*, 2nd Edition, Scheaffer and McClave.

JTR/mlm

cc: R. Hsu, Kvaerner (e-mail)
T. Berglund, Masada (e-mail)
C. Babb, HGI (e-mail)
S. Laird, HGI (e-mail)
J. Lukas, HGI (e-mail)

J. Ranney, HGI (e-mail)
D. Sexton, HGI (e-mail)
A. Slayton, HGI (e-mail)
File .0410, .4225

Appendix C

Osmonics Data Tables Acids and Sugars

LIQUID CHROMATOGRAPHY - QC - ACIDS

Data Filename: 100702A1

Date: 10/07/02

Description of Sample(s): Masasa Osmonics Samples

[illegible]

J. H. Holmes
5/11/2010
OsmonicsSamples

LIQUID CHROMATOGRAPHY - QC - SUGARS

Data Filename: 100702S1 Date: 10/07/02
Description of Sample(s):

CONTROL STANDARDS					
Date	Inj. No.	Analyte	Known Concentration mg/mL	Determined Concentration mg/mL	% Recovery
10/7/2002	2	QC-Glucose			
10/7/2002	2	QC-Xylose			
10/7/2002	2	QC-Galactose			
10/7/2002	2	QC-Arabinose			
10/7/2002	2	QC-Mannose			
10/7/2002	3	Std-Glucose			
10/7/2002	3	Std-Xylose			
10/7/2002	3	Std-Galactose			
10/7/2002	3	Std-Arabinose			
10/7/2002	3	Std-Mannose			
10/7/2002	11	Std-Glucose			
10/7/2002	11	Std-Xylose			
		Std-Galactose			
10/7/2002	11	Std-Arabinose			
		Std-Mannose			
10/7/2002	21	Std-Glucose			
10/7/2002	21	Std-Xylose			
10/7/2002	21	Std-Galactose			
10/7/2002	21	Std-Arabinose			
10/7/2002	21	Std-Mannose			

Date Submitted:	10/16/2002	Laboratory No.:		Requested By:	jeff Ranney		Notebook Page:
Date Wanted:		For:		Address:			Analyzed by: J. Holmes / J. Patterson
Date Reported:	10/8/2002 0019QBN		Charge to Account No.:	Request Approved By:	Jacq		

Remarks, methods, etc.: Osmonics

Lab. No.	Consignor's Number	Sugars - Concentration (g/L)							Acids - Concentration (g/L)					
		Glucose	Xylose	Galactose	Arabinose	Mannose	% H2SO4	Sp. Gr.	Lactic Acid	Glycerol	Acetic Acid	Ethanol	HMF	Furfural
7379	Permeate 0 - 25%													
738.0	Permeate 25 - 50%													
7381	Permeate 50 - 75%													
7382	Permeate 75 - 95%													
7383	concentrate													
No Dilution														
7379	Permeate 0 - 25%													
738.0	Permeate 25 - 50%													
7381	Permeate 50 - 75%													
7382	Permeate 75 - 95%													

LIQUID CHROMATOGRAPHY SUMMARY SHEET

ACIDS

Data File Name:

Project:

Date:

[illegible]

LIQUID CHROMATOGRAPHY SUMMARY SHEET

SUGARS

Data File Name:

Project:

Date:

[illegible]

% Sulfuric Acid						
Lab. No.	Consignor's	N NaOH	Meq. Wt.	Wt. of Sample	mL of NaOH	% H2SO4
7379						
7379B						
7380						
7380B						
7381						
7381B						
7382						
7382B						
7383						
7383B						

Appendix D

Baker Hughes Acid Neutralization and Gypsum
Precipitation

May 16th, 2001

BAKER PROCESS

May 16, 2001

email: ed.gerber@kvaerner.com

Kvaerner Process
7909 Parkwood Circle Drive
Houston, TX 77036

Attention: Ed Gerber

Subject: Testing Letter Report

Reference: MASADA / Orange Recycling Facility
Acid Neutralization / Gypsum Dewatering Testing

Dear Ed:

Following is a brief letter report outlining the results of our recent testing. [REDACTED]

Background

MASADA has developed a treatment process for conversion of municipal solid waste (MSW) to ethanol. The primary unit operations involve acid digestion of the biomass, acid recovery, neutralization, evaporation and fermentation. Baker Process' involvement in the process deals primarily with the acid neutralization of the material following acid recovery. Baker Process was contracted to neutralize approximately 800-1,000 gallons of the weak acid/strong sugar solution following the acid recovery operation and perform additional testing necessary for equipment sizing and prediction of process performance related to the acid neutralization.

Testing

A small-scale continuous sedimentation pilot apparatus including recycle of precipitated solids was used for neutralization of the acid/sugar solution. High calcium lime was used for neutralization to [REDACTED] for the samples tested. A small portion of the overflow material from the sedimentation apparatus was collected for subsequent bench-scale testing necessary for equipment sizing and process performance analysis. The balance of this overflow material was filtered with the filtrate collected and refrigerated for subsequent testing by other vendors.

Summary of Results

For a full-scale processing rate of approximately [REDACTED]

Technical Specification 99-10544-7006, Rev C dated February 21, 2001, expected process results would be as follows:

Parameter	Units	Value
Clarified Effluent (to Evaporators)		
TSS	mg/L	
Soluble Ca	mg/L	
Soluble SO ₄	mg/L	
HBF Filter Cake (coarse material)		
Cake Solids	wt%	
Cake Production (dry solids)	lb/h	
Filter Press Cake (fine material)		
Cake Solids	wt%	
Cake Production (dry solids)	lb/h	
Lime Consumption (as CaO)	lb/h	
Flocculant Dosage	lb/ton dry solids	
Overall Sugar Recovery	%	

Other

Chemical Analysis of Treated Effluent

	Units	Target (1)	Analysis
Sulfate	mg/L		
Ca	mg/L		
Cr	mg/L		
Fe	mg/L		
Ni	mg/L		
Al (2)	mg/L		
Mg	mg/L		
Cu	mg/L		
Zn	mg/L		
Na	mg/L		

Notes:

- 1. Target values were provided by Harris Group.

We look forward to working with you further on the project. Please feel free to contact me if you should have any questions or need additional information.

Sincerely,
BAKER PROCESS

Gene Haas
District Manager/Northwest U.S.
Chemical Engineer/Sales

cc:	John Lukas-HGI/e ✓
	Bill Timmins-SLC/e
	Jim Allen-SLC/e
	Vaughn Weston-SLC/e
	Kurt Wilson-SLC/e
	Don Taylor-SLC/e
	file

Appendix E

Acid Recovery and Sugar Concentration

June 2003

EXECUTIVE SUMMARY

Masada Resources Group has contracted Koch Membrane Systems to investigate the feasibility of employing highly engineered, SelRO[®] nanofiltration membranes for the recovery of sulfuric acid (H₂SO₄) and concentration of sugars from the Oxynol[™] process stream. As part of this study, KMS has provided process engineering services and in-house piloting equipment to conduct trials.

Masada Resources Group developed the Oxynol[™] process to treat solid matter through a biomass process, which includes material recovery, cellulose to sugar conversion and ethanol production units.

The objectives of this pilot study were:

- To demonstrate membrane stability in sulfuric acid/sugars streams.
- To optimize membrane flux (i.e. permeability).
- To determine the effect of varying system operating parameters such as temperature, cross flow velocity and pressure.
- To develop membrane cleaning procedures.
- To identify any potential fouling or plugging.
- To establish a design for an industrial scale system sized for 380 gpm feed.

The pilot study successfully met the program objectives. The results of the tests using SelRO[®] nanofiltration membranes indicated good membrane stability in sulfuric acid.

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INTRODUCTION

In the process of biomass treatment, sulfuric acid is used in the conversion of cellulose to sugars.

To reduce the costs of sulfuric acid consumed for the process Masada Resources Group has become interested in technologies to purify the acid. Membrane technology was considered for this application. KMS SelRO® acid stable spiral membranes were tested in the lab for this application, showing promising results. To further investigate the SelRO® product, Masada Resources Group ordered a KMS in-house pilot study for a two-month period.

The degree of purity of acid is measured in terms of acid to sugar ratio. The target for the membrane separation process [REDACTED]:1 or higher. At the same time, the sugars are being concentrated in the concentrate side. The concentrate stream will be used in the ethanol production sub-plant. The target concentration factor was set [REDACTED] [REDACTED] which was later increased [REDACTED] at the client's request.

This report summarizes the tests done and the results obtained.

Section 1 (test objectives) lists the goals of the pilot work.

Section 2 (test plan) highlights the overall test approach and gives the general test procedure.

Section 3 (setup) discusses the test equipment including the pilot unit, the membrane, auxiliary equipment and analytical procedures.

Section 4 (tests description) contains the narrative of the events and the different operating modes.

Section 5 (Results) summarizes the test results, including performance data, and membrane cleaning.

Section 6 (Conclusions and recommendations) contains a summary of achievements and recommendations for optimization and design of a commercial membrane separation system.

The following personnel participated in the testing:

Personnel

Company

[REDACTED]	
------------	--

SECTION 1: TEST OBJECTIVES

The objective of the pilot test was to demonstrate the ability of the SelRO® membrane to concentrate sugars from spent sulfuric acid liquor and to establish the design process parameters for an industrial system.

The feed stream is originating from the CES Oxynol™ process, developed by Masada Resources Group, which converts organic matter into fuel ethanol, CO₂, and industrial by-products.

The detailed goals are:

- To confirm the ability of the SelRO® MPS-34 spiral membrane to concentrate sugars from spent sulfuric liquor and to increase the acid purity. The target is to increase the *acid: sugar* ratio from 10:1 in the feed to 25:1 or higher in the permeate.
- To study the membrane performance and to provide a process design for a commercial unit to treat 200,000 lbs per hour (approximately 380 gpm).
- To study the membrane fouling and element plugging characteristics in this application.
- To assess the stability of the SelRO® spiral membrane in the specific stream and the required temperature (120-140°F).
- To study the effect of the different operating parameters on the NF process and to establish an optimal set of operating parameters.
- To develop a cleaning regime for the application.

The feed to the NF system consists of 8% sulfuric acid (ranging from 6-9%), 0.45% Glucose (ranging from 0.18-0.57%), 0.105% Mannose (ranging from 0.02-0.14%), 0.065% xylose (ranging from 0.04-0.09%) and other components at lower concentration. The detailed composition is given in Appendix 1.

Most of the developmental work during the pilot tests was conducted using a Model feed solution. The composition of the Model solution is shown in Appendix 2. The model feed solution was considered by Masada & KMS to be representative of the actual feed that the commercial NF unit will be processing.

SECTION 2: TEST PLAN

2.1 Phase 1: Study and Optimization of Process Parameters

The test program includes the study of the effect of the operating parameters on the membrane flux and rejection rates.

- Develop flux data as a function of temperature using a clean 6, 8 and 10% sulfuric acid. Temperature of the test solution ranges between 80°F to 140°F.
- Develop flux and rejection data as a function of fluid flow conditions

- Develop flux and rejection data as a function of operating pressure between [REDACTED] psi TMP, at low (CF=1), medium (CF=2) and high (CF=7) concentration range. During these tests operating parameters was maintained at [REDACTED] gpm-circulation flow and 104-105°F.

- Develop flux and rejection data as a function of operating temperature between 113-140°F (45-60°C) at low (CF=1), medium (CF=2) and high (CF=7) concentration factors. During these tests the pressure will be set to the maximum allowed pressure, per the pressure-temperature envelope for the MPS-34 membrane (see membrane Data Sheet, Appendix 3). Circulation flow was maintained at 4 gpm.

2.2 Phase 2: Concentration runs using Model and Pilot feed solution

Conduct concentration runs, at the optimal operating conditions found in phase 1, using Model feed solution and Pilot feed solution provided by Masada Resources Group (definition of Model and Pilot Feed solutions is given in section 4.1 page 13). Perform cleaning cycles to confirm the effectiveness of the cleaning procedure developed.

2.3 Phase 3: Study the extended performance at the design Process Parameters found in phase 1.

The test program includes long runs to establish extended performance data.

- Establish procedure for membrane cleaning.
- Develop flux and rejection data as a function of time at low, medium and high concentration. The different concentrations will be selected to simulate a stages-in-series system performance.

¹ TMP - Average Trans Membrane Pressure - The difference between the average pressure at the feed side of the membrane to the pressure at the permeate side. [REDACTED]

- Confirm the condition of the membrane by testing it for standard QC markers (5% glucose in water). QC tests were conducted frequently during the runs.

SECTION 3: SETUP AND EQUIPMENT

3.1 [REDACTED] pilot unit

The tests were conducted using a pilot unit model M104A-SW. A general flow schematic of the pilot unit and the additional auxiliary equipment is shown in Figure 1. A picture of the [REDACTED] pilot unit is shown in Figure 2.

The unit is operated manually. Its main components are:

- Feed pump and cartridge filter
- High-pressure pump and piping
- 35-gallon feed/rinse tank
- Housings for 2.5"X40" spiral wound membrane
- Controls

Construction materials of the wetted parts are Hastelloy C, [REDACTED]

Figure 1: Schematic Drawing of [REDACTED] Pilot Setup for Masada Project

Figure 2: [REDACTED]

3.2 Membrane

SelRO® 2540-MPS-34 spiral membrane, [REDACTED] The SelRO® MPS-34 is [REDACTED] membrane [REDACTED] with superior pH and temperature stability. Main characteristics and operating limits of the 2540 are shown in the membrane Data Sheet, Appendix 3.

The spiral was installed in a Hastelloy C276 housing, rated for 600 psi pressure. A SelRO® spiral installed in housing is shown in Figure 3.

Figure 3: SelRO® spiral modules in Hastelloy C276 high-pressure housings

Figure 4: General flow schematics of (a) closed loop operation mode (b) batch mode (c) modified batch mode

SECTION 4: TEST DESCRIPTION

4.1 Feed Streams

The application has been developed for a future plant; therefore, actual feed solution for the pilot tests was not available. The membrane tests were conducted using the following feed solutions.

- "Model" Feed Solution

Model feed was prepared before each membrane test. A recipe was formulated to simulate the expected feed composition, as shown in Appendix 1. The recipe for the **Model** solution is shown in Appendix 2.

Model feed solution was mixed for 16 hours or more prior to introduction into the membranes.

- "Pilot" Feed Solution

Two samples of **Pilot** solution, produced in pilot plant conditions, were received from Masada Resources Group. The amount of **Pilot** feed solution received from Masada was 28 gallons for each sample. **Pilot** solution was produced in pilot runs of the Oxynol process by Masada. The supply of this material is very limited. Koch received about 45-50% of the total inventory of the material.

The terms **Pilot** solution and **Model** solution are used throughout this report, per the definitions above.

Although the analytical data showed that the Model solution simulates well the Pilot feed solution, there was a visual difference between the two samples. The Pilot solution had a yellow color, while the Model solution had a very light blue color. The blue color is best seen in large containers. It is hardly seen in a small beaker.

In addition, the Pilot solution had a profound smell of spoiled organic matter, indicating low MW components present in the feed. Figure 5 shows Model feed solution and Pilot feed sample.

Figure 5: Pilot feed solution (Left) and Model feed solution (Right)

4.2 Narrative of Events

The tests were conducted in 3 phases:

- Parametric study to establish an optimal set of operation conditions.
- Concentration runs with Model and Pilot feed solutions
- Extended runs at constant concentration factors

SECTION 5: RESULTS

A summary of the performance of the MPS-34 membrane shows the following:

5.1 Effect of operating conditions on membrane performance

he
id
dy
.

SECTION 6: CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

The membrane performance while processing sulfuric acid from biomass exceeded the process objectives.

Very small flux decline was observed for 5 days of operation, flux decay vs. concentration was moderate, cleaning was reproducible and efficient, and permeate quality was satisfactory.

Autopsy of the membrane after 3 months of exposure to Model and Pilot feed material confirms that the membrane element is stable in the application fluid.

These observations lead to the conclusion that the sulfuric acid stream from biomass is appropriate for nanofiltration membrane processes using SelRO membranes.

Overall, based on the pilot results, there is a high level of confidence in designing and successfully operating an industrial system to process sulfuric acid from biomass, at the expected composition⁴ and to reach [REDACTED] volumetric recovery.

Due to the small amount of Pilot feed solution, the experience gained in processing sulfuric acid from biomass to a 90% volumetric recovery is limited.

Other conclusions are:

- [REDACTED]
- At the selected operating conditions, it is possible to recover [REDACTED] the acid (by volume) when a feed solution at the expected composition⁴ is processed.
- During the test period it was demonstrated that more than 95% of the sugars are removed by the membranes, on a spot basis.
- Membrane performance in Pilot and Model feed solutions is reproducible with respect to flux and rejection.
- [REDACTED]

⁴ Expected composition - As shown in Appendix 1, column designated as "Expected"

⁵ [REDACTED]

Appendix 1: Feed composition of spent sulfuric acid

Nanofiltration Feed Estimate							
Component (see note 1)	Units	Expected	Range Min	Max			
Primary Components (See note 2 & 3)							
Suspended Solids	ppm						
Glucose	%						
Xylose	%						
Mannose	%						
Galactose	%						
Arabanose	%						
Total sugar	%						
Sulfuric acid	%						
Acid/Sugar	Ratio						
Ethanol	ppm						
Acetic acid	%						
HMF	%						
Furfural	%						
Levulinic Acid	%						
Lactic Acid	%						
Glycerol	%						
Metals/Cations (See note 4)							
Al	mg/L						
Sb	mg/L						
As	micro-g/L						
Ba	mg/L						
Cd	mg/L						
Ca	mg/L						
Cr	mg/L						
Cu	mg/L						
Fe	mg/L						
Pb	mg/L						
Mg	mg/L						
Mn	mg/L						
Ni	mg/L						
P	mg/L						
K	mg/L						
Si	mg/L						
Na	mg/L						
Sn	mg/L						
V	mg/L						
Zn	mg/L						
Anions (See note 5)							
Cl	mg/L						
Fl	mg/L						
NH4	mg/L						
Note 1: Components determined from combination of analytical results and process modelling							
Note 2: Sugar and organic acid contents by TVA HPLC methods							
Note 3: Sulfuric acid by titration at TVA							
Note 4: Metal/Cations by TVA ICP methods							
Note 5: Anions by combination of TVA IC and anion selective probe methods, and or Hazen chemical gravometric method							

Appendix 2: Recipe of Model feed solution for pilot tests.

Gallons of Solution	Gal				
Pounds of Solution	lb				
SG					
Water	Balance		RO Water	DI Water	
Glucose	%		99% Glucose	Glucose	
Xylose	%		98.5% Xylose	Xylose	
Mannose	%		99% Glucose	Glucose	
Sulfuric acid	%		98% Sulfuric Acid	Sulfuric acid	
Ethanol	mg/L		100% Ethanol	Ethanol	
Acetic acid	%		100% Acetic Acid	Acetic acid	
Levulinic Acid	%		100% Levulinic Acid	Levulinic Acid	
Al	mg/L		Al Salt	KAl((SO4)2 12H2O	
Ca	mg/L		Ca 2+ salt	CaCl2 2H2O	
Cr	mg/L		Chromate	Na2Cr2O7 2H2O	
Fe	mg/L		Fe Salt	FeSO4 7H2O	
Mg	mg/L		Mg 2+ salt	MgSO4	
Mn	mg/L		MnF2	MnF2	
Ni	mg/L		Ni Salt	NiCl2 6H2O	
P	mg/L		Phosphoric acid	H3PO4	
K	mg/L		K+ Salt	KAl((SO4)2 12H2O	
Na	mg/L		Chromate salt and NaCl	NaCl	
Zn	mg/L		Zn Salt	ZnCl2	
Cl	mg/L		HCl	HCl	
F	mg/L		NaF	NaF	
NH4	mg/L				

Appendix 3: MPS-34 Membrane Data Sheet

SeIRO[®] MPS-34 - pH Stable Membrane
Nanofiltration Spiral Module Series - 2540, 4040

PRODUCT DESCRIPTION	Membrane Chemistry: Membrane Type: Construction: Major Applications: Options:				Proprietary Composite Nanofiltration Membrane pH stable Nanofiltration Membrane Spiral-Wound element Acid and caustic recovery, Product concentration Feed Channel spacers: 30 and 57 mil Permeate tubes: Stainless steel, CPVC							
SPECIFICATIONS	Model	Rejection		30 mil Spacer				57 mil Spacer				
		glucose/ sucrose	NaCl	Permeate Flow		Membrane Area		Permeate Flow		Membrane Area		
	Percent	Percent	gpd	m ³ /d	ft ²	m ²	gpd	m ³ /d	ft ²	m ²		
	MPS-34 2540	95 / 97	35	600	2.3	17	1.6	450	1.7	13	1.2	
	MPS-34 4040	95 / 97	35	2,100	8.1	60	5.6	1,500	5.8	43	4.0	
* Test Conditions: RO water at 440 psi (30 bar), 86°F (30°C). Feed solution for rejection tests are 3% glucose / 3% sucrose or 5% NaCl												
OPERATING & DESIGN INFORMATION	Typical Operating Pressure:						220-510 psi (15-35 bar)					
	Operating Temperature Range:						40-158°F (5-70°C)*					
	Cleaning Temperature Range:						95-158°F (35-70°C)*					
	Allowable pH - Continuous operation:						0-14**					
	Allowable pH - Clean-In-Place (CIP):						0-14**					
Maximum pressure drop per element:						10 psi (0.7 bar)						
Maximum pressure drop per vessel (5 in series):						50 psi (3.5 bar)						
* Please refer to the Temperature-Pressure envelope when temperature is higher than 122°F (50°C)												
** Corrosive acids should be avoided when a stainless steel permeate tube is being used												

PRODUCT DIMENSIONS

Model	a		b		c		d	
	inches	(mm)	inches	(mm)	inches	(mm)	inches	(mm)
MPS-34 2540	38.0	(965)	2.4	(61)	0.75	(19.05)	40	(1016)
MPS-34 4040	38.0	(965)	3.9	(99)	0.75	(19.05)	40	(1016)

STABILITY IN ACIDS AND BASES*

S - Stable	
5% HCl	S
37% HCl	S
15% H ₂ SO ₄	S

* Alternate operation of MPS-34 membrane

The information contained in this publication is believed to be accurate and reliable, but is not to be construed as implying any warranty or guarantee of performance. We assume no responsibility, obligation or liability for results obtained or damages incurred through the application of the information contained herein. Refer to Standard Terms and Conditions of Sale and Performance Warranty documentation for additional information.

SeIRO® MPS-34 - pH Stable Membrane

Membrane Characteristics:

SeIRO® Composite nanofiltration membrane in a spiral wound configuration, with superior pH and temperature stability.

Performance:

Performance specifications shown on the front side of this document are nominal values. Individual element permeate flow rates may vary $\pm 20\%$ from the values shown.

Operating Limits:

- **Operating Pressure:** Maximum operating pressure for SeIRO® MPS-34 is 510 psi (35 bar). Actual operating pressure is dependent upon system flux rate, as well as feed, recovery and temperature conditions.
- **Maximum Allowed Permeate Pressure:** 3 psi (0.2 bar).
- **Differential Pressure:** Maximum differential pressure limit is 10 psi (0.7 bar) per element. Maximum differential pressure for any length vessel is 50 psi (3.5 bar).
- **Temperature:** Maximum operating temperature is 158°F (70°C) with stainless steel permeate tube and 113°F (45°C) with CPVC permeate tube. For guidelines of recommended temperature and pressure please refer to the "Recommended Envelope for Code 30 membranes" in this document.
- **pH:** Allowable range for continuous operation is 0-14 with CPVC permeate tube. When a Stainless steel permeate tube is used, corrosive acids should be avoided.

Water Quality for cleaning and Diafiltration:

Turbidity: Maximum feed turbidity is 1 NTU.

Guidelines: For more detailed information please consult with KMS Process Technology.

- **Chlorine and Chemical Exposure:**
 - It is not recommended to expose the SeIRO® MPS-34 to chlorine or other oxidants, as it may affect the membrane performance.
 - Sodium metabisulfite (without catalysts such as cobalt) is the preferred chemical to eliminate free chlorine or similar oxidizers in the feed.
 - It is not recommended to expose the SeIRO® MPS-34 to organic solvents, such as alcohol, acetone, etc.
- **Feed Flow Rate:** Maximum and Minimum flow rate for the MPS-34 spiral module are as follows:

2540	Min. 2 gpm (7.5 liter/min)	Max. 5 gpm (19 liter/min)
4040	Min. 6 gpm (22 liter/min)	Max. 17 gpm (65 liter/min)

Actual feed flow rate is dependent upon system flux rate, feed characteristics, fouling tendency and system design.

Operating Envelope For Code 30 Membranes:

It is important to follow the pressure - temperature relationship guidelines, in order to prevent irreversible compaction and performance deterioration. The following diagram should be used as a guideline to operating the MPS-34 spiral module.

Module Handling:

- **Recommended Cleaning Materials:** Depending on the nature of the feed material, a choice can be made from the following cleaning agents:
 - 0.1-5% w/w sodium hydroxide at 122°F (50°C)
 - 0.2-1% w/w nitric or phosphoric acid at 122°F (50°C)
 - 0.1-0.5% w/w detergent mix KLD-II or KLD-III
 - 0.5% Anionic surfactant (such as SDS) at 122°F (50°C)

Consult KOCH regarding the use of other cleaning materials.

- **Lubricants:** For element installation, use only water or glycerin to lubricate seals. The use of petroleum or vegetable-based oils or solvents may damage the element and will void any warranty.
- **Preservation:** Should be made with:
 - Short Term (up to two weeks): 0.25 w/w Sodium metabisulfite
 - Long Term: 0.7% w/w Roccal (Benzalkonium chloride, Sigma Part Number B1383)

Note that concentrated glycerin should not be used to preserve the MPS-34 spiral membrane.

- **Storage:** The membrane module should not get dry. It should be stored in a sealed bag, in a temperature ranging from 36°F - 86°F (2°C - 30°C).

Service and Ongoing Technical Support

Koch Membrane Systems has an experienced staff of professionals available to assist you to optimize existing systems and support with the development of new applications. We have a comprehensive product development program to ensure the availability of state-of-the-art products. Koch Process Technology and Technical Service Departments will provide knowledgeable assistance whether it is staff training, review of system operations, or recommendations for fine tuning your system.

Koch's Capability

Koch Membrane Systems is the world leader in crossflow membrane technology, manufacturing reverse osmosis, nanofiltration, ultrafiltration and microfiltration membrane systems. The industries served include food, dairy, and beverages, semiconductors, automotive, water and wastewater, chemical and general manufacturing. Koch adds value by providing top quality membrane products and by sharing our experience in the design and supply of thousands of crossflow membrane systems worldwide.

Appendix 4: Analytical results

Sample Description	Sample Details	Sugars Concentration (g/L)					Total Sugars (g/L)	Rejection to Total sugar	H ₂ SO ₄ Conc. (%)	Rejection to H ₂ SO ₄	acid/sugar
		Glucose	Fructose	Sucrose	Lactose	Mannose					
Feed	CF=1 Model Feed										
Permeate	CF=1 parametric study										
Permeate	CF=1 parametric study										
Permeate	CF=1 parametric study										
Permeate	CF=1 parametric study										
Permeate	CF=1 parametric study										
Permeate	Total Permeate to CF=1										
Feed	CF=2 Model Feed										
Permeate	CF=2 parametric study										
Permeate	CF=2 parametric study										
Permeate	CF=2 parametric study										
Permeate	CF=2 parametric study										
Permeate	CF=2 parametric study										
Permeate	CF=2 parametric study										
Permeate	Total Permeate from CF=2 to CF=5										
Feed	CF=5 Model Feed										
Permeate	CF=5 parametric study										
Permeate	CF=5 parametric study										
Permeate	CF=5 parametric study										
Permeate	CF=5 parametric study										
Permeate	CF=5 parametric study										
Permeate	CF=5 parametric study										
Feed	CF=5 Model Feed										
Permeate	CF=5 parametric study										
Permeate	CF=5 parametric study										
Permeate	CF=5 parametric study										
Feed	Concentration Run model Solution										
Permeate	Concentration Run model Solution										
Feed	Concentration Run model Solution										
Permeate	Concentration Run model Solution										
Feed	Concentration Run model Solution										
Permeate	Concentration Run model Solution										
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Feed	Concentration Run Real Solution CF=1										
Feed	Concentration Run Real Solution CF=1										
Permeate	Concentration Run Real Solution CF=1										
Feed	Concentration Run Real Solution CF=1.2										
Permeate	Concentration Run Real Solution CF=1.2										
Feed	Concentration Run Real Solution CF=1.6										
Permeate	Concentration Run Real Solution CF=1.6										
Feed	Concentration Run Real Solution CF=3.6										
Permeate	Concentration Run Real Solution CF=3.6										
Feed	Concentration Run Real Solution CF=4.1										
Permeate	Concentration Run Real Solution CF=4.1										
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Feed	Concentration Run Real Solution CF=1.9										
Permeate	Concentration Run Real Solution CF=1.9										
Feed	Concentration Run Real Solution CF=2.4										
Permeate	Concentration Run Real Solution CF=2.4										
Feed	Concentration Run Real Solution CF=4.5										
Permeate	Concentration Run Real Solution CF=4.5										
Feed	Concentration Run Real Solution CF=11										
Permeate	Concentration Run Real Solution CF=11										

Appendix F

Kvaerner Hydrolyzate Fermentation Testing TVA

May 7th, 2002

May 7, 2002

PROJECT MEMORANDUM 42010/05
MASADA PROCESS FERMENTATION TESTING
PILOT PLANT HYDROLYZATE (2000/01)
FERMENTATION (2001/02)

1. SUMMARY

The results of the 2001/02 fermentation trials at TVA are presented here. These fermentation tests used pilot-plant-produced MSW-derived sugars made from the Masada process. The tests focused on the investigation of nutrient options and optimization of the nutrient source and concentration. Fermentation testing shows that corn steep liquor (CSL) is an effective nutrient. CSL can be used as a replacement for the more expensive TVA-developed nutrient mix. With CSL added at the 1% level to both the inoculum and the fermentation, an over 98% ethanol yield at 24 hours was observed for testing at the 16-liter scale. Using CSL only in the inoculum or in the inoculum and at a reduced rate in the fermentation results in yields in excess of 90% but with fermentation time increasing with decreasing CSL concentrations. As previously demonstrated, the TVA nutrient mix also results in fermentation efficiencies in excess of 90%. As with the CSL, adding the TVA nutrient to only the inoculum results in an increased time to achieve full glucose utilization and higher ethanol yields.

Several sources of CSL were tested with similarly effective fermentation regardless of the CSL source. Flask scale testing also resulted in over 90% ethanol yields with CSL as the nutrient source. The average ethanol yield is 98.5% for tests using CSL in both the inoculum and the fermentation broth when data from flask tests in February 2002 with Cerestar CSL and 16-liter tests in March 2002 with GPC CSL are considered.

This experimental data indicate that an over 90% yield of ethanol (as a function of glucose and mannose conversion) has been consistently achieved using the MSW-derived sugar source and CSL nutrient sources. When CSL is added at the full 1%

rate to both the inoculum and the broth, ethanol yields in excess of 95% are observed.

2. INTRODUCTION

Extensive fermentation testing has taken place at TVA using MSW-derived sugars. Previous studies primarily used a nutrient mix optimized by TVA for the fermentation of hydrolysis-derived substrates. More recent studies investigated alternative nutrient sources. These studies used a MSW-derived hydrolysis sugar. This sugar was produced during the 2000/01 Masada process pilot trials designed to mimic the commercial process as closely as possible for the pilot operation.

A number of nutrients were tested based on the likelihood of success and estimated nutrient costs. Table 1 shows an estimation of the nutrient costs for some potential options. The most cost-effective nutrients were selected for further testing. The TVA nutrient mix was tested as a control. Corn steep liquor from several different sources was tested and biopeptides were tested. Yeast Food P was tested at the flask level with encouraging results, but was not further tested due to the high nutrient cost. The Alltech yeast food grain was not tested as no samples were available for TVA to use in test fermentations.

Table 1
Estimated Nutrient Costs
Basis: WinGEMS Rev-W, 4/1/02 (65% MRF)

Nutrient	Nutrient add to:		
	Inoculum Only	Inoculum and Fermentation	Inoculum and 50% to Fermentation
CSL	\$ 48,327	\$ 531,592	\$ 289,959
TVA	\$ 460,759	\$ 5,068,352	\$ 2,764,556
Yeast Food P	\$3,044,192	\$33,486,112	\$18,265,152
Biopeptides – low	\$ 8,268	\$ 90,952	\$ 49,610
AYF Grain – low	\$ 9,114	\$ 100,258	\$ 54,686
Biopeptides – high	\$ 34,521	\$ 379,727	\$ 207,124
AYF Grain – high	\$ 38,052	\$ 418,576	\$ 228,314

3. RESULTS

The results from the 2001/02 fermentation trials at TVA are summarized in the attached graphs. Detailed reports from TVA on these trials will be included in the design report appendix. Testing was conducted at the flask scale for preliminary evaluation and in the 16-liter fermentation test units for confirmation of flask results.

The results from the 16-liter fermentation are presented first because they are the most commercially relevant.

Figure 1A 16-Liter Fermentations

Here the results for the 16-liter fermentation tests are shown. The ethanol yields are shown as a function of fermentation time for several different concentrations of CSL in the fermentation broth. The figure shows that by 24 hours over 98% ethanol yield was observed when CSL was added to both the inoculum and the fermentation at the full rate. As the CSL rate to the fermentation was reduced to 30% and 0%, the time for the fermentation to complete increased to 38 and 60 hours, respectively. This figure shows 90+ % conversions can be achieved using CSL in place of the TVA nutrient mix and that less than a full addition of CSL to the fermentation can be effective.

In all cases the sugar was Masada process derived, the inoculum rate was 10%, and 1% CSL was added as a nutrient to the inoculum. Rates of nutrient (CSL) added to the fermentation varied.

Figure 2A 16-Liter Fermentation

In this figure the ethanol yields and glucose utilization for the three 16-liter fermentation tests are shown. As expected, the ethanol yield and glucose utilization track each other in all experiments. This data is the same as shown in Figure 1A, which presents the fermentation time as a function of amount of CSL added as a nutrient. In these cases CSL from GPC was used as the nutrient. Glucose utilization is defined as 1 minus the amount of glucose remaining, divided by the amount of glucose at the start of fermentation.

Figure 3A Corn Steep Liquor versus TVA Nutrients

In this figure the ethanol yield using the TVA nutrient mix is compared to the ethanol yield when CSL from two sources is used as the nutrient. Ethanol yields in excess of 96% are reported for all the experiments. The data is from flask scale experiments, with the exception of the last GPC nutrient experiment, which is from a 16-liter test. These experiments demonstrate that CSL from both sources is at least as effective as the TVA nutrient mix. For these experiments, nutrients were added both to the inoculum and the fermentation broth.

Several of the flask experiments using GPC as the nutrient resulted in ethanol yields in excess of 100%. TVA indicated that several factors could lead to this results including the conversion of some C-5 sugars, analytical accuracy limitations, and the potential unaccounted for

presence of sugar in the CSL nutrient. (Conversions of galactose, xylose, and arabanose averaged 14.8%, 20.0%, and 49.4% for the set of CSL experiments during which yields of over 100% were observed. Conversion of these sugars are not used by TVA to estimate ethanol yield.)

Figure 4A Nutrient in Only Inoculum versus in Fermentation and Inoculum

Figure 4A shows the ethanol yields for experiments using CSL and the TVA nutrients as a function of whether the nutrient is added to inoculum only or to both the inoculum and the fermentation. For both the CSL and TVA nutrients, a drop-off is seen in yields when no nutrient is added to the fermentation. Using a reduced level of 0.3% CSL (30% of normal) level in the fermentation results in an improvement over the no nutrient result and suggests that a nutrient level between the 1% case and the 0.3% case might be optimum.

All conversions are based on the results after approximately 24 hours of fermentation. As Figure 1A illustrated, higher conversions at lower nutrient rates are achieved at extended fermentation times.

Figure 5A Nutrient Evaluation (in both inoculum and fermentation)

Here the yields are presented for a series of different nutrients. Nutrients were added to both the fermentation broth and inoculum. The TVA nutrient mix, two SCL sources, and the DMS Yeast Food P all gave acceptable results.

The Alltech yeast food was lower in yield and the biopeptide nutrients gave a poor yield. Alltech later recommended an alternative yeast food for testing, citing the high cost of this particular alternative. The alternative yeast food was not available for testing at the time of these experiments. TVA indicated that the low yields for the biopeptide may have been caused by a low activity yeast culture (not verified). Given the low cost of the biopeptides, they were further tested along with the TVA mix and the CSL. The DMS yeast food was eliminated from further testing based on the high cost of this nutrient material. Lower levels of this nutrient may be effective but were not tested because a low-cost successful nutrient source was identified.

Figure 6A Nutrient Evaluation (in inoculum only)

In this figure a number of flask fermentations are shown for a variety of nutrient sources. In these tests, the nutrient was added only to the

inoculum. As shown, ethanol yields are lower when nutrients are only added to the inoculum, regardless of the nutrient source. Although in this case the TVA nutrient did perform better than CSL, both nutrients require addition to the fermentation broth. The cost of the CSL to both fermentation and inoculum is less than the cost of the TVA nutrient, even at a reduced rate of the TVA nutrient to fermentation. The other nutrient alternatives tested, no nutrient and biopeptides, resulted in lower ethanol yields than both the TVA mix and the CSL. The lower yields for the biopeptides come without a significant cost reduction compared to CSL.

Magnesium (Mg) spiking results are inconclusive for several reasons: (1) because the Mg levels were inadvertently spiked only in the 10% inoculum, and (2) because lower fermentation rates without nutrient added to the beer make it difficult to separate nutrient effects from Mg level effects. Further testing of Mg levels is planned.

JTR/mlm
Attachments

cc:

1.8 Fig. 1A

1.8 Fig. 2A

1.8 Fig. 3A

Corn Steep Liquor v. TVA Nutrients
10% Inoculum, Nutrients in inoculum and fermentation.
CSL Levels, 1%

1.8 Fig. 4A

Nutrient in only Inoculum vs. in Fermentation and Inoculum

1.8 Fig. 5A

1.8 Fig. 6A

Nutrient Evaluation
(In inoculum only, fermentation yields poor)
2001 Pilot Plant Hydrolyzate, 2001-02 Flask Fermentation

Appendix G

Seattle University Report

Masada Co-Products

June 3rd, 2002

Harris Group Inc.
Engineering for Optimum Performance.®

CO-PRODUCT ENHANCEMENT AND DEVELOPMENT FOR THE MASADA OXYNOL PROCESS

PRESENTED TO:

HARRIS GROUP INC.

June 3, 2002

BY:

**ENGINEERING DESIGN TEAM CEE 02.2
CIVIL & ENVIRONMENTAL ENGINEERING DEPARTMENT
SEATTLE UNIVERSITY**

June 3, 2002

Harris Group Inc.
1000 Denny Way, Suite 800
Seattle, WA 98109-5338

Co-Product Enhancement and Development for the Masada OxyNol Process

We are submitting to you and the Harris Group our final report evaluating the anaerobic treatment process designed to treat the wastewater originating from the Masada fermentation process. The report analyzes the waste stream for specified parameters (pH, alkalinity, chemical oxygen demand, biochemical oxygen demand, and sulfide), determines an optimum hydraulic retention time, characterizes methane gas production efficiency, establishes ideal alkalinity requirements, and presents an economic analysis of a potential full-scale reactor.

As a design team we have truly enjoyed working with you and the Harris Group on this challenging and rewarding design project and we look forward to potential future projects. If you have any questions regarding the contents of this report, please do not hesitate to contact any member of the team.

Sincerely,

Seattle University Civil/Environmental Engineering Design Team CEE 02.2

Cc: Dr. Phillip Thompson, Dr. Nirmla Gnanapragasam

CO-PRODUCT ENHANCEMENT AND DEVELOPMENT FOR THE MASADA OXYNOL PROCESS

Project Sponsor
Harris Group Inc.

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Science and Engineering Project Center Director
Dr. Patricia D. Daniels

June 3, 2002

EXECUTIVE SUMMARY

The Harris Group is currently designing an innovative solid waste treatment facility capable of producing ethanol through a fermentation process. As a result of fermentation, an abnormally high-strength wastewater is generated and must be treated before it is disposed of by evaporation. An anaerobic process was selected for this task due to its relative advantages. Anaerobic treatment can efficiently degrade high-strength wastewater and also produces methane, a combustible energy source, in the process.

The purpose of this project was to optimize the operational parameters for treating the waste stream. Laboratory experiments were performed to analyze relevant components of the waste stream and attempt to maximize methane production. Other tasks included a literature review of anaerobic treatment, construction of a bench-scale reactor, verification of an ideal hydraulic retention time, and an economic analysis of a full-scale reactor.

Conclusions

- An anaerobic reactor, while providing methane production and sufficient mitigation of the wastewater, requires costly chemical additions (sodium hydroxide, chlorine, etc.) that may negate its potential fiscal benefits relative to other treatment options.
- A significant amount of methane gas can be generated from the incoming wastewater which is about 75 percent biodegradable under anaerobic conditions.
- [REDACTED] methanogenic sludge granules are able to completely degrade the high-concentration COD introduced into the reactor.
- Sulfate is completely reduced by the anaerobic treatment system.

Recommendations

- Application of Upflow Anaerobic Sludge Blanket treatment will yield the most efficient methane production and degradation of the wastewater.
- Maintaining a strict mesophilic temperature range (30 – 40 °C) creates an optimum temperature for biological activity.
- A concentration of [REDACTED] of NaOH should be added to wastewater prior to treatment to maintain an advantageous pH of 7.0.
- [REDACTED] of alkalinity as CaCO_3 should be added to the reactor before treatment to buffer the large initial acidity flux. Sodium bicarbonate effectively provides this demand.
- Respective $\text{COD}:\text{SO}_4$ and $\text{COD}:\text{S}$ ratios of 5 and 15 should be maintained to ensure successful methanogen competition and subsequent methane production.
- Sulfate removal prior to biological treatment may result in significant savings in terms of annual chemical costs.

ABSTRACT

The Harris Group is developing a new technology in solid waste disposal. The state-of-the-art technology converts municipal solid waste into carbon dioxide, methane, and fuel-grade ethanol, all of significant commercial value, through concentrated acid hydrolysis-fermentation. Our team devised an efficient anaerobic treatment process to allow the high-strength industrial wastewater, originating from the fermentation process, to be discharged into evaporators for further disintegration. Additionally, the team identified critical components of the influent waste stream and optimized all parameters for maximum methane production. Laboratory bench-scale experiments were designed, constructed, and performed over several months to investigate ideal anaerobic treatment conditions.

ACKNOWLEDGEMENTS

We would like to thank the following individuals and organizations for their assistance and advice in contributing towards the goals of our successful design project:

- Harris Group Inc.
- Masada Co.
- [REDACTED]
- Seattle University Chemistry Department
- Seattle University Physics Department
- Seattle University Project Center
- Seattle University Writing Center
- Dr. Phillip Thompson
- Dr. Jeff Ranney and Mr. John Lukas
- Dr. Rolf Skrinde and Dr. Nirmala Gnanapragasm

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I. INTRODUCTION

A. Background

Harris Group Inc. was contracted by Masada to design a unique solid waste processing facility in Middletown, New York. The innovative facility is capable of recycling 90 percent of incoming solid waste, whereas standard facilities recycle only 20 percent (Masada Resource Group, 1998). The facility also produces a marketable industrial grade ethanol to be used as a renewable and clean-burning fuel or as an additive to gasoline. However, a high-strength wastewater is generated by the ethanol production and a treatment process must be utilized to reduce the strength of the wastewater before it is evaporated. An anaerobic wastewater treatment process was selected for this demand, as it effectively mitigates high-strength wastewater and additionally has the benefit of producing methane, which is a significant source of energy and resulting cost savings for the solid waste facility.

B. Statement Of Problem

The Harris Group and Masada needed to identify the operational parameters of the anaerobic process, which treats the waste stream generated from ethanol production. The tasks assigned to the design team included: characterization of the wastewater's relevant components, laboratory experiments analyzing the wastewater's potential, and investigating ideal anaerobic treatment conditions.

C. Purpose of Project and Overview

The goal of this project was to assist in the design of an anaerobic treatment system for the high-strength wastewater generated by the solid waste processing facility. The initial design step was to perform a literature review for present and past research to gather background on the problem. The literature review consisted primarily of collecting and evaluating relevant information on anaerobic wastewater treatment as well as examining materials collected from previous efforts on this project, during the 2000-2001 academic year. The team's main objective for research was to become familiar with issues associated with anaerobic wastewater treatment and to anticipate future problems. Table 1 lists the design parameters that were the focus of the literature review, contained in Section II.

II. Methods and Design Approach

A. Overview

For comprehensive analysis, testing was performed either daily or weekly in accordance with a testing protocol. In addition to quantifying the reactors' potential for methane production, influent and effluent measurements were taken of chemical oxygen demand (COD), 5-day biochemical oxygen demand (BOD₅), pH, and alkalinity (ALK) in compliance with *Standard Methods* (Eaton, Clesceri, and Greenburg, 1995). Measurement of off-gas production efficiency was also recorded and analyzed for the percentage of methane, carbon dioxide and hydrogen sulfide. The details for these procedures are located in Appendix B.

All wasted sludge was retained for de-watering and future testing at another location. All effluent samples were preserved, labeled, and refrigerated at 4 °C for further analysis. Samples were categorized by combinations of date, reactor number, or sampler's initials.

B. Treatment Criteria

Upflow Anaerobic Sludge Blanket Design

An Upflow Anaerobic Sludge Blanket (UASB) reactor will be utilized for this project. In a UASB the influent wastewater flows upward through the receiving tank, allowing for greater contact between the wastewater and the sludge blanket. The treated wastewater then lies on top of the sludge and the generated biogas can be collected at the top of the tank. The primary advantages for using UASB anaerobic treatment are lower hydraulic retention time, generally compact size and minimal footprint, and its ability to attain a high percentage of methane conversion and COD degradation (Metcalf and Eddy, 2003).

Treatment Conditions

Table 2 lists the expected range of design conditions for a number of different parameters of the wastewater.

TABLE 2: MAXIMUM DESIGN CONDITION

Description	Unit	Expected Range
Operating period	Hr/day	
	Days/Week	
	Hr/Year	
Total flow rate to waste water treatment	gpm	
Temperature	°C	
Acidity/ Alkalinity range	pH	
COD	mg/L	
BOD ₅	mg/L	
TSS	mg/L	
Sulfate	mg/L	
NH ₃	mg/L	
TKN	mg/L	
Oil/Fat/Grease	mg/L	
Aluminum	mg/L	
Calcium	mg/L	
Cadmium	mg/L	
Chromium	mg/L	
Copper	mg/L	
Iron	mg/L	
Magnesium	mg/L	
Potassium	mg/L	
Zinc	mg/L	
Chloride	mg/L	
Nickel	mg/L	
Arsenic	mg/L	
Lead	mg/L	
Phosphorus	mg/L	
Sulfur	mg/L	
Cadmium	mg/L	
Selenium	mg/L	
Cobalt	mg/L	
Vanadium	mg/L	
Silver	mg/L	
Barium	mg/L	

The treatment process used for experimentation was an anaerobic system, which used biological degradation to mitigate the high-strength wastewater. A fill and draw batch reactor was used for treatment. Temperature was maintained in the mesophilic range at 30-40 °C throughout the

treatment process, because, in an anaerobic setting, digestion optimally occurs at a temperature of 35 °C (Reynolds and Richards, 1996).

Anaerobic treatment utilizes a mixed culture of anaerobic microorganisms to hydrolyze, ferment, and ultimately convert organic material (fats, proteins, polysaccharides, etc.) to methane and carbon dioxide. Usually 50 percent of the organic solids content of the sludge can be reduced by this method (Lester and Birkett, 1999). The basic concept of anaerobic digestion is expressed in Equation 1:

There are three main reactions undergone by organic wastes in anaerobic digestion by means of enzymes produced by different kinds of bacteria.

- 1) Hydrolysis: Organic molecules are de-polymerized by extracellular enzymes. These undergo further degradations producing acetic acid, long chain fatty acids, and carbon dioxide.
- 2) Acetic Acid Formation: Different bacteria degrade the long chain fatty acids producing acetic acid, molecular hydrogen, and carbon dioxide. Acetic acid is also produced from some carbohydrates. Acetogens are the bacteria that produce enzymes for such reactions.
- 3) Methane Production: Acetic acid is eventually degraded and methane is produced by a group of bacteria called methanogens. Their activity depends on the conversion of fatty and acetic acid within a system, so that an overabundance of acid does not occur and consequently lower the system's pH, which in a well balanced system ranges between 7 and 8 (Lastella et al, 2000).

C. Reactor Design, Construction and Operation

The six reactors were evaluated on a comparative basis. While both reactor types were identical in design, reactors 1-3 were fed a solution containing a specific amount of glucose to facilitate methanogenic activity and thus acted as *control reactors*. Initially, reactors 4-6 mirrored the feeding schedule of reactors 1-3 to provide an experimental basis. Then, for experimental purposes, reactors 4-6 received the wastewater provided by Masada requiring treatment. Thus, reactors 4-6 played a variable role in experimentation and are referred to as *experimental reactors*.

The basic reactor design consisted of one two-liter and two one-liter Erlenmeyer flasks interconnected by plastic tubing and operated with two valves, as shown in Figure 1. The system used a General Electric maritime-type caulking to ensure airtight, anaerobic conditions and accurate displacement.

The reactors were initially seeded with chemical additions to facilitate biological activity. To the 2-liter flask, 100 g of the sludge granules provided by Biothane and 1800 ml of a prepared solution were added. The prepared solution consisted of 8.26 g of sodium bicarbonate, 12.5 mg of glucose, and the nutrients listed in Table 3.

TABLE 3: NUTRIENT CONCENTRATION

<u>Nutrient</u>	<u>Concentration, mg/L</u>
KNO ₃	
Ca(NO ₃) ₂ •4(H ₂ O)	
NH ₄ H ₂ PO ₄	
MgCl ₂	
Micronutrients*	
Fe-EDTA	

(* Includes KCl, H₃BO₃, MnSO₄ • H₂O, ZnSO₄ • 7H₂O, CuSO₄ • 5H₂O, H₂MoO₄)

Although an anaerobic treatment process primarily produces methane gas, additional gases were produced in the anaerobic reactor including carbon dioxide (CO₂), hydrogen sulfide (H₂S), and hydrogen (H₂), which in conjunction with methane is called biogas. The system was designed and configured so that the biogas generated in the anaerobic reactor is stripped of both CO₂ and H₂S, using a sodium hydroxide solution (1 M NaOH). After exiting the trap, the biogas, now consisting of methane and a small percentage of H₂ gas, passes into the third flask, which is inverted and filled with de-ionized water. Water is displaced when methane enters the inverted beaker, allowing the amount of methane produced to be measured. Evaporation was also accounted for in displacement measurements.

FIGURE 1: BENCH-SCALE REACTOR SET-UP

D. Theoretical Background

The design team found nine of the expected wastewater characteristics to be of significant importance.

Alkalinity

Alkalinity is the capacity of a system to act as a buffer to influxes of acidity. Therefore, alkalinity was essential to the overall project design since it maintained an optimal pH to

promote maximum biological activity in the system. Alkalinity is primarily comprised of carbonate species as seen in Equation 2:

$$\text{Total Alkalinity} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \quad (2)$$

Within a given anaerobic system, the amount of alkalinity follows a cycle. The entrance of the influent into the system initially causes a decrease in alkalinity due to the formation of volatile fatty acids (VFAs). However, as the influent resides in the system, the VFAs are metabolized by biological processes and the alkalinity increases significantly due to the breakdown of organic nitrogen. Thus, effluent concentrations normally surpassed influent concentrations. The effluent amount could be further increased, if deemed necessary, by the addition of urea or excess ammonia to the waste stream (Sterling et al, 2001). The raised alkalinity of the effluent can also be recirculated through the system for cost and operational benefits (Lettinga et al, 1997). Alkalinity should range from 1,000-5,000 mg/L as CaCO_3 (Reynolds and Richards, 1996). The wastewater tested has an alkalinity of [REDACTED] as CaCO_3 and there was no value provided by the Harris Group.

Biochemical Oxygen Demand and Chemical Oxygen Demand

Biochemical oxygen demand is the amount of oxygen used by bacteria in the stabilization of a decomposable organic waste material. Chemical oxygen demand (COD) is the measure of organic materials in wastewater in terms of the oxygen required to oxidize the organic materials chemically. The loading rate of COD has significant effects on its removal. Each gram of methane emitted corresponds to 4 grams of COD removed in a typical anaerobic digester (Fang and Zhou, 1993).

Methane

Biogas production is a mix of methane (60-70%) and carbon dioxide (30-40%), as well as hydrogen sulfide, nitrogen, hydrogen, oxygen and water vapor (Energy from Waste: Anaerobic Digestion, 2001). Methane is a resource that provides energy, making its operation cost-effective (Quick Reference Guide, 2001). The majority of methane, 72 percent, is produced from acetic acid (Reynolds and Richards, 1996). This is the result of methanogens producing large quantities of methane and carbon dioxide, which is called methane fermentation (Parkin and Speece, 1982). Available hydrogen gas can combine with carbon dioxide to produce more methane as well (Riggle, 1998).

Methanogens use ammonia and sulfide as nitrogen and sulfur sources respectively. They also require trace elements, such as iron, cobalt, molybdenum, and nickel. Nickel addition can increase the acetate utilization rate of methanogens (Bitton, 1994).

Methanogens and sulfate-reducing bacteria may compete for the same electron donors. Sulfate-reducing bacteria have the potential to out-compete methanogens for acetate under low acetate conditions. This is due to sulfate-reducing bacteria having a higher affinity than methanogens for acetate. Sulfate-reducing bacteria are very competitive at COD: SO_4 ratios between 1.2-1.7. However, increasing this ratio favors methanogens, while decreasing it favors the sulfate-

reducing bacteria (Bitton, 1994). The waste stream to be tested has a relatively high expected COD:SO₄ ratio of [REDACTED]

As bacterial activity and gas production increase, essential sulfides may be stripped from solution. The sulfur sinks that cause this include hydrogen sulfide gas production and precipitation of sulfides by heavy metals. Therefore, it is necessary to carefully maintain the COD:SO₄ ratio in order to achieve the highest rate of methane production possible (Kayhanian and Rich, 1995).

Volatile Acids

Volatile acids or “organic fatty acids”, as they are more commonly called, are a result of the anaerobic biodegradation of organics such as carbohydrates, proteins, fats, and oils (Reynolds and Richards, 1996). Normal anaerobic biodegradation results in the production of acetic and butyric acid among others. In the overall process of biogas production, volatile acids are produced as an intermediary step, between hydrolysis and methane production. The creation of volatile acids naturally has the effect of lowering a reactor’s pH thereby acidifying or “spoiling” the reactor and consequently destroying the methanogenic environment of the reactor. Propionic acid in particular displays high toxicity to methanogens (Bitton, 1994). A balance is needed between acid production and acid consumption for a stable process running at a high rate to be maintained. The ideal method to accomplish this balance is to buffer the reactor for acidity with the addition of alkalinity in the form of carbonates (Plaza et al, 1996).

Sulfate reduction

Under anaerobic conditions, sulfates are chemically reduced to sulfides and to hydrogen sulfide by bacteria (Metcalf and Eddy, 1979) as in Equations 3 and 4.

High levels of sulfate make conditions unfavorable in the anaerobic treatment process, especially at the start of digestion. Methanogens produce methane and other biogas components from acetic acid, as well as from the combination of available hydrogen gas and CO₂. Sulfate stimulates the growth of sulfate reducing bacteria, which out compete methanogens for substrates (acetate and H₂), thereby inhibiting methane production. Concentrations of the toxic H₂S, which inhibit methane production by [REDACTED] Sulfides are also responsible for precipitating non-alkali metals in reactors, making them unavailable to methanogens. Acidic pH increases sulfide toxicity through the increase in sulfide concentration due to stoichiometric relations. A high COD:S ratio promotes methanogenesis, but when the ratio is less than 10 both sulfate reduction and methane production fail (Percheron et al, 1997).

Studies have shown that addition of trace metals, such as iron and cobalt promoted anaerobic digestion. In these cases the iron supply was needed to precipitate the sulfide before cobalt addition to prevent the cobalt from being precipitated by the sulfide, thereby making it unavailable for microorganisms (Percheron et al, 1997).

Total Kjeldahl Nitrogen

Total Kjeldahl Nitrogen (TKN) is the measure of total organic and ammonia nitrogen, including both ammonia and ammonium species, within a system. The organic nitrogen in the waste stream consisted primarily of amino acids and polypeptides, which are derivatives of ammonia. TKN is beneficial by giving a system the ability to build new cells, since nitrogen is the primary nutrient required for microbial synthesis. The operational load of TKN entering the Masada anaerobic treatment process was [REDACTED]. With this high loading of TKN, high ammonification with negligible N₂ formation and almost complete reduction of sulfates to sulfides was expected (Krylova et al, 1997).

High levels of ammonia nitrogen can affect methanogenic activity in anaerobic treatment, with NH₃ inhibiting methane production more than NH₄ (Lay et al, 1998). Excess ammonia nitrogen inhibits the destruction of organic compounds and the production of volatile fatty acids. Experimental analysis showed a significant decline in biogas [REDACTED] and methane [REDACTED] at an NH₄Cl concentration of [REDACTED]. A significant decrease in bacteria of all physiological groups was observed at concentrations higher than [REDACTED] (Krylova et al, 1997). Ammonia nitrogen concentrations also affect the time required for the methanogens to adapt to their environment before they produce significant amounts of methane, called the lag phase time.

III. WASTEWATER CHARACTERIZATION

B. Experimental Results

Wastewater Characteristics

The procedures used for wastewater analysis are located in Appendix B. Experimental results for wastewater constituents are shown in Table 4 and are compared to the expected values provided by the Harris Group in September 2000.

Description	Unit	Expected Maximum	Experimental Result
Acidity/ Alkalinity range	pH	[REDACTED]	
Alkalinity	mg/L as CaCO ₃		
COD	mg/L		
BOD ₅	mg/L		
TSS	mg/L		
Sulfate	mg/L		

TABLE 4: WASTEWATER RESULTS

pH

The results of daily pH testing gave a good indication of the general health of the reactors (Figure 2). On day 9, reactors 1-6 were restarted due to pH levels that exceeded the optimum pH range of [redacted]; reactors 1-3 averaged a pH of [redacted] and reactors 4-6 had an average pH of [redacted]. The relatively high reactor pH was due to adding a feed solution that was too alkaline (pH = 10) and caused a significant decrease in methane production.

On day 53 the control reactors were restarted for the second time. This first substantial low pH level (day 53) was a result of increasing the COD loading rate into both the experimental and control reactors on day 48. The COD was increased in the reactors by shifting the daily COD feed from [redacted] on Day 48; the control reactors were fed [redacted]

Restarting the reactors with a relatively high initial COD resulted in another significant pH drop (day 55), forcing a third restart of the reactors. After the third restart, COD was stabilized at [redacted] initially and pH was more closely monitored. When pH drops occurred the reactors were adjusted by the addition of a naturally alkaline solution of 1 N NaOH. Changes in pH did not occur once the feed solution was buffered with sodium bicarbonate.

As previously mentioned, pH was the basic variable utilized to evaluate reactor health. Towards the end of the project, beginning on day 51, pH was consistently within the optimum range of [redacted]. This optimization of the pH consequently allowed a maximization of the methane production (Figure 3). On day 74 the daily feed of wastewater to the experimental reactors increased from [redacted]. This corresponded to a 45-day hydraulic retention time (HRT).

FIGURE 2: DAILY PH RESULTS (DAYS 1-47)

FIGURE 3: DAILY PH RESULTS (DAYS 48-87)

Alkalinity

The alkalinity of the experimental reactors stayed fairly consistent with a noticeable increase as the days progressed. This was due to the addition of [REDACTED] wastewater feeding solution. The control reactors were also buffered by the addition of [REDACTED]

FIGURE 4: REACTOR ALKALINITY

It should be noted that the alkalinity concentrations in Figure 4 were not solely bicarbonate or carbonate species. In the process of sulfate reduction, bisulfide ion (HS^-) is generated and contributed to the measurement of total alkalinity in the system. The testing method that was used (titration) was unable to distinguish between carbonate and sulfide buffering systems.

Chemical Oxygen Demand

The following COD and methane data analyses were for the first stable period of reactor performance following the last re-start due to pH decline. The first period of analysis is from day 69 through 73 (60-d HRT) and the second period is for days 74-84 (45-d HRT). Figure 5 depicts the COD of the effluent from the experimental and control reactors for days 69 through 73. In Figure 6 the COD of the effluent from the experimental and control reactors is plotted for days 73 through 84.

FIGURE 5: EFFLUENT COD (60-DAY HRT)

FIGURE 6: EFFLUENT COD (45-DAY HRT)

Methane Production

The cumulative results of methane production testing are shown in Figure 7, and the average methane production values for the control and experimental reactors are located in Table 5. The theoretical methane production for the controls was determined with Equation 5 which indicates a stoichiometry of 2.4 millimoles of methane for every millimole of glucose (Rittmann & McCarty, 2001).

These results also

Experimental results were evaluated in accordance with hydraulic retention times (HRTs) of 45, and 60 days. To accomplish this goal without overloading the experimental reactors and causing their acidification or spoiling (see Section II C *Volatile Acids*), a modified feeding duration of 60 days was initially established, corresponding to [REDACTED] into the experimental reactors. This was followed by an HRT of [REDACTED]. The methane production results are summarized in Table 5 and indicate that about [REDACTED] were produced for every gram of COD loading. This value will be used in Section IV to estimate the value of methane that could be produced by the full-scale system.

TABLE 5: AVERAGE METHANE PRODUCTION ± 1 S.D.

<u>Reactor</u>	<u>Average Methane Production (L/d)</u>
Control	
Experimental (60 day HRT)	
Experimental (45 day HRT)

FIGURE 7: METHANE PRODUCTION

Sulfate

The influent concentration of sulfate was found to be about [REDACTED]. Every day 30 mL of wastewater was fed to the reactors, therefore the reactors were receiving [REDACTED] of sulfate per day as shown in Equation 6. In terms of electron demand, sulfate reduction accounted for less than [REDACTED] of the electrons donated per day by the substrate. Thus, competition between sulfate reducing bacteria and methanogens for COD was low.

$$[REDACTED] \quad (6)$$

The sulfate loading to the full-scale reactor is calculated in Equation 7.

$$[REDACTED] \quad (7)$$

$$[REDACTED] \quad (8)$$

As shown in Figure 8, the experimental reactors were determined to degrade virtually 100% of the influent sulfate, as effluent levels of sulfate were found to be near zero.

FIGURE 8: EFFLUENT SULFATE

The system will reduce the entire amount of sulfate to hydrogen sulfide, therefore producing approximately [REDACTED]

[REDACTED] (9)

For treatment of hydrogen sulfide by stripping with chlorine the following Equation applies:

[REDACTED] (10)

The amount of HOCl necessary to treat the hydrogen sulfide is dependent on the molar ratio.

[REDACTED] (11)

The mass of [REDACTED]

[REDACTED] (12)

Assuming an efficiency of [REDACTED] would be needed to treat the hydrogen sulfide (Equation 13). It should also be noted that other means of sulfide removal (e.g. precipitation with iron) might be also be considered.

[REDACTED] (13)

Biodegradability of Wastewater

To determine the biodegradability of the Masada wastewater, a mass balance on COD was attempted. However, the variability of the COD in the reactors generally exceeded the sensitivity required for such an analysis. Table 6 illustrates the difficulty in performing a COD mass balance. [REDACTED]

On the following day, the average concentration was [REDACTED] percent. For the 1.8 L reactors, the average data for these two days indicated that [REDACTED] of COD had been destroyed [REDACTED]

[REDACTED] On the contrary, data for days 77 and 78 indicated that only about 10 percent of the COD had been degraded. These large fluctuations in results were a function of reactor variability, as the COD method itself showed a precision or reproducibility of greater than 95 percent. [REDACTED]

TABLE 6: EXAMPLE MASS BALANCE ON COD CONVERSION

<u>Date</u>	<u>Day</u>	<u>Reactor COD (g/d)</u>	<u>Std. Dev. Of Reactor COD</u>	<u>COD Added, mg</u>	<u>Initial COD Concentration, mg/L</u>
51702	76	[REDACTED]			
51802	77				
51902	78				

A second approach for understanding the degradation of the wastewater involved an electron balance on the substrate. [REDACTED]

Table 7 summarizes the electron balance. The total number of electrons that were added to each reactor during the experimental period was [REDACTED]. Measuring the methane that was produced provided an estimate of the electrons donated by the substrate that were used for cell energy requirements. Since about [REDACTED] of methane were produced during the analysis period, then [REDACTED]. Another [REDACTED] would be required to reduce the entire mass of sulfate added during the period to hydrogen sulfide. If it is assumed that [REDACTED] of the available electrons went to cell synthesis, the electron balance yields an unused fraction of about [REDACTED] of the available electrons. [REDACTED]

TABLE 7: ELECTRON BALANCE FOR EXPERIMENTAL REACTORS.

Electron Donor	
Maximum meq Donated by Substrate	
Electron Acceptor	
meq CO ₂ Reduced to methane	
meq Used to Reduce Sulfate	
meq Used for Cell Synthesis	
Unused Electrons (by difference)	
Total	

IV. Conclusions

A. Full-Scale Reactor Design

A UASB reactor at full-scale has a volumetric loading rate of [REDACTED] (Metcalf and Eddy, 2003). The volume (V) and the hydraulic retention time (HRT) are calculated in Equations 14 and 15 respectively.

$$[REDACTED] \quad (14)$$

$$[REDACTED] \quad (15)$$

Thus, the volume of the reactor is [REDACTED] with a hydraulic retention time of approximately [REDACTED] days.

B. Economic Analysis

Upflow Anaerobic Sludge Blanket

The cost of a full scale UASB reactor was determined from a unit cost of [REDACTED] (Biothane, 2001). Using Equation 16, [REDACTED]

$$[REDACTED] \quad (16)$$

[REDACTED]

Methane

Methane

The annual value of methane produced by the potential full scale UASB reactor was found by calculating the total annual volume of methane that theoretically should be produced. The COD conversion to methane was [redacted] COD Loaded (see Section III B *Methane Production*).

The estimated value of methane is [redacted]. Using

Sodium Hydroxide

An addition of sodium hydroxide, NaOH, is required to adjust the pH of the wastewater from [redacted] [redacted]. The amount of NaOH necessary to adjust the pH was experimentally found to be [redacted]

Sodium Bicarbonate

An addition of alkalinity in the form of NaHCO₃ was also determined to be needed appropriate operation of the reactor. The amount of NaHCO₃ required per day was experimentally

Hydrogen Sulfide

To treat the hydrogen sulfide gas produced in the system chlorine is needed to strip the gas. The

Sulfate Removal

As determined by last year's Design Team CEE 01.1 Sulfate can be removed prior to treatment in the UASB reactor with a series of treatments. [REDACTED]

TABLE 8: APPROXIMATE CAPITAL COSTS FOR SULFATE TREATMENT

Equipment	Cost
Ion Exchange	[REDACTED]
Settling Tank	[REDACTED]
Sand Filters	[REDACTED]
Equalization Basin	[REDACTED]
	[REDACTED]
Total Initial Cost	[REDACTED]

Economic Analysis

The cumulative results of the economic analysis are presented in Tables 9 and 10. The design team's findings point towards an annual cost of [REDACTED] which includes the cost of the chlorine for hydrogen sulfide treatment (Table 8). Table 9 presents annual cost calculations based on removal of sulfate prior to treatment in the UASB. Removal of sulfate prior to treatment allows the amount of methane production to increase substantially. The adjusted cost [REDACTED]

TABLE 9: ANNUAL COST CALCULATIONS
(with hydrogen sulfide stripping)

Annual Value of Methane	[REDACTED]
Annual Cost of UASB	[REDACTED]
Annual Cost of NaOH	[REDACTED]
Annual Cost of NaHCO ₃	[REDACTED]
Annual Cost of Cl ₂	[REDACTED]
Annual Labor	[REDACTED]
	[REDACTED]
Total Annual Cost	[REDACTED]

TABLE 10: ANNUAL ADJUSTED COST CALCULATIONS
(with sulfate removal)

Annual Value of Methane	[REDACTED]
Annual Cost of UASB	[REDACTED]
Annual Cost of NaOH	[REDACTED]
Annual Cost of NaHCO ₃	[REDACTED]
Annual Cost of Sulfate Removal	[REDACTED]
Annual Labor	[REDACTED]
	[REDACTED]
Total Annual Value	[REDACTED]

C. External Constraints

This project was not severely limited by economic, environmental, sustainability, manufacturability, ethical, health and safety, social, or political constraints. Time was the overriding limiting factor.

V. Recommendations

pH Adjustment

The pH of the wastewater was found to be a relatively

Alkalinity Addition

Sulfate Removal

VI. References

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APPENDIX A: REQUEST FOR PROPOSAL

REQUEST FOR PROPOSAL

Phase I

Review and update the literature report on anaerobic wastewater treatment from the previous project. The objective is for the design team to become familiar with primary issues associated with wastewater treatment and to review and update the issues previously developed.

Phase II

Analysis and characterization of the waste stream for those constituents listed in Table 1. Establish six anaerobic bench-scale reactors operating as batch reactors.

Phase III

Evaluate the hydraulic retention time for optimum methane production by evaluating bench-scale experiments at 15, 30, and 45 days. Measure the influent and effluent pH, alkalinity, COD, BOD₅, TSS, and VSS. Ensure continuous gas flow measurements in order to quantify the gas production of carbon dioxide, methane, and hydrogen sulfide. Maintain a mesophilic environment at 35 °C. Analyze the effluent for pH, alkalinity, and COD. Retain all effluent samples for further analysis.

APPENDIX B: EXPERIMENTAL PROCEDURES

pH Meter Calibration

The pH of each reactor was measured via a Beckman 32 pH Meter. In order to provide a precise and accurate measurement, the meter was calibrated before any measurement of pH was taken or recorded. The Beckman 32 pH Meter is calibrated as follows.

After the Beckman 32 pH Meter has been supplied with power, the “STD” (standard) button is pressed to begin the calibration. The pH probe is then immersed in a standardized liquid with a pH of 4, which is colored pink for discrimination purposes. The standard is confirmed by an eye icon flashing during adjustment and then stopping once the given pH has been achieved. The pH probe is then fully rinsed with deionized water so as to not cross-contaminate systems and maintain a standardized liquid. The above procedure is then repeated again with a standardized liquid of pH 7. Once the meter has been calibrated towards a pH of 4 and a pH of 7, normal measurements of unknown systems are allowed to proceed in full confidence. Measurements are taken by immersing the pH rod in the sample and pressing the “pH” button. Mixing the sample while taking pH measurements ensures a more accurate reading.

Alkalinity

The pH of a given system is buffered by the alkalinity present, predominately the carbonate group. Therefore, an estimation of alkalinity is essential to maintain a proper pH in the system.

A titration method was used to determine the alkalinity present in a system. To prepare for the titration, 50 mL from the control reactors and 25 mL from the experimental reactors were gravimetrically measured into 100 ml and 50 ml beakers. Next, the pH of the sample was measured and recorded once the pH meter has been properly calibrated. The titration begins using a 1 N H₂SO₄ solution. The volume of titrant required to reach a pH of 4.3 (V_{mo}) is then recorded. The volume of titrant to achieve a pH of 8.3 (V_p) is not measured because the wastewater samples from the reactors were in the range of 7.0 and 7.5. Therefore V_p is equals to zero.

Table A1 was used to calculate the various alkalinity species contained within a system, where V equals the volume of sample analyzed and N equals the normality of H₂SO₄.

TABLE A1: ALKALINITY SPECIES CALCULATIONS

Condition	Predominant forms of alkalinity	Species, moles/L
$V_p = V_{mo}$	CO_3^{2-}	$[CO_3^{2-}] = V_p \times N / V$
$V_p = 0$	HCO_3^-	$[HCO_3^-] = V_{mo} \times N / V$
$V_{mo} = 0$	OH^-	$[OH^-] = V_p \times N / V$
$V_{mo} > V_p$	CO_3^{2-} & HCO_3^-	$[CO_3^{2-}] = V_p \times N / V$ $[HCO_3^-] = (V_{mo} - V_p) \times N / V$
$V_p > V_{mo}$	OH^- & CO_3^{2-}	$[CO_3^{2-}] = V_{mo} \times N / V$ $[OH^-] = (V_p - V_{mo}) \times N$

Chemical Oxygen Demand

The Hach COD method utilizes an incubator preheated to 150 °C. Using volumetric flasks, pipettes, and deionized water, samples were diluted so the COD would fall within the testing range of 0-150 mg/L. 2 mL of the diluted sample was pipetted into the testing vial. The contents of the vial was mixed and placed in the COD incubator for 2 hours. All samples were tested against blanks, which were created using the above steps but with deionized water substituted for

the sample solution. After all the samples were cooled to room temperature, the blanks were inserted into a spectrophotometer for calibration. After proper calibration, the sample vials were inserted into the spectrophotometer set to 400 nm and the percent transmittance (%T) was read. Using Table A2, a Hach spectrophotometer conversion table, the percent transmittance was converted to COD (mg/L). For example, T = 57% would be read on the 50 %T row along the left, then across horizontally to the 7 to get a reading of 68.8 mg/L COD.

TABLE A2: HACH LOW RANGE CALIBRATION TABLE, 0-150 MG/L COD

	%T									
%T, Tens	0	1	2	3	4	5	6	7	8	9
10	--	--	--	--	--	--	--	--	--	--
20	--	--	--	--	--	--	--	--	--	--
30	--	--	--	--	--	0	3.7	7.5	11.3	15.0
40	18.7	22.2	25.6	28.9	32.1	35.3	38.4	41.4	44.4	47.3
50	50.2	3.0	55.8	58.5	61.2	63.8	66.3	68.8	71.3	73.8
60	76.2	78.6	80.9	83.2	85.5	87.7	89.9	92.1	94.2	96.3
70	98.4	100.4	102.4	104.3	106.2	108.2	110.1	112.0	113.9	115.8
80	117.6	119.4	121.1	122.8	124.5	126.2	127.9	129.6	131.2	132.8
90	134.5	136.1	137.7	139.3	140.9	142.5	144.1	145.6	147.0	148.6

The Bioscience COD method was similar to the Hach COD method by utilizing the same incubator (at 150 °C) and spectrophotometer (at 440 nm). However, rather than using Table A2, a calibration curve was constructed by the preparation of determined dextrose solutions (mg/L) of 10, 50, 100, and 150 prepared with a 1000 ppm glucose stock solution. 2.5 mL of all samples were then pipetted into the Bioscience reagent vials and then heated for 2 hours. The 150 mg/L sample is used to zero the spectrophotometer. After the meter is properly calibrated, the remaining determined dextrose solutions were used to develop a calibration curve. The unknown samples were then inserted into the spectrophotometer, read for percent transmittance, and matched to the derived calibration curve.

Trial and error was used for both methods to establish dilution requirements to obtain a result in the necessary 0-150 mg/L ranges of the spectrophotometer.

Biochemical Oxygen Demand

This test required fifteen biochemical oxygen demand (BOD) samples to be produced with experimental solution, seed water, and dilution water. The seed water, a commercial-product called *PolySeed* (Fisher Scientific), consisted of reconstituted freeze-dried bacteria in a buffered solution. The dilution water was aerated and buffered in accordance with *Standard Methods*.

All fifteen BOD bottles were filled halfway with dilution water. Five blanks were made by the addition of 2 mL of seed water. To another five BOD bottles 2 mL of seed water and 5 mL of glucose solution were added. To the remaining five bottles 2 mL of seed water and 20 mL of diluted wastewater (1:1000) were added. All bottles were then completely filled with dilution water and labeled appropriately.

The bottles were then transferred (except for one designated sample blank, glucose, and wastewater) to the 20 °C incubator. The oxygen concentration of each designated sample was then determined using a dissolved oxygen (DO) meter; see DO meter calibration instructions below. An oxygen measurement was then taken 5-days later for the twelve remaining bottles placed in the incubator.

The dissolved oxygen meter used was a *YSI model 58 DO meter*. To operate the meter, the probe is placed in moist air and the O_2 Zero knob is adjusted until the display reads 00.0. The function switch is then turned from Zero to % and the probe is allowed to stabilize for 15 minutes. After 15 minutes, the O_2 Calib knob is adjusted until the meter reads 98. The probe is then placed into the sample BOD and when the reading has stabilized the oxygen measurement is recorded. The salinity knob is positioned at 0 for freshwater and altitude is accounted for by correcting the number on the screen of the meter by a percentage for the corresponding altitude.

Methane Production

Methane production was estimated from the volume of water displaced by an inverted flask filled with approximately 1000 mL of deionized water, over a 24-hour period. To account for the evaporation rate three beakers were utilized (similar in surface area and volume to the beakers containing the displaced water). This evaporation amount was then added to the water that was displaced for each beaker over a 24-hour period. Methane production results were obtained and recorded once or twice daily.

Wasting and Feeding of Reactor

Every day a 120 g sample was taken from each reactor. The reactor was then fed a nutrient solution (for control reactors) or the actual wastewater (for experimental reactors). In order to waste sludge from the reactor, the design team employed a series of valves in combination with nitrogen gas to pressurize the 2-liter reactor and force the sludge to travel back up the feed tube where a sample could be collected, as shown in Figure 1. Before the nitrogen gas was applied, Valve No.1 was closed and Valve No.2 was opened to allow the gas to travel directly to the reactor to pressurize it so a sample could be taken.

The feed solution for the control reactors was similar to the solution used in the start-up of the reactors. Beginning on day 10, the reactors were switched to a glucose-based feed solution, whose six-carbon chain more closely resembled the five-carbon chain of the actual wastewater. 12.5 g of glucose was substituted for the acetic acid in 2-liters of the control feed solution. 120 mL of this solution was likewise fed to the reactors every day.

The experimental reactors were given the same feed solution as the control reactors until they were restarted using wastewater feed on day 48. The 2-liter wastewater feed solution consisted of undiluted wastewater, 60 mL of 1 M NaOH to raise the pH into the optimum range, and 10 g of $NaHCO_3$ to buffer incoming acidity. The experimental reactors were initially wasted 30 g and fed 30 ml each day. That amount was increased to 45 (g or ml) on day 74 and to 60 (g or ml) on day 84.

Sulfate

Sulfate concentrations were measured with a Dionex Bio-LC equipped with a AS4A separation column. The mobile phase was pumped at a rate of 2.0 ml/min and was prepared by adding 0.25 g of sodium bicarbonate and 0.93 g of sodium carbonate to four liters of deionized water. The

regenerant consisted of 0.025 N sulfuric acid and was pressurized at 5 psi. Standards were made from two separately prepared 1000 mg/L stock solutions of sulfate from calcium sulfate salt. Every other standard beginning with 0.5 mg/L was made from stock solution 1 while stock solution 2 was used for the remaining standards. After a minimum five point calibration (0.5, 1, 5, 10 and 15 mg/L), blind repeats of standards were analyzed at least every 10 samples (and at the end of each run), so that the integrity of analytical accuracy was maintained. Reactor samples were tested without dilution. Solids were removed from the samples prior to analysis by microfuge centrifugation.

APPENDIX C: DATA SHEETS

TABLE A3: EXPERIMENTAL PH DATA

Event			Reactor Number					
	Date	Day	1	2	3	4	5	6
1*	2-Mar	1						
	3-Mar	2						
	4-Mar	3						
	5-Mar	4						
	6-Mar	5						
	7-Mar	6						
	8-Mar	7						
	9-Mar	8						
	10-Mar	9						
	11-Mar	10						
	12-Mar	11						
	13-Mar	12						
	14-Mar	13						
	15-Mar	14						
	16-Mar	15						
	17-Mar	16						
	18-Mar	17						
	19-Mar	18						
	20-Mar	19						
	21-Mar	20						
	22-Mar	21						
	23-Mar	22						
	24-Mar	23						
	25-Mar	24						
	26-Mar	25						
	27-Mar	26						
	28-Mar	27						
	29-Mar	28						
	30-Mar	29						
	31-Mar	30						
	1-Apr	31						
	2-Apr	32						
	3-Apr	33						
	4-Apr	34						
	5-Apr	35						
	6-Apr	36						
	7-Apr	37						
	8-Apr	38						
	9-Apr	39						
	10-Apr	40						
2*	11-Apr	41						

"ND" indicates no data / erroneous data

1*: Restart all reactors.

2*: Switched feeding solution from acetate to glucose.

TABLE A3: EXPERIMENTAL PH DATA— CONT'D

Event	Date	Day	Reactor Number					
			1	2	3	4	5	6
3*	12-Apr	42						
	13-Apr	43						
	14-Apr	44						
	15-Apr	45						
	16-Apr	46						
	17-Apr	47						
	18-Apr	48						
	19-Apr	49						
	20-Apr	50						
	21-Apr	51						
4*	22-Apr	52						
	23-Apr	53						
	24-Apr	54						
5*	25-Apr	55						
	26-Apr	56						
	27-Apr	57						
	28-Apr	58						
	29-Apr	59						
	30-Apr	60						
	1-May	61						
	2-May	62						
	3-May	63						
	4-May	64						
6*	5-May	65						
	6-May	66						
	7-May	67						
	8-May	68						
	9-May	69						
	10-May	70						
	11-May	71						
	12-May	72						
	13-May	73						
	14-May	74						
	15-May	75						
	16-May	76						
	17-May	77						
	18-May	78						
	19-May	79						

"ND" indicates no data / erroneous data

3: Masada wastewater introduced to reactors 4-6.*

4: Reactor 1-3 restarted.*

5: Restart all reactors.*

6: Wastewater fed to reactors 4-6 changed from 30 mL to 45 mL.*

TABLE A3: EXPERIMENTAL PH DATA- CONT'D

			Reactor Number:
<u>Event</u>	20-May	80	
	21-May	81	
7*	22-May	82	
8*	23-May	83	
	24-May	84	
	25-May	85	
	26-May	86	
	27-May	87	
	28-May	88	
	29-May	89	

"ND" indicates no data / erroneous data

7: Reactor #3 at 50 °C.*

8: Wastewater fed to reactors 4-6 changed from 45 mL to 60 mL.*

TABLE A4: EXPERIMENTAL METHANE PRODUCTION DATA

			<u>Average Methane Production (mL/day)</u>		<u>Std Dev Methane Production</u>	
<u>Event</u>	<u>Date</u>	<u>Day</u>	<u>Reactor 1-3</u>	<u>Reactor 4-6</u>	<u>Reactor 1-3</u>	<u>Reactor 4-6</u>
	18-Mar	17				
	19-Mar	18				
	20-Mar	19				
	21-Mar	20				
	22-Mar	21				
	23-Mar	22				
	24-Mar	23				
	25-Mar	24				
	26-Mar	25				
	27-Mar	26				
	28-Mar	27				
	29-Mar	28				
	30-Mar	29				
	31-Mar	30				
	1-Apr	31				
	2-Apr	32				
	3-Apr	33				
	4-Apr	34				
	5-Apr	35				
	6-Apr	36				
	7-Apr	37				
	8-Apr	38				
	9-Apr	39				
	10-Apr	40				

"ND" indicates no data / erroneous data

TABLE A4: EXPERIMENTAL METHANE PRODUCTION DATA – CONT'D

Event			Average Methane Production (mL/day)		Std Dev Methane Production	
	Date	Day	Reactor 1-3	Reactor 4-6	Reactor 1-3	Reactor 4-6
1*	11-Apr	41				
	12-Apr	42				
	13-Apr	43				
	14-Apr	44				
	15-Apr	45				
	16-Apr	46				
	17-Apr	47				
2*	18-Apr	48				
	19-Apr	49				
	20-Apr	50				
	21-Apr	51				
	22-Apr	52				
3*	23-Apr	53				
	24-Apr	54				
4*	25-Apr	55				
	26-Apr	56				
	27-Apr	57				
	28-Apr	52				
	29-Apr	53				
	30-Apr	54				
	2-May	61				
	3-May	62				
	4-May	63				
	5-May	64				
	6-May	65				
	7-May	66				
	8-May	67				
	9-May	68				
5*	10-May	69				
	11-May	70				
	12-May	71				
	13-May	72				
6*	14-May	73				
	15-May	74				
	16-May	75				
	17-May	76				
	18-May	77				
	19-May	78				
	20-May	79				

"ND" indicates no data / erroneous data

1*: Switched feeding solution from acetate to glucose.

2*: Masada wastewater introduced to reactors 4-6.

3*: Reactors 1-3 restarted.

4*: Restart all reactors.

5*: Changed NaOH Gas Trap.

6*: Wastewater fed to reactors 4-6 changed from 30 mL to 45 mL

TABLE A4: EXPERIMENTAL METHANE PRODUCTION DATA – CONT'D

Event	Date	Day	Average Methane Production (mL/day)		Std Dev Methane Production	
			Reactor 1-3	Reactor 4-6	Reactor 1-3	Reactor 4-6
7*	21-May	80				
	21-May	81				
	22-May	82				
	22-May	82				
	23-May	83				
8*	23-May	83				
	24-May	84				
	25-May	85				
	25-May	85				
	26-May	86				
	27-May	87				
	27-May	87				
	28-May	88				

"ND" indicates no data / erroneous data

7*: Reactor #3 at 50 °C.

8*: Wastewater fed to reactors 4-6 changed from 45 mL to 60 mL.

TABLE A5: EXPERIMENTAL ALKALINITY DATA

Testing Date	Day	Alkalinity, mg/L as CaCO ₃					
		Reactor Numbers					
		1	2	3	4	5	6
19-May	79						
20-May	80						
21-May	81						
22-May	82						
23-May	83						
24-May	84						
25-May	85						
26-May	86						
27-May	87						

"ND" indicates no data / erroneous data

TABLE A6: EXPERIMENTAL SULFATE DATA

Control Reactors					Experimental Reactors				
Date	Day	Reactor#	Average	Stdev	Date	Day	Reactor#	Average	Stdev
5/9/02	69	2			-	-	-		
5/10/02	70	3			-	-	-		
5/11/02	71	3			-	-	-		
5/13/02	73	1			5/13/02	73	4		
5/14/02	74	1			-	-	-		
5/15/02	75	1			-	-	-		
5/16/02	76	1			5/16/02	76	4		
5/17/02	77	1			5/17/02	77	4		
5/18/02	78	1			5/18/02	78	4		
5/19/02	79	1			5/19/02	79	4		
5/20/02	80	1			5/20/02	80	4		
5/21/02	81	1			5/21/02	81	4		
5/22/02	82	1			5/22/02	82	4		
5/23/02	83	1			5/23/02	83	4		
5/24/02	84	1			5/24/02	84	4		

TABLE A7: EXPERIMENTAL COD DATA

Controls					Experimental				
Date	Day	Average	STD Dev	K of Var., %	Date	Day	Average	STD Dev	K of Var., %
8-May	44				8-May	44			
9-May	45				9-May	45			
10-May	46				10-May	46			
11-May	47				11-May	47			
13-May	48				13-May	48			
14-May	49				14-May	49			
15-May	50				17-May	52			
16-May	51				18-May	53			
17-May	52				19-May	54			
18-May	53				20-May	55			
19-May	54				21-May	56			
20-May	55				22-May	57			
21-May	56				23-May	58			
24-May	60				24-May	59			
Average			Average,%		Average			Average,%	

APPENDIX D: RESUMES

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