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January 27, 2011

Mr. Timothy Edman
Manager, Regulatory Administration
Xcel Energy, Inc.
414 Nicollet Mall
Minneapolis, MN 55401

Dear Mr. Edman:

Subject: Quarterly Progress Report Entitled "Mitigation of Hydrogen Sulfide with Concomitant Enhancement of Microbial Methane Production in Biomass Digesters"
Contract No. RD3-68; EERC Fund 9967

Enclosed please find the subject report. If you have any questions, please contact me by phone at (701) 777-5247 or by e-mail at dstepan@undeerc.org.

Sincerely,

Daniel J. Stepan
Senior Research Manager

DJS/kmd

Enclosure

Energy & Environmental Research Center, University of North Dakota
15 North 23rd Street, Stop 9018, Grand Forks, ND 58202-9018

Project Title: Mitigation of Hydrogen Sulfide with Concomitant Enhancement of Microbial Methane Production in Biomass Digesters

Contract Number: RD3-68 Milestone Number: 8 Report Date: January 27, 2010

Principal Investigator: Daniel J. Stepan Contract Contact: Tobe M. Larson

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Congressional District: Not Applicable

Congressional District: Not Applicable

MILESTONE REPORT

Summary: The overall goal of this Energy & Environmental Research Center (EERC) project is to test and demonstrate a novel biotechnology to convert biomass into a biogas with increased methane content and significantly reduced hydrogen sulfide. The project is being conducted at both the bench and pilot scale. Laboratory screening tests have established baseline operating conditions. The EERC has teamed with Haubenschild Farm Dairy, Inc., Princeton, Minnesota, to conduct the project.

During this reporting period, key milestones included the conclusion of pilot-scale experiments using Haubenschild Farm Dairy manure supplemented with scavenger and additive to compare process performance of the experimental plug flow anaerobic digester to the full-scale plug flow anaerobic digester that acts as a control. Operation, data collection, shutdown, and disassembly of the pilot anaerobic digester system were completed.

The pilot system is a 2-ft-diameter, 20-ft-long vessel with a nominal operating volume of 235 gallons. Work performed included operation of the pilot digester with addition of the EERC additive and scavenger to obtain operational data to compare with the full-scale anaerobic digester which served as a control. The addition of scavenger and additive did result in lower H_2S concentrations in the biogas of the pilot digester.

Work planned for the next reporting period includes final data reduction and analysis, performing an economic analysis on the cost of additive and scavenger addition for the full-scale digester at Haubenschild Farm Dairy and preparation of the final technical project report.

Project funding was provided by customers of Xcel Energy through a grant from the Renewable Development Fund.

Technical Progress: During this reporting period, the project team continued operation of the pilot-scale digester system previously installed at Haubenschild Farm Dairy, near Princeton, Minnesota. The digester was operated as long as possible given weather and budget constraints. This allowed pseudo-steady-state performance to be obtained with respect to reactor loading. Difficulties were encountered when collecting gas production rate data because of a leak in the feed end gate valve and a power outage from an early winter snowstorm that resulted in a process upset. Despite the challenges encountered, sufficient data were collected to allow for conclusions to be derived from the pilot-scale test. The full-scale Haubenschild Farm Dairy digester was also operational and continuously producing a combustible biogas during the period of time the pilot digester was in operation. Qualitative information from the full-scale system indicated it also experienced an operational upset because of the power outage from the early winter storm.

Laboratory Screening Experiments

No new laboratory screening experiments were initiated during this reporting period, but additional data were collected from ongoing experiments that were initiated during the previous reporting period. Table 1 lists the test conditions established for those experiments.

Table 1. Experimental Design for Laboratory Screening Experiments

Condition	Fresh Manure, g	Seed, g	Additive, units of concentration	Scavenger, units of concentration
Seeded Control	36	4	0	0
Seeded Additive	36	4	0.25	0
Seeded Additive	36	4	0.5	0
Seeded Additive and Scavenger	36	4	0.25	0.5
Seeded Additive and Scavenger	36	4	0.25	1
Seeded Additive and Scavenger	36	4	0.5	0.5

The samples were periodically removed from the incubator, and the headspace gas of the samples was sampled with a gas-tight syringe and analyzed using gas chromatography to determine the methane, carbon dioxide, and hydrogen sulfide content of the generated biogas.

Results of the laboratory screening experiments are illustrated in Figures 1 and 2. Figure 1 shows cumulative methane production versus time, and Figure 2 is cumulative hydrogen sulfide versus time. The data previously reported included the results through 32 days of incubation. The results provided here include the measurement of methane and H_2S production through 61 days of incubation. The conclusions after 61 days of incubation are consistent with those made after 32 days: all test conditions showed an increase in the amount of methane generated and a significant decrease in the amount of sulfide in the headspace gas versus the control. The use of the additive and scavenger producing the lowest amount of H_2S were found for test conditions with 0.25 units of additive, 1 unit of scavenger and 0.5 units of additive, 0.5 units of scavenger conditions. However, because the condition with 0.25 units of additive, 0.5 units of scavenger provided good H_2S generation control at a low cumulative chemical addition rate, it was initially

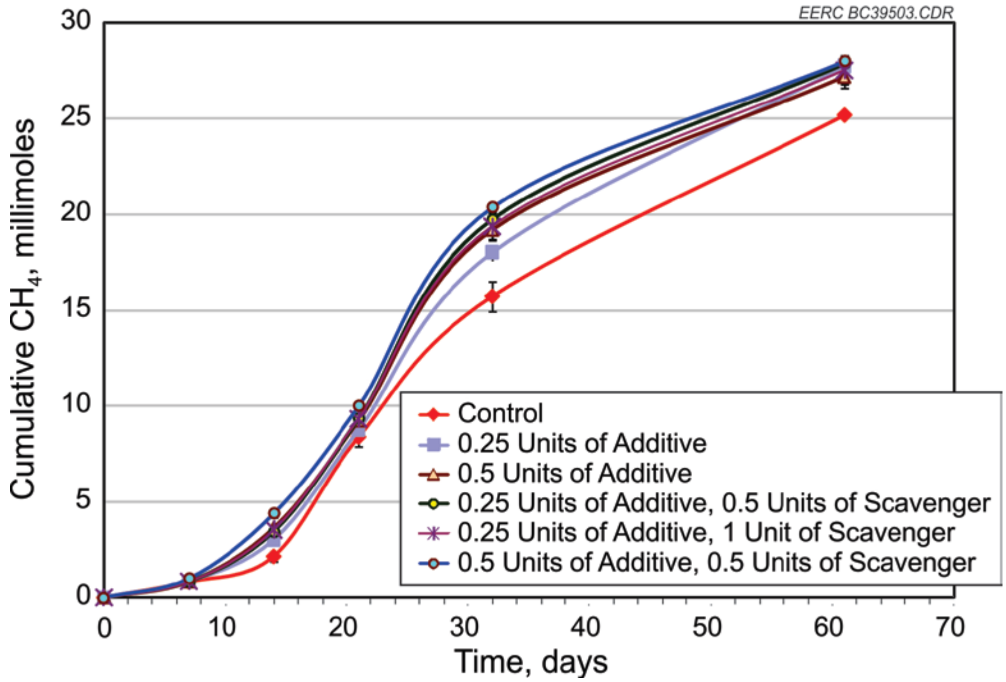


Figure 1. Effects of the scavenger and additive dosages on methane production in serum bottles fed Haubenschild manure. The error bars represent the standard error of the triplicates. Where not shown, the error bars are within the symbols.

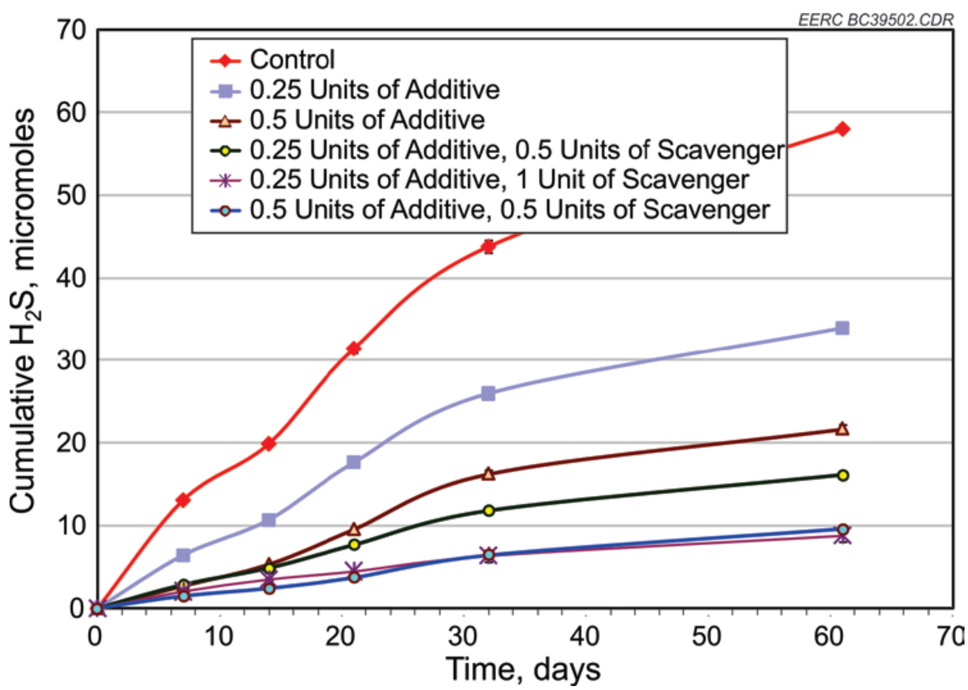


Figure 2. Effects of the scavenger and additive dosages on hydrogen sulfide production in serum bottles fed Haubenschild manure. The error bars represent the standard error of the triplicates. Where not shown, the error bars are within the symbols.

selected for use in the pilot-scale digester. Test conditions in the pilot digester were later increased to 0.25 units of additive and 1.0 units of scavenger.

Pilot-Scale Digester

During this reporting period, the pilot digester continued in operation at Haubenschild Farm Dairy until a winter storm produced a power outage that necessitated a discontinuation of the pilot testing. The power outage resulted in cold-temperature operation that impacted the microbial population and also allowed condensation to accumulate in the biogas line and mass flow sensor, which resulted in its failure. Given the anticipated microbial recovery time, time required for repair/replacement of the mass flow sensor, the available data collected to date, and the remaining project budget, a decision was made to discontinue operation of the pilot digester. On November 20, 2010, the pilot-scale digester was shut down, emptied, disassembled, and transported back to the EERC. Data were collected at two different additive loading conditions and showed that the addition of scavenger and additive did result in lower H_2S concentrations in the biogas of the pilot digester.

Details on the day-to-day operation of the digester were provided in Milestone Report 7. All of the data plots presented in this report include data collected over the entire pilot-scale digester operating period, including data collected from August 13, 2010, to September 30, 2010 (Milestone Report 7). The data presented herein include temperature, mass, biogas flow rate data for the pilot-scale digester, and gas composition (methane and H_2S) for both the full-scale and pilot-scale digesters.

Figure 3 illustrates pilot digester temperature as measured by the two temperature control thermocouples and by manual measurements of digester effluent. The target operating temperature was 95°F. Table 2 presents the mean, standard deviation about the mean, minimum, maximum, and median temperature data, which are shown graphically in Figure 3. The averages for the control thermocouples were higher than those for the manual measurements, but none of these averages was statistically different (greater than one standard deviation) from the target value of 95°F. The lowest observed average daily temperatures were observed on days when power outages at the farm led to a lack of availability of hot water for use in regulating the digester temperature. Typically, there was no discernable upset in digester operation. However, in one instance, November 14, 2010, a winter storm caused a power outage that resulted in a temperature drop in both the pilot-scale and full-scale digesters. The gas production rate for the full-scale digester subsequently decreased sufficiently to result in a shutdown of the genset. A corresponding reduction in biogas production by the pilot-scale digester was apparent but difficult to quantify because of failure of the feed inlet gate valve on the digester, which created a leak sufficient to prevent accurate gas production rates. In addition, the power outage led to the condensation in the biogas line and mass flow sensor, which led to the malfunction and failure.

Figure 4 illustrates the total mass of the operating digester. The nominal operating mass is approximately 1300 kg. From August 12, 2010, to September 30, 2010, the mass was maintained within 5% of this value, with a total average daily value ranging between 1234 and 1370 kg. Near the end of that time, the digester exhibited a relatively rapid increase in mass. Over the

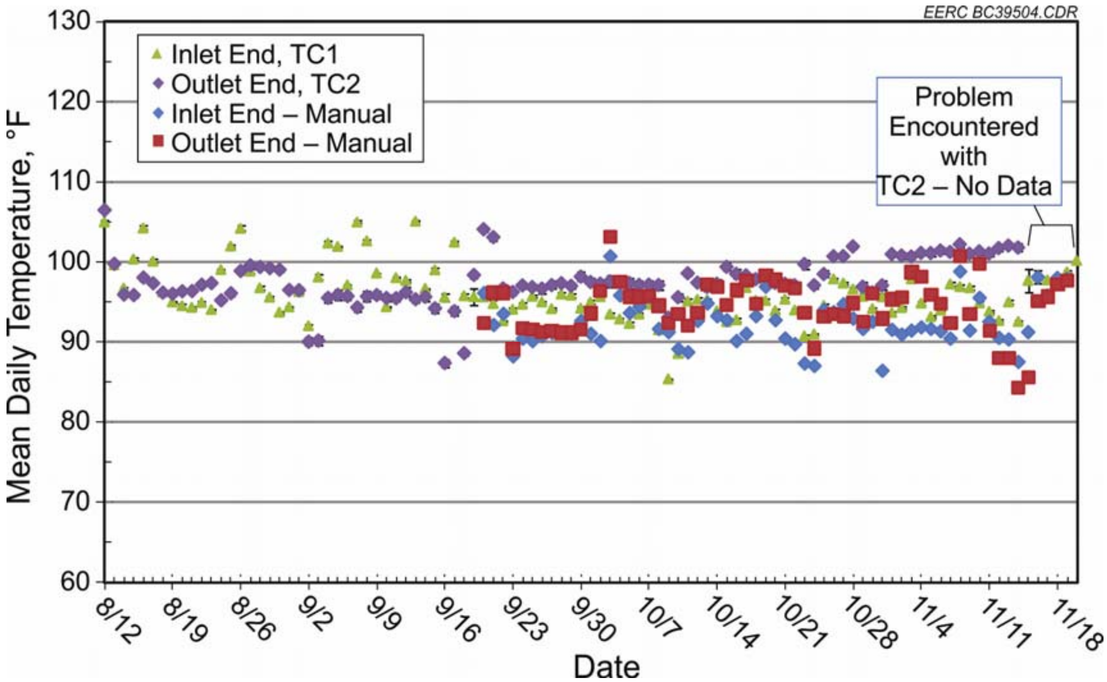


Figure 3. Pilot-scale digester temperature. Error bars represent ±1 95% confidence interval of the daily mean.

Table 2. Average (mean), Minimum, Maximum, Median Temperatures of the Pilot-Scale Digester

	TC1, inlet	Manual Inlet Temp.	TC2, outlet	Manual Outlet Temp.
Average	96.1	92.3	97.6	94.2
Std. Dev.*	3.4	3.0	3.0	3.5
Minimum	85.3	86.4	87.3	84.3
Maximum	105.1	100.7	106.5	103.1
Median	95.5	91.6	97.2	94.7

* Standard deviation.

operating period from October 1 to November 19, the mass of the digester varied between 1237 and 1453 kg, with a mean of 1317 ±48 kg. The maximum value during this period was 11.8% greater than the target. Solids accumulation was attributed to higher solids content of the feed manure (as high as 12% on some days) and the nature of plug flow digester operation.

Figure 5 illustrates the mean biogas production rate for the pilot-scale digester. The expected nominal flow rate based on the lab-scale digester was 1.5 slpm (standard liters per minute). Initially, the flow rate was less than that level because the digester began operation on digested solids from the full-scale digester. A high rate of variability was observed during initial feeding operations and was attributed to daily ambient temperature variations that were warmer than the

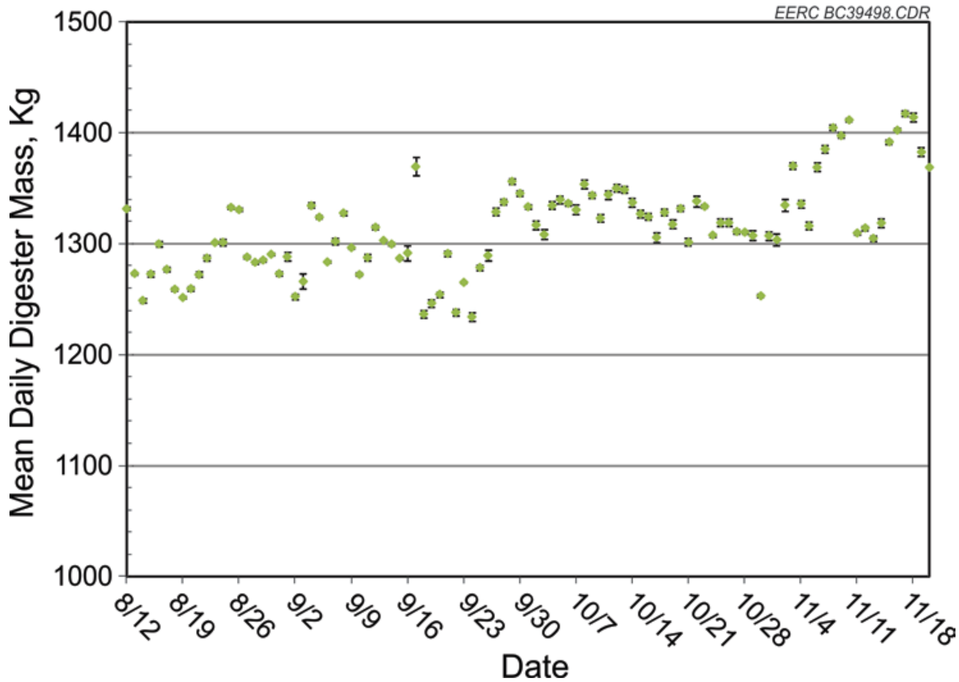


Figure 4. Mean daily digester mass. Error bars represent ±1 95% confidence interval of the daily mean.

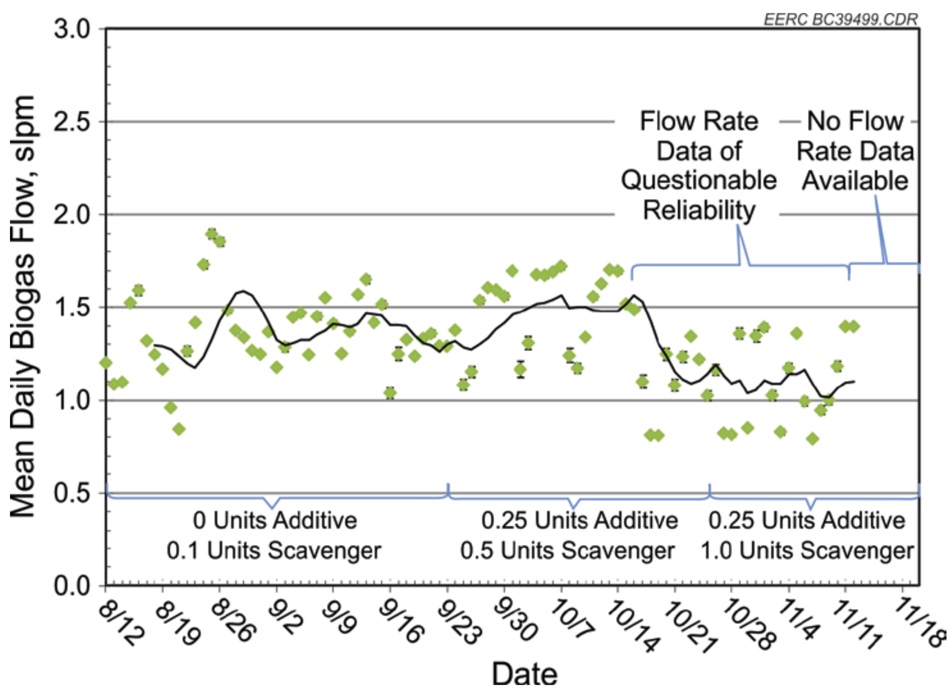


Figure 5. Mean daily biogas flow. Error bars represent ±1 95% confidence interval of the daily mean. The trend line provided is the 7-day moving average.

target operating temperature, which affected the microbial population dynamics. The period from August 29 to September 23 was considered steady-state operation under control conditions. The corresponding gas flow rate was 1.36 ±0.13 slpm. The first day of the EERC additive and scavenger addition was September 24. The data appear to suggest a gas flow rate increase from steady-state control conditions to a 7-day moving average of close to 1.5 slpm. On October 17, the average was observed to decrease to around 1.2 slpm. Behavior of the system as noted by the operators indicated the likely presence of a slow and/or intermittent leak or leaks. Efforts were made to find and seal all possible leaks with limited success, and it was observed that on certain days, it was difficult to measure gas flow after closing reactor valves after feeding operations. A failure of the mass flowmeter occurred on November 12. Attempts were made to measure gas flow with a rotameter with limited success. A persistent leak did not allow sufficient pressure to build up for accurate gas flow determinations using a rotameter, which operates at higher differential pressure than the mass flowmeter.

Figure 6 illustrates biogas methane content for both the pilot-scale and full-scale digesters. The values from both digesters are essentially equivalent, with the average value for the pilot digester being 59.1% and for the full-scale digester being 59.9%.

Figure 7 illustrates hydrogen sulfide content for both the pilot-scale and full-scale digesters. Two sets of analytical data are shown for each digester. The data sets labeled as Haubenschild Digester and EERC Pilot Digester are results of gas chromatography, while the data sets labeled EERC Kitagawa and Haubenschild Kitagawa were collected on-site using Kitagawa tubes. It

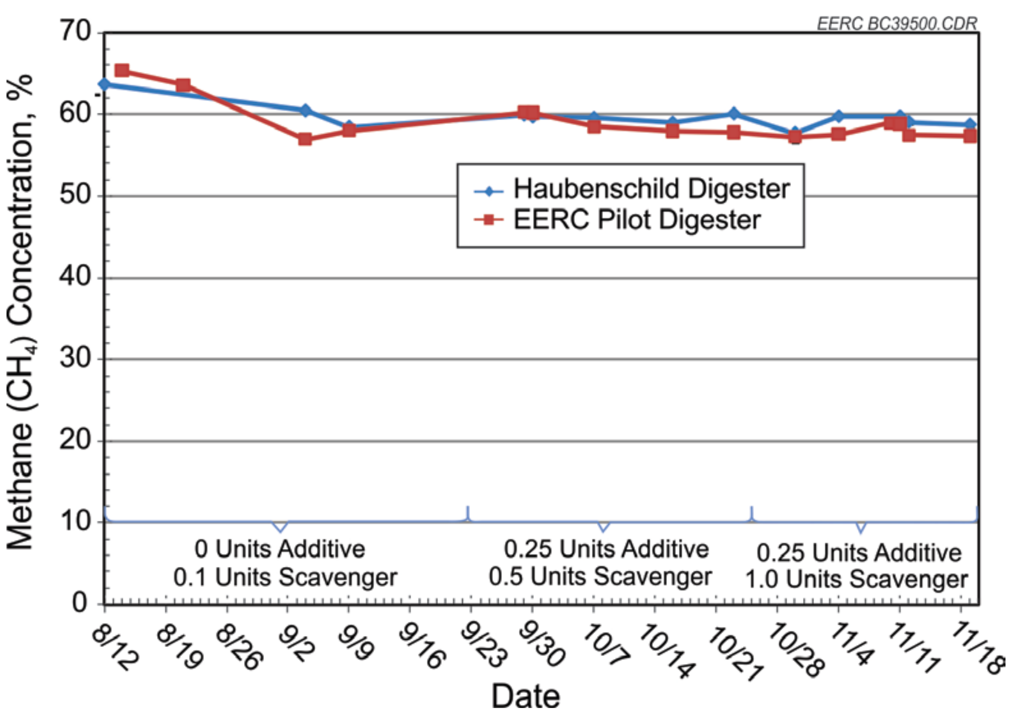
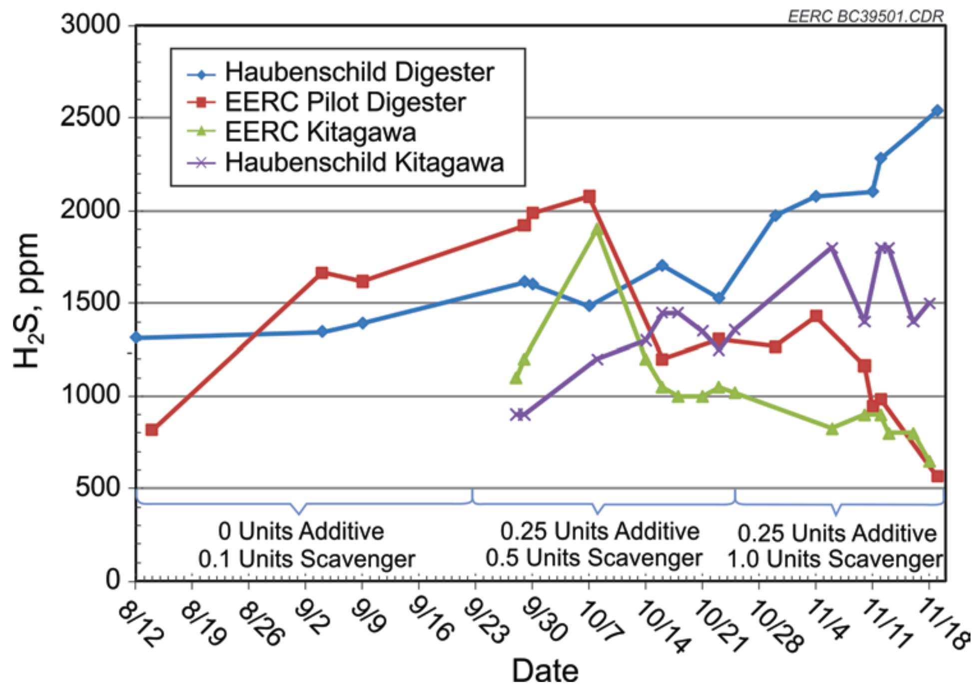


Figure 6. Methane concentration in full-scale (Hubenschild) and pilot-scale (EERC) digesters. Error bars based on ±1 standard deviation are not visible because they are smaller than the size of the symbol.



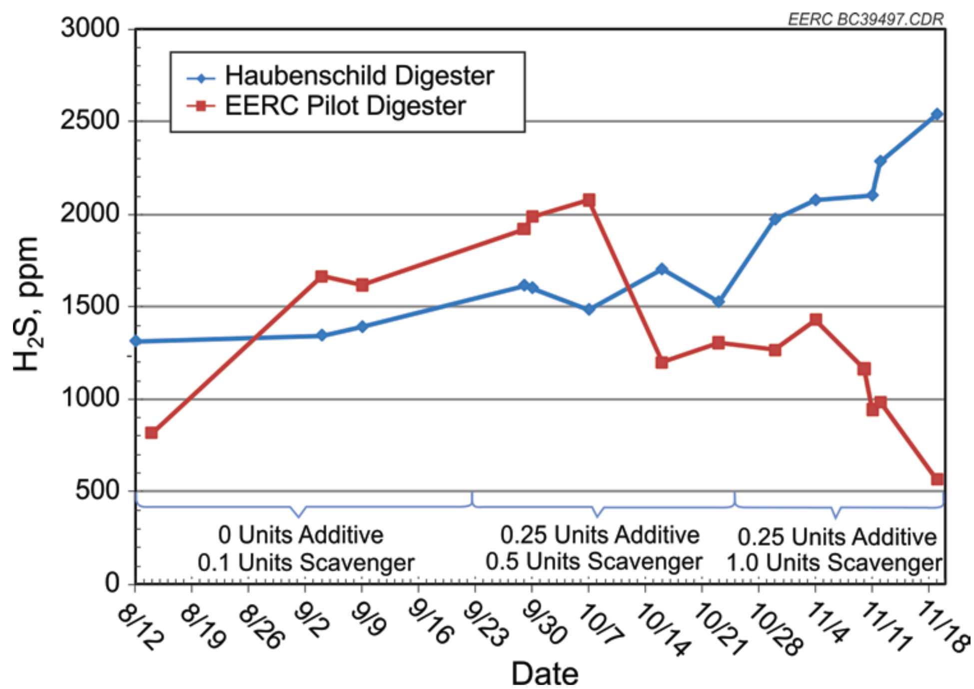


Figure 7. Hydrogen sulfide concentration in full-scale (Hubenschild) and pilot-scale (EERC) digesters. Error bars of ±1 standard deviation for the gas chromatography data (blue diamond and red square) are not visible because they are smaller than the size of the symbol.

appears that the Kitagawa tube analyses tended to underestimate H_2S concentrations but were nonetheless effective at providing confirmation of the general trend of H_2S generation.

The timing of the observed decreases in H_2S concentration for the pilot-scale digester confirms the efficacy of using the EERC additive and scavenger. The first decrease in H_2S from between 1620 and 2080 ppm to levels between 1200 and 1430 ppm occurred sometime between 10 and 15 days following the addition of 0.5 units of additive and 0.25 units of scavenger to the pilot digester feed manure. The second decrease from the 1200 to 1430 ppm range to the 565 ppm (and, apparently, still decreasing) value started between 10 and 15 days, following the increase in scavenger concentration to 1.0 units. This behavior is consistent with the results from the serum bottle experiments (Figure 2), which revealed the 0.25 units of additive, 1.0 units of scavenger condition provided better control of H_2S production than the 0.25 units of additive, 0.5 units of scavenger condition.

Additional Milestones: Pilot-scale testing was completed.

Project Status: Although technical difficulties were encountered, the project remained on schedule and within overall budget, close to the projected spending plan. Key milestones for the upcoming quarter include final data reduction and analysis, performing an economic analysis on the cost of additive and scavenger addition for the full-scale digester at Haubenschild Farm Dairy, and preparation of the final technical project report.