

April 30, 2010

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/cs

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: 5 Report Date: April 30, 2010

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

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Congressional District: Not Applicable

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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 will be conducted at both the bench and pilot scale. Laboratory screening tests will establish baseline operating conditions prior to bench- and pilot-scale testing. The EERC has teamed with Haubenschild Farm Dairy, Inc., Princeton, Minnesota, to conduct the project.

During this reporting period, key milestones included the continuation of bench-scale experiments using Riverview Dairy manure to compare process performance of control and experimental plug flow anaerobic digesters, incorporation of recycle and a decreased residence time to aid in digester operation, and batch serum bottle experiments to decide on the appropriate recycle rate, residence time, and scavenger concentration. The serum bottle tests confirmed that a 10% recycle should provide significant benefit to stable operation of the plug flow digester and that use of the sulfide scavenger should further reduce H₂S generation. The results from operation of the bench-scale digester confirmed the benefit of 10% recycle, confirmed both digesters perform in a similar manner when operated without additive, and confirmed that supplying additive decreased the concentration of H₂S in the produced gas. Some decrease in gas production rate was noted for the additive digester, but the composition of the gas showed an increase in methane concentration.

The work planned for the next reporting period includes design and fabrication of the pilot-scale digester and shipment to the field site, additional serum bottle studies on the combined use of additive and scavenger, and continued operation of the bench-scale digesters.

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

Technical Progress:

Laboratory Screening Experiments

Additional laboratory screening experiments were conducted during this reporting period. These consisted of an inoculum size experiment and a scavenger experiment. For the inoculum size experiment, the seed culture (effluent from the lab-scale control digester) and fresh manure were homogenized separately using a blender. The homogenized seed manure was dispensed into the serum bottles followed by introduction of the fresh manure. In the scavenger experiment, the seed culture was mixed with the fresh manure, the mixed sample was then homogenized in a blender, and this mixture was transferred into serum bottles. Samples were prepared in an anaerobic glove box as described in the Milestone 2 quarterly report. All tests were performed in triplicate.

The samples were periodically removed from the incubator; 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.

Effects of Inoculum Size on Production of Methane and Hydrogen Sulfide

Results from previous batch serum bottle experiments and previous bench-scale digester runs suggested that decreasing the hydraulic residence time of the digesters and incorporating sludge recycle might help improve performance. Sufficient volatile solids destruction and methane formation could be accomplished at the shorter residence time by inoculation of the fresh manure with a healthy culture of methanogenic microorganisms through the use of recycle. Further, the shorter residence time should avoid the potential for regrowth of sulfidogenic organisms that might have caused the failure of the digester in November 2009 and early in this reporting period (data not shown). Before incorporating these changes in the lab-scale plug flow digesters, a batch serum bottle study was performed to select the appropriate recycle rate (seed culture size) and residence time. Table 1 shows the experimental design for the study. It included the use of a “no seed” control, three levels of seed addition to represent three different recycle rates, and the observation of the methane and hydrogen sulfide production in these cultures over time to represent residence time in an ideal plug flow digester. All serum bottles received additive at the normal concentration of 0.5 units. It should be noted that real digesters have dispersion (mixing) that will minimize the need for recycle. A tracer study can be conducted on a real system to get a measure of the amount of dispersion.

Table 1. Experimental Design for Seed Size Serum Bottle Experiment

Condition	Fresh Manure, g	Seed, g	Additive, mL, (0.5 units)
No Recycle, 0%	40	0	5
5% Recycle	38	2	5
10% Recycle	36	4	5
15% Recycle	34	6	5

Results of the seed size experiments are plotted in Figures 1 and 2. From Figure 1, it is apparent that recycle of digester effluent would significantly increase the rate of methane production, which could be obtained in a plug flow digester fed the fresh manure used in this experiment. The amount of benefit obtained by increasing the % seed used was most pronounced at 10 days, where the 10% and 15% seed cultures had produced almost twice as much methane as the 5% seed culture. By 20 days, the methane production by the 5% seeded culture was similar to that observed for the 10% and 15% cultures. The unseeded (0%) cultures had produced less than 1/5 the amount of methane by Day 20 than that observed for the seeded cultures. By Day 20, the 5%, 10%, and 15% seeded cultures produced 654%, 715%, and 663% more methane, respectively, than the unseeded cultures. This very large increase in methane production is not expected to be observed for a real plug flow reactor. Dispersion in a reactor will accomplish some amount of inoculation of the freshly added manure. Therefore, recycle in a real plug flow digester should only provide moderate benefits.

From Figure 2, it is apparent that addition of the seed culture did not increase the production of H_2S like it increased the production of methane, thus improving the ratio of methane to H_2S in the produced gas. It is also apparent that for all three of the seeded cultures, the rate of H_2S production was very low for the first 10 days. The rate of H_2S formation appeared to increase dramatically after 10 days of incubation. These data were interpreted as an indication that the benefit of the additive may have been exhausted by 10 days, allowing for regrowth of sulfidogenic microbes.

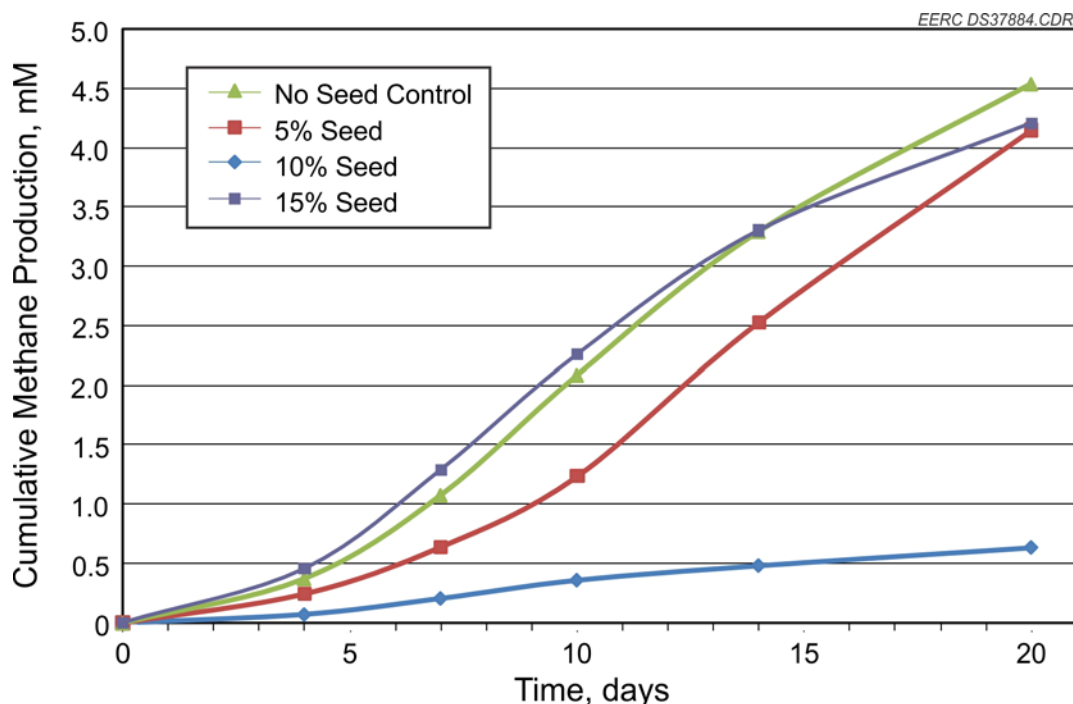


Figure 1. Effects of the inoculate (seed) size on methane production in serum bottles fed Riverside Dairy manure.

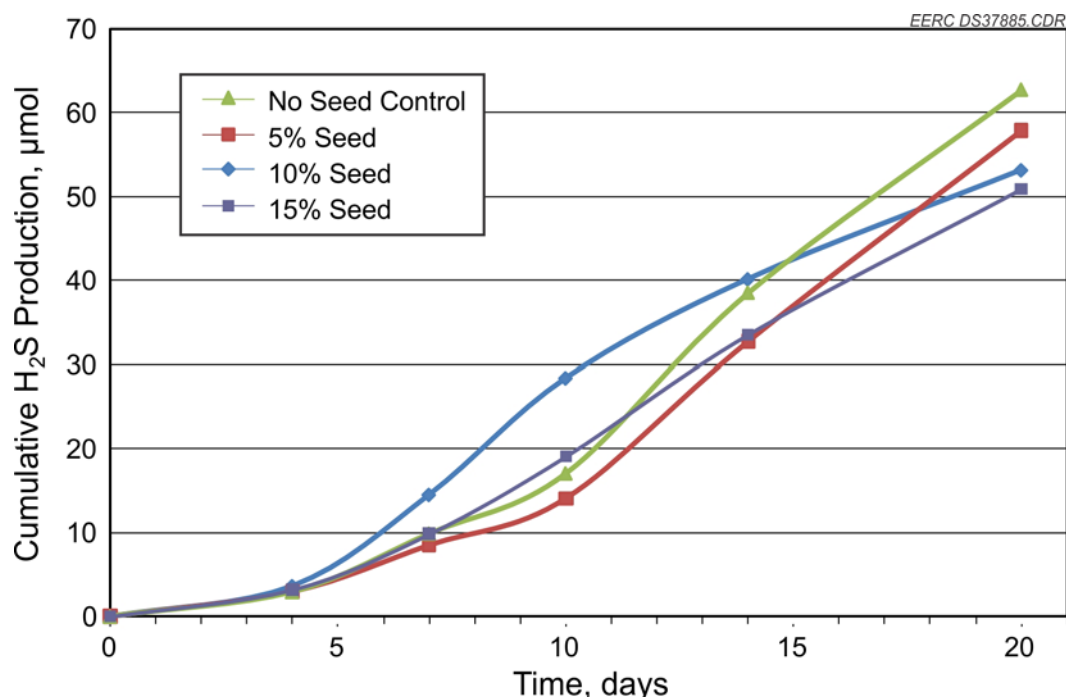


Figure 2. Effects of the inoculate (seed) size on formation of hydrogen sulfide in serum bottles fed Riverside Dairy manure.

Based on these results, operation of the bench-scale digesters was switched to a 10-day hydraulic retention time (HRT) with a 10% recycle rate.

Effects of H₂S Scavenger Addition on Production of Methane and Hydrogen Sulfide

Additional serum bottle experiments were conducted to further investigate the use of a sulfide scavenger to be added in conjunction with the EERC additive. The scavenger is designed to capture any sulfide that is produced and keep it from being emitted as H₂S. The design of this experiment is given in Table 2. The experiment included the use of seed culture at 10% additive at 0.5 units and scavenger at 0, 1, 2, and 4 units of concentration. The experiments were run for 20 days to determine if the scavenger might prevent the increased H₂S production rate observed after 10 days in the previous experiment. If it did, it might allow the use of longer residence times in the digester without the apparent sulfidogenic microorganism regrowth. The longer residence time would allow for greater volatile solids (VS) destruction and more methane production.

Results of the scavenger experiments are plotted in Figures 3 and 4. From Figure 3, it is apparent that addition of the scavenger had a very substantial effect on methane production. While the addition of the additive increased the 20-day methane production from 1.37 mmol for the control to 3.95 mmol, the addition of scavenger further increased this to 9.05, 11.1, and 10.7 mmol for the 1, 2, and 4 units of scavenger added, respectively. This increase in methane

Table 2. Experimental Design for Use of Scavenger in Control of H₂S Production

Condition	Fresh Manure, g	Seed, g	Additive, units of concentration	Scavenger, units of concentration
Seeded Control	36	4	0	0
Seed + Additive	36	4	0.5	0
Seed + Additive + 1 Unit of Scavenger	36	4	0.5	1
Seed + Additive + 2 Units of Scavenger	36	4	0.5	2
Seed + Additive + 4 Units of Scavenger	36	4	0.5	4

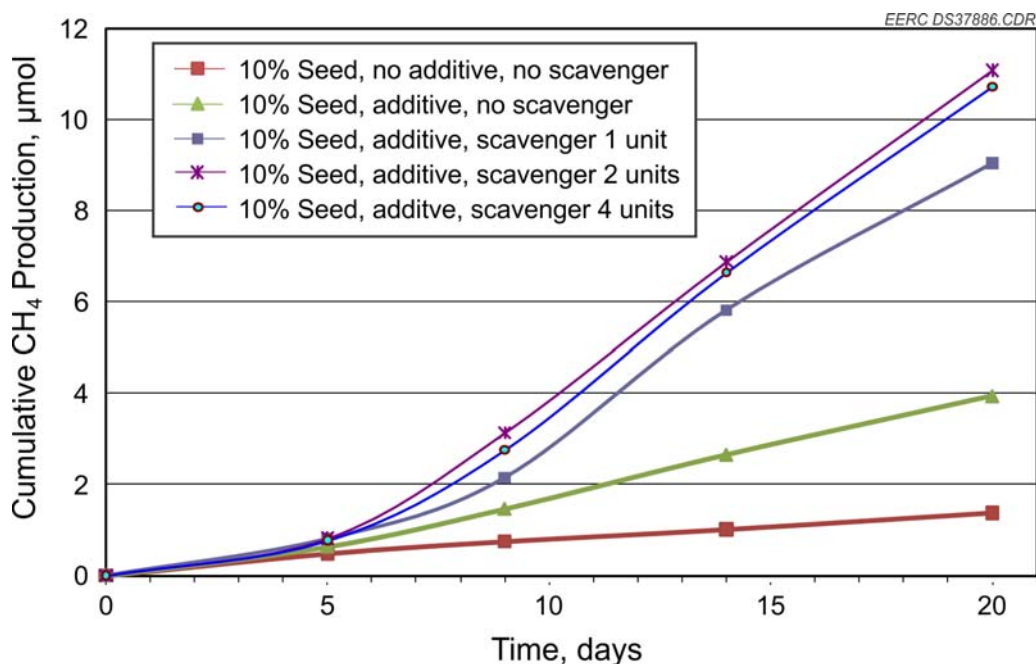


Figure 3. Effect of additive and scavenger addition on cumulative methane production in serum bottles fed Riverside Dairy manure.

production as a result of scavenger addition was not expected. It is surmised that it may be because of changes in nutrient availability. A serum bottle study designed to investigate this will be performed during the next quarter.

Figure 4 contains the H₂S production data for the scavenger experiment. From the data presented in Figure 4, it is apparent that the additive delayed the production of H₂S, with the rate of production increasing with time of incubation as was seen in the previous serum bottle study. The 9-day cumulative H₂S generation in the additive test was 32% of that seen in the control. At 20 days, the benefit decreased to where the additive test had produced 65% of the H₂S produced in the control. For the condition where the scavenger was added at 1 unit (along with the additive), there was an additional benefit observed at 5 and 9 days of incubation but no

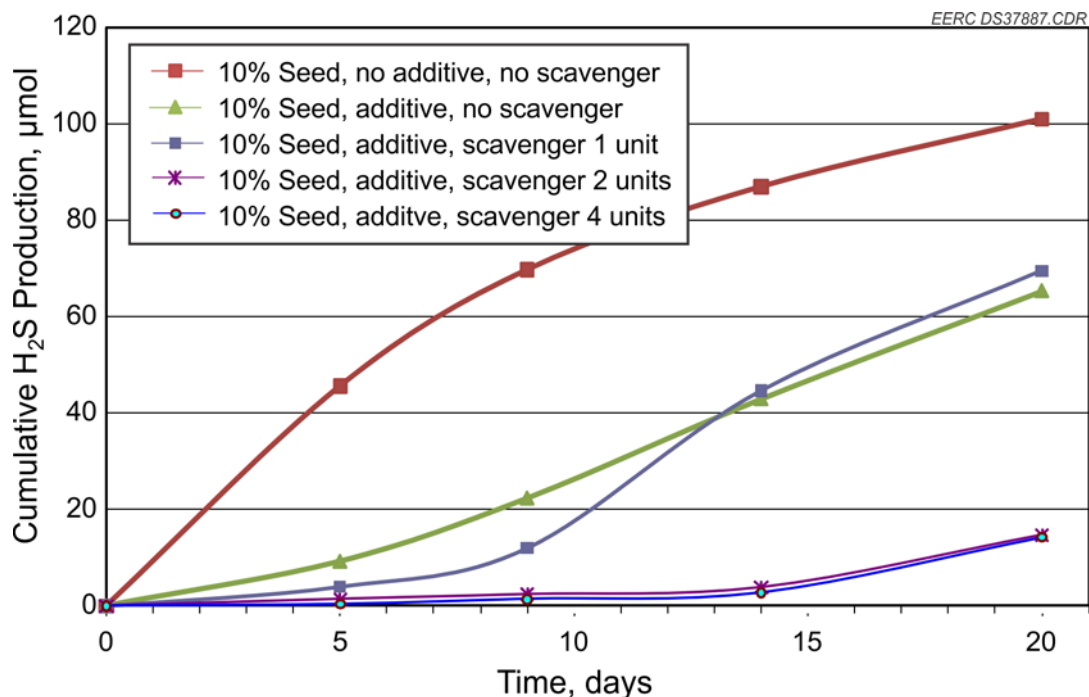


Figure 4. Effect of additive and scavenger addition on cumulative H₂S production in serum bottles fed Riverside Dairy manure.

additional benefit after 14 and 20 days. The 2 and 4 units of concentration of scavenger conditions provided almost complete control of H₂S formation for 14 days, with production of only 2.0% to 3.4% of the H₂S of the no additive control, respectively. At 20 days, the observed H₂S formation was 14% of that observed for the no additive control. These results suggest that the combined use of additive and scavenger should allow for operation of the digester at residence times of at least 14 days with almost no H₂S production and may allow for successful operation at residence times as long as 20 days with very little H₂S production.

During the next reporting period, a serum bottle test will be run with the scavenger alone and in concert with the EERC additive. The scavenger will be incorporated as part of the feed to the bench-scale digester, and the residence time will be increased in order to increase methane production and VS destruction.

Bench-Scale Digester Experiments

Digester Operation and Maintenance

Work conducted this quarter consisted of the continuation of bench-scale experiments including routine operation, maintenance, and data. Because of concerns about leaks and contamination, new control and experimental digesters were constructed. Each digester consists of an 8-inch-diameter by 10-foot-long polyvinylchloride (PVC) pipe with an operating volume of 13 gallons (49 L), a condenser for biogas moisture removal, and a continuous biogas flowmeter. A more

complete description of the bench-scale digesters and their operation has been given in previous quarterly milestone reports.

The changes that were introduced in this reporting period included decreasing the residence time from approximately 20 days to approximately 10 days by increasing the amount of fresh manure added to each digester each day. Previously each digester received 2.5 L of fresh manure mixed with 400 mL of digester effluent. During this reporting period, the feed to the digesters was increased to 5.0 L/d, with 500 mL of effluent from the control reactor added as recycle/inoculum. Early in the reporting period, the digesters had been operated at the 20-day HRT with additive fed to the additive digester, but this led to failure of the additive digester. The digesters were cleaned out and restarted at the 20-day HRT, with both digesters operated without any additive. Feed volumes were then increased gradually to drop the HRT to 10 days. After steady-state operation was achieved at the 10-day HRT with both digesters operated in the identical manner (no additive), the use of additive was initiated. This change was made on Day 40 after restart. As of the end of this reporting period, the additive digester was receiving 0.5 units of concentration of additive in the 10% recycle feed, and the control digester was receiving the same feed without additive. The manure used during this reporting period came from Riverview Dairy, located in Morris, Minnesota.

Testing Results and Discussion

Figures 5 and 6 contain the methane and H₂S gas production flow rates calculated from the average daily gas flow rate and gas composition data collected for both bench-scale plug flow digesters. The data are given for all dates that both gas composition and flow rate data were available for both digesters for the period of operation from the last digester restart date until the end of the reporting period. The data in Figure 5 show similar methane production rates for both digesters over the entire period. Variations in the observed methane production rate were associated with alterations in feed (fresh manure is collected at the farm every 14 to 18 days) and wastage (changes in the amount of digested sludge are made occasionally to help control the volume of material in the digesters).

The H₂S data given in Figure 6 show a similar pattern in the amount of H₂S produced in both digesters until after Day 40 when the delivery of additive to the additive digester was initiated. Each day following initiation of additive feed to the reactor showed a decrease in H₂S production from the day before. With the 10-day HRT, it is expected to take at least 10 days to reach the maximum decrease in H₂S production rate – the data shown illustrate only the first 4 days of effect of additive addition. On Day 44, the H₂S production rate in the additive feed digester was 72% of the H₂S production rate in the control digester.

Additional Milestones: None.

Project Status: Although difficulties have been encountered, the project remains on schedule and within budget. Key milestones for the upcoming quarter include the completion of the bench-scale anaerobic digestion experiments, design and fabrication of the pilot-scale digester, and shipment of the digester to the field site.

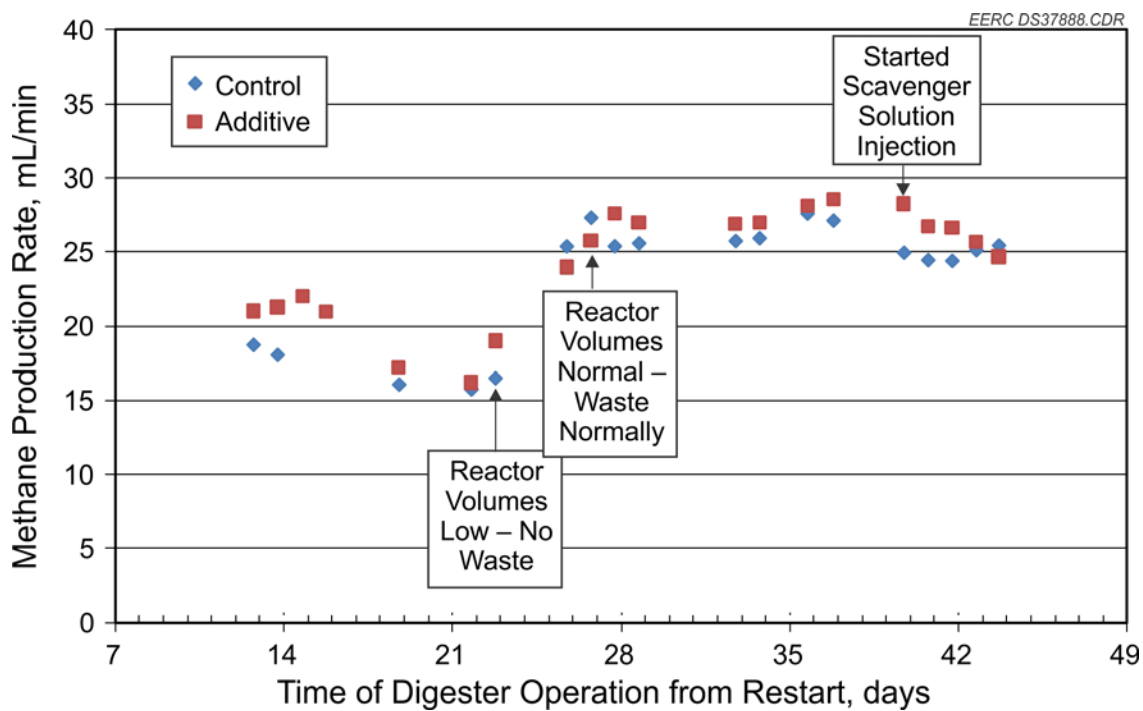


Figure 5. Methane production rate observed in the control and additive test digester.

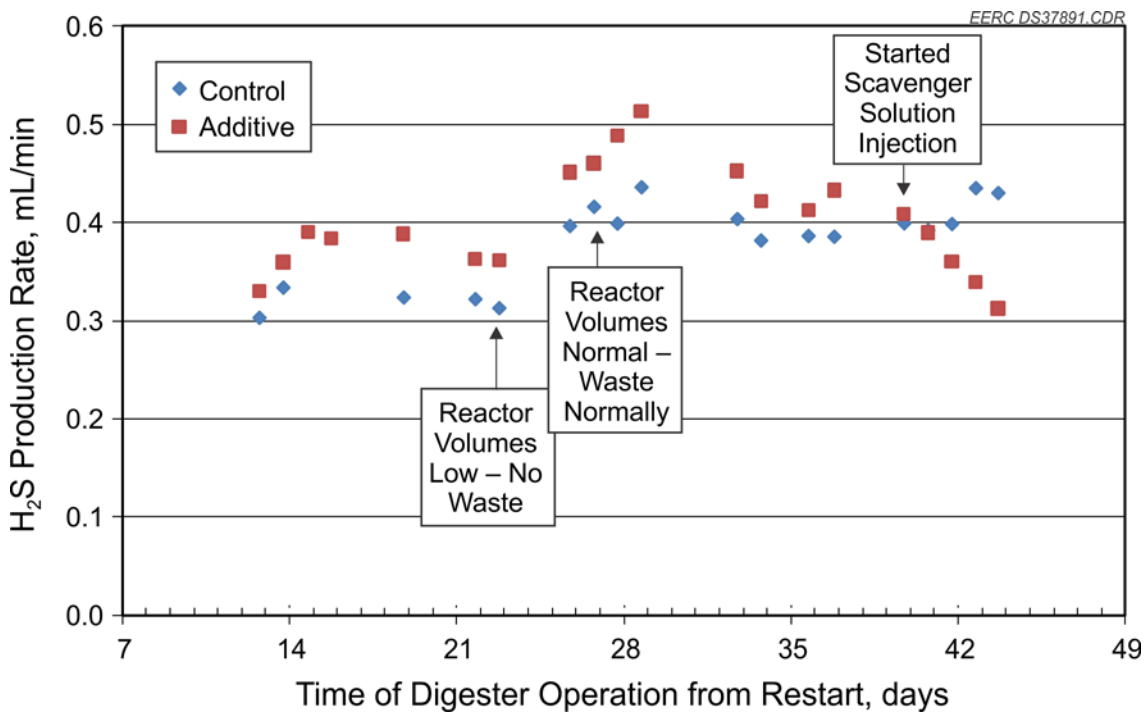


Figure 6. H₂S production rate observed in the control and additive test digester.

It is anticipated that final analysis of the bench-scale data and completion of the interim report detailing the bench-scale testing procedures and results will slip into the first month (July 2010) of the following quarter.

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