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Production of Volatile Sulfur Compounds during Thermophilic Anaerobic Digestion of Municipal Wastewater Sludge

Paper # 1037

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ABSTRACT

This study compares the effect of a rapid (from 54 to 58^{0}C in two weeks) and a slow increase of the thermophilic digester temperature (from 54 to 57^{0}C at a rate of 0.55^{0}C per month) on full-scale thermophilic anaerobic digestion. Rapidly increasing the digester temperature caused elevated production of volatile sulfur compounds, most notably methyl mercaptan, whereas volatile solids destruction and methane production were not significantly affected. The increase of the volatile fatty acid to alkalinity ratio from 0.1 to over 0.3 during the rapid temperature increase indicated a transient biochemical instability, which could be reversed by lowering the temperature. In contrast, the steady-state test showed no effect on digester performance when the temperature was slowly increased to 57.2^{0}C over several months of operation. Production of methyl mercaptan was detected in trace amounts, but only at the highest temperature tested (57.2^{0}C). These tests suggest that the thermophilic digester temperature can be increased to 57^{0}C without an effect on digester performance by allowing sufficient time for microbial populations to adapt to higher temperatures. Further research is warranted to accurately determine the temperature limit for thermophilic anaerobic digestion in full-scale applications.

INTRODUCTION

In full-scale thermophilic anaerobic digestion, thermophilic digester temperatures are usually in the lower end of the thermophilic temperature range (50 to 55 ^{0}C). Anaerobic digestion above 60 ^{0}C has only been investigated in lab-scale studies, focusing on process performance[1,2], pathogen removal[3] and microbial population dynamics.[4] Based on common practice criteria, it is usually recommended to keep the temperature below 60 ^{0}C[5], although experiences on a full scale are very limited.

The City of Los Angeles Bureau of Sanitation has conducted series of full-scale tests at the Hyperion Treatment Plant (HTP) for evaluation of EQ biosolids production by thermophilic anaerobic digestion.[6,7,8,9,10,11,12] A two-stage continuous-batch process has been implemented to comply with the Class A pathogen reduction requirements of U.S. EPA 40 CFR Part 503.[13] In October 2002, the thermophilic digesters were temporarily operated with the temperature rapidly being increased from 54 to 58 ^{0}C to evaluate the compliance with the time-temperature relationship for batch disinfection as specified in Alternative 1 of 40 CFR 503.32 (T≥56.3 ^{0}C at

16 hours holding). This rapid increase of the temperature coincided with an increase of odor complaints from neighboring communities and it was postulated that the increase of odor emissions could have been caused by a change in the digester biochemistry.[14] A similar observation was made at the City of Los Angeles Terminal Island Treatment Plant, where rapidly increasing the thermophilic digester temperature to 65^0C caused elevated production of volatile fatty acids (VFA) and volatile sulfur compounds (VSC) as well as reductions in volatile solids destruction and methane production.[14]

The aforementioned observations could have been a transient response to a changing environment in the digesters of that of a rapidly increasing temperature. Alternatively, these observations may also have been an intrinsic effect of the temperature being raised beyond the maximum temperature for thermophilic anaerobic digestion of wastewater sludge. In order to better understand the effect of the digester temperature, this contribution compares the performance of HTP's digesters during rapidly increasing the temperature (transient test) with the performance of a dedicated digester for which the temperature was slowly increased from 54 to 57^0C over several months of operation (steady-state test). Apart from the digester temperature, digester operation parameters were similar in both tests, which allowed for a direct comparison of VSC production, biochemical stability (VFA to alkalinity ratio) and digestion parameters (volatile solids destruction, methane production). Disinfection results are not presented herein as HTP has consistently met the Class A pathogen reduction requirements after complete conversion of the plant to thermophilic operation in October 2002.[8,11,15,16]

MATERIALS AND METHODS

Plant Description and Experimental Setup

Hyperion Treatment Plant

HTP is located in Playa del Rey, California. It has three batteries with 6 (batteries D1 and D2) or 8 (battery E) egg-shaped digesters (Figure 1a). Each digester has a volume of 9,500 m^3. The plant's feed to the digesters consisted of a mixture of primary sludge and TWAS at average rates of 11,300 and 3,000 m^3/day, respectively. The digesters were operated in a two-stage process. The first stage contained 16 digesters operated in a continuous mode at an average HRT of 11 to 12 days. The second stage contained 4 digesters operated in a batch mode with 32-hour cycles of sludge feeding, holding and withdrawal (Figure 1b). The holding time was 16 hours and each batch digester was fed/withdrawn up to approximately 60- 70% of its total volume during one cycle.

Digester temperatures

The transient test with rapidly increasing and decreasing digesters temperatures was conducted on plant-scale and involved all first- and second-stage digesters. Since most of the digestion process occurred in the first-stage digesters (HRT of about 10 days) rather than the second stage (holding time of 16 hours), digester performance was related to the temperature in the first-stage.

Figure 1a. Schematic of two-stage continuous-batch thermophilic anaerobic digestion.

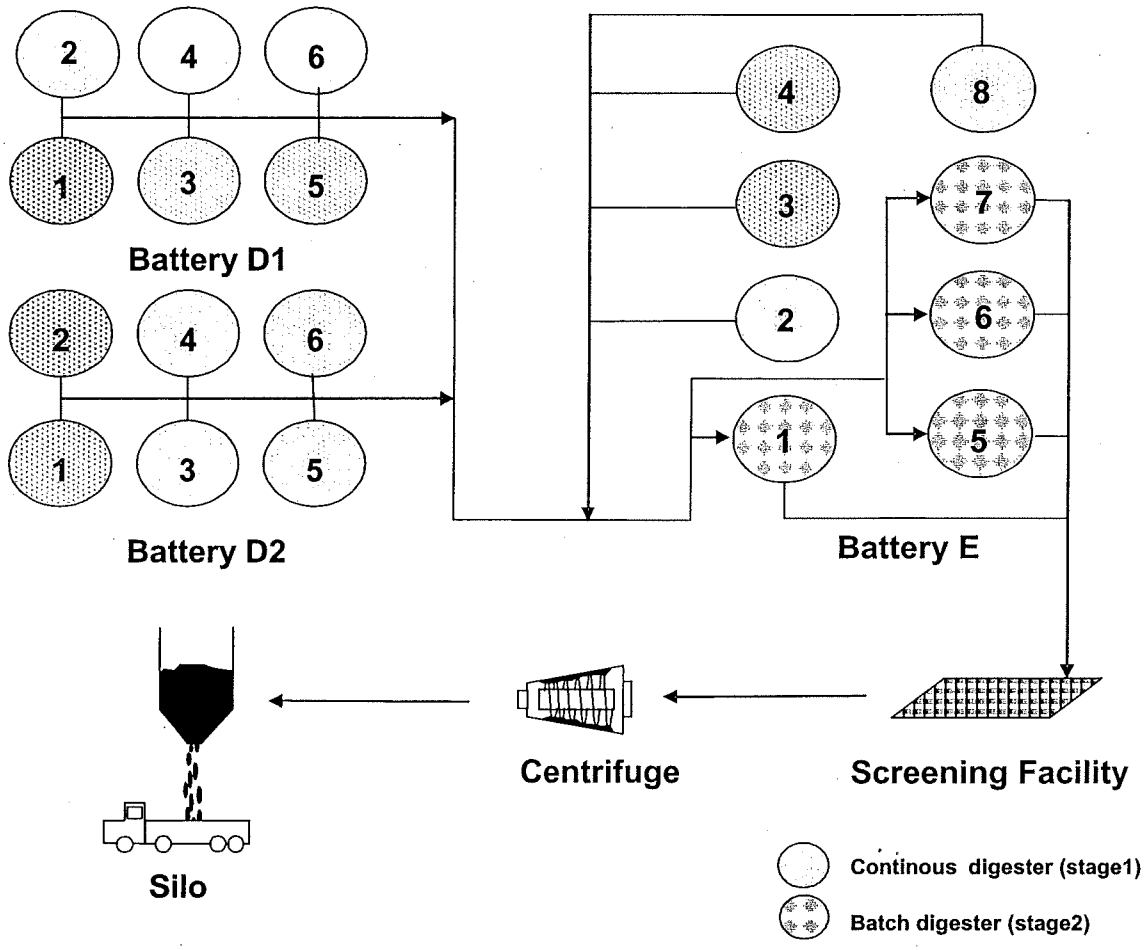


Figure 1b. Digester cycles for batch operation.

Digester	Sequence #1	Sequence #2	Sequence #3	Sequence #4
Hours	0 8	16	24	32
1E	F	H	H	W
5E	W	F	H	H
6E	H	W	F	H
7E	H	H	W	F

F = feed, H = hold, W = withdraw

Second-stage digester temperatures were 1-2^{0}C lower than first –stage digester temperatures. Figure 2a shows that in the last week of September 2002, the average temperature of the first-stage digesters was rapidly increased from 54.4 ^{0}C to around 58 ^{0}C and held constant for a period of three weeks in October 2002. In November 2002, the average first-stage digester temperature was reduced to about 53 ^{0}C.

Digester 1D1 in battery 1 was selected for the steady-state test while the temperature of the other digesters was kept constant at around 53-54^{0}C. The temperature of digester 1D1 was increased in steps of 0.55^{0}C per month from 53.9^{0}C in February 2003 to 57.2^{0}C in September 2003, as shown in Figure 2b.

Sampling

For the transient test, samples were taken from the combined digester outflow of the first stage and analyzed for VFA, total alkalinity, total solids and volatile solids destruction (TSD and VSD, respectively). Digester gas samples were collected from the combined outflow of the first and second stage and analyzed for methane, carbon dioxide and VSC. For the steady-state test, biosolids and digester gas samples were taken from sampling ports dedicated to digester 1D1. Sampling frequencies are shown in Table 1.

Analytical procedures

Analyses were conducted by the Environmental Monitoring Division at HTP according to the procedures summarized in Table 1.

Figure 2a. Transient – First-stage digesters average temperature.

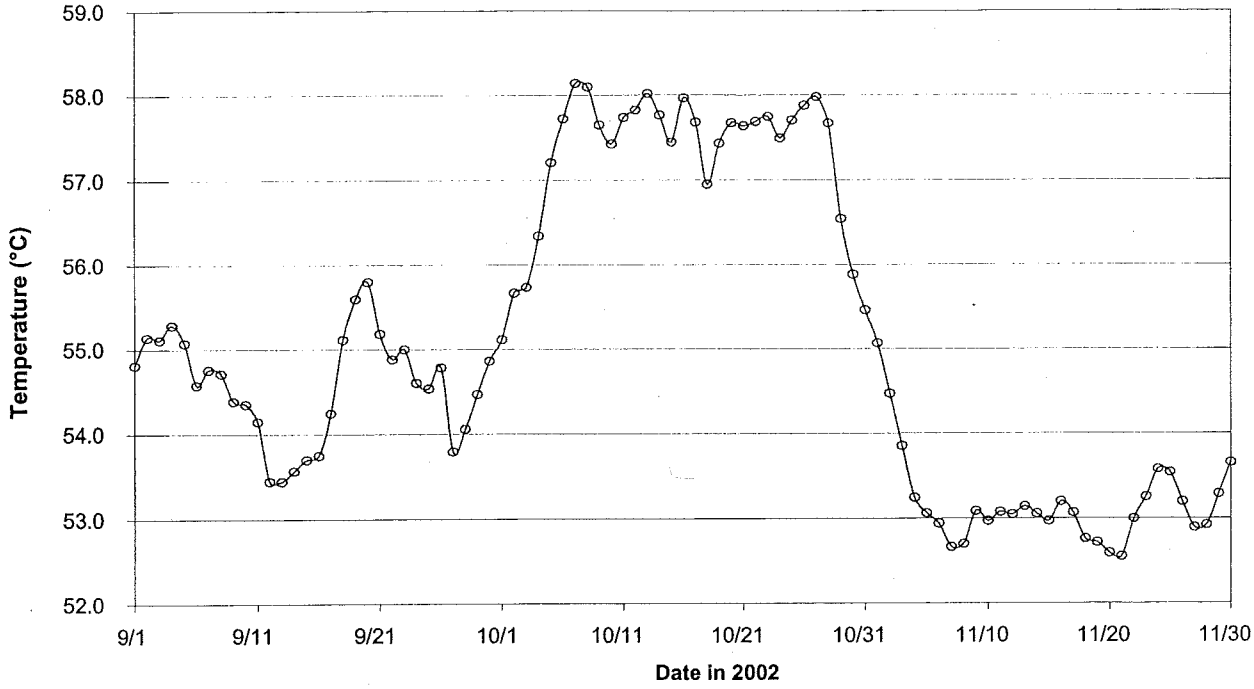


Figure 2b. Steady state – Digester 1D1 temperatures.

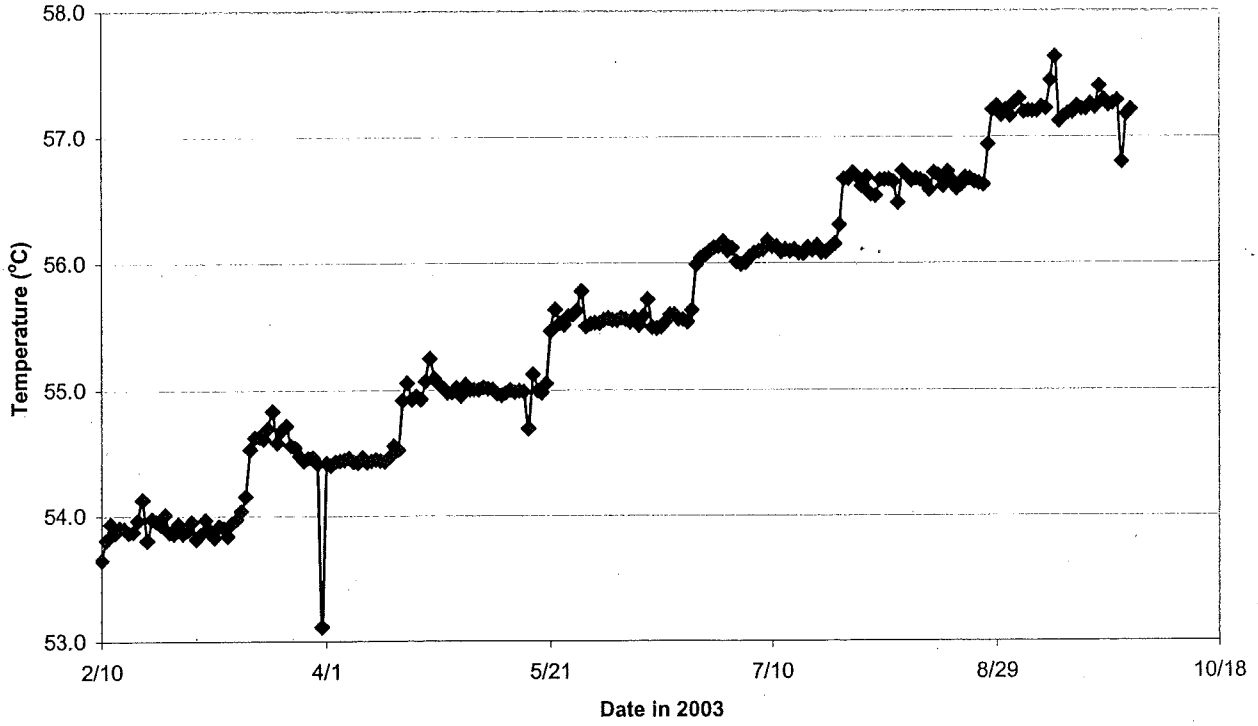


Table 1. Laboratory procedures.

Parameter	Method	Sampling frequency	
		Transient test	Steady-state test
CH_4	EPA Method 18[17]	Daily	Twice weekly
CO_2	EPA Method 18[17]	Daily	Twice weekly
Total alkalinity	Titration, SM 2320 B[18]	Twice weekly	Daily to twice weekly
Volatile fatty acids	Distillation and titration, SM 5560 C[18]	Twice weekly	Daily to twice weekly
Total solids	Gravimetric, 1003-105 C, SM 2540 B[18]	Daily	Daily to twice weekly
Volatile solids	Gravimetric, 550 C, SM 2540 E[18]	Daily	Daily to twice weekly
pH	Electrometric, SM 4500-H^+ B[18]	Twice weekly	Daily to twice weekly
$CH_3SH/(CH_3)_2S$	SCAQMD Method 307-91[18]	Daily	Daily
H_2S	Colorimetric tube or SCAQMD Method 307-91[19]	Daily	Daily

RESULTS

Transient Test with Rapid Temperature Increase

Operation summary

First-stage continuous digesters were biochemically stable and did not produce excessive odors at an average temperature of approximately 54 ^{0}C during August and the first part of September 2002. Odor complaints from residential areas close to HTP rose in frequency, however, when increasing the temperature to 58 ^{0}C in a two-week period from September to October 2002. Subsequently, the number of odor complaints sharply dropped when the digester temperatures were lowered in November 2002. Table 2 shows that first-stage digester operation was constant and monthly averages of first-stage digester operation parameters were very similar in October and November 2002. Hence, changes in digester performance could be attributed to changes in the digester temperature.

Table 2. Operation parameters during transient test (16 first-stage digesters; 4 second-stage digesters).

Parameter[a]	October 2002	November 2002
PS feed rate (m^3/d)	10166 ± 1365	9361 ± 805
TS in PS (%)	3.4 ± 0.3	3.7 ± 0.3
VS in PS (% of TS)	78.5 ± 1.3	78.9 ± 1.0
TWAS feed rate (m^3/d)	3049 ± 396	2993 ± 459
TS in TWAS (%)	5.7 ± 0.56	5.6 ± 1.0
VS in TWAS (% of TS)	83.1 ± 1.0	82.9 ± 0.5
First-stage HRT (d)	11.3 ± 1.2	12 ± 0.6
Second-stage holding time (h)	16	16

[a] Average ± standard deviation. Abbreviations: PS; primary sludge; TWAS: thickened waste activated sludge; TS: total solids; VS: volatile solids; HRT: hydraulic retention time.

Production of VSCs

A large increase of the methyl mercaptan concentration (up to 375 ppm_v) and an increase of the dimethyl sulfide concentration (up to 40 ppm_v) were observed in the digester gas when the digester temperature was increased to 58 ^{0}C (Figure 3). Both concentrations sharply dropped when the temperature of the digesters was reduced to approximately 53 ^{0}C. The hydrogen sulfide concentration in the digester gas was relatively constant in the range of 100 – 200 ppm_v. Production of carbonyl sulfide, ethyl mercaptan, 2-propyl mercaptan or 1-propyl mercaptan was not observed.

Biochemical stability

A close correlation but with a delayed response of about one week was observed between the average VFA concentration in first-stage digester biosolids and the digester temperature (Figure 4). When the temperature was rapidly increased to 58 ^{0}C, the VFA concentration rose from approximately 400 mg/l to over 1,000 mg/l (as acetic acid). When the digester temperature was lowered, the VFA concentration declined as well. The total alkalinity ranged from 3,000 mg/l to 3,700 mg/l (as $CaCO_3$) and was not significantly influenced by the digester temperature. Hence, the trend of the VFA to total alkalinity ratio versus the digester temperature, shown in Figure 5, was very similar to that of the VFA concentration versus the digester temperature. The VFA to total alkalinity ratio increased to a maximum of about 0.33 at 58 ^{0}C.

Digestion parameters

Methane and carbon dioxide concentrations in the digester gas (Figure 6) and VSD (Figure 7) remained about the same during the transient test. Although the pH increased from approximately 7.2 to 7.7, there was no apparent correlation with the digester temperature, neither was there an effect on the NH_3 concentration in the biosolids. Overall, these results indicated that the rapid increase and decrease of the digester temperature in the range of 54 and 58^{0}C did not have a marked effect on digestion parameters.

Steady-state Test with Slow Temperature Increase

Operation summary

Table 3 demonstrates that the composition and feed rates of primary sludge and thickened waste activated sludge to digester 1D1 were constant. The average HRT in digester 1D1 was 11.3 days with very little variation over 8 months of testing.

Production of VSC

The concentration of H_2S in digester gas appeared to slightly increase with the digester temperature (Figure 8), but the concentrations during this test were in general in the same range as earlier observed during the transient test. However, when the digester temperature was slowly increased, the digester gas did not contain methyl mercaptan and dimethyl sulfide (Figure 8).

Figure 3. Transient – Volatile sulfur compounds in digester gas.

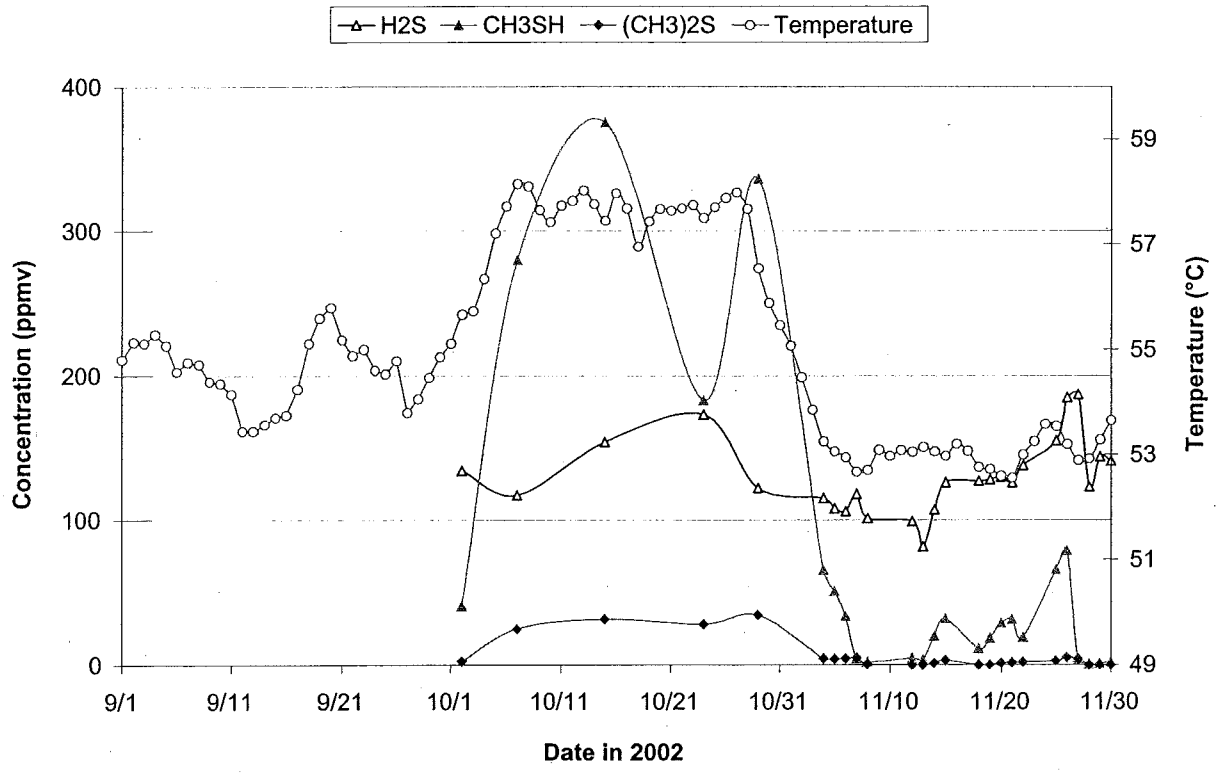


Figure 4. Transient – VFA in first-stage digester biosolids.

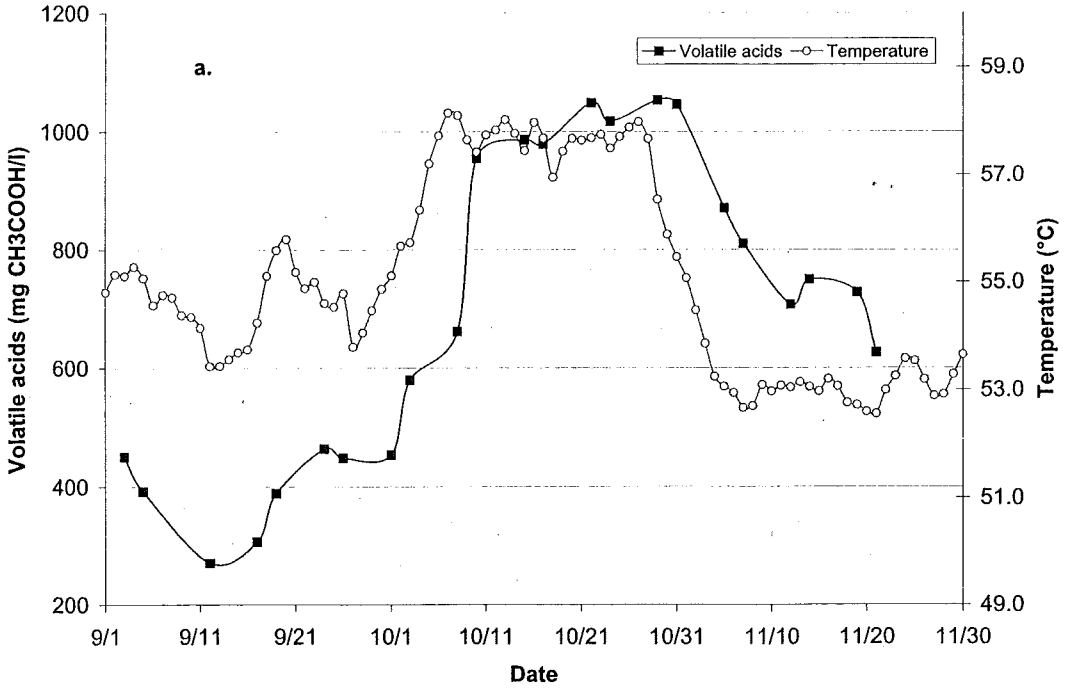


Figure 5. Transient – VFA to total alkalinity in first-stage digester biosolids.

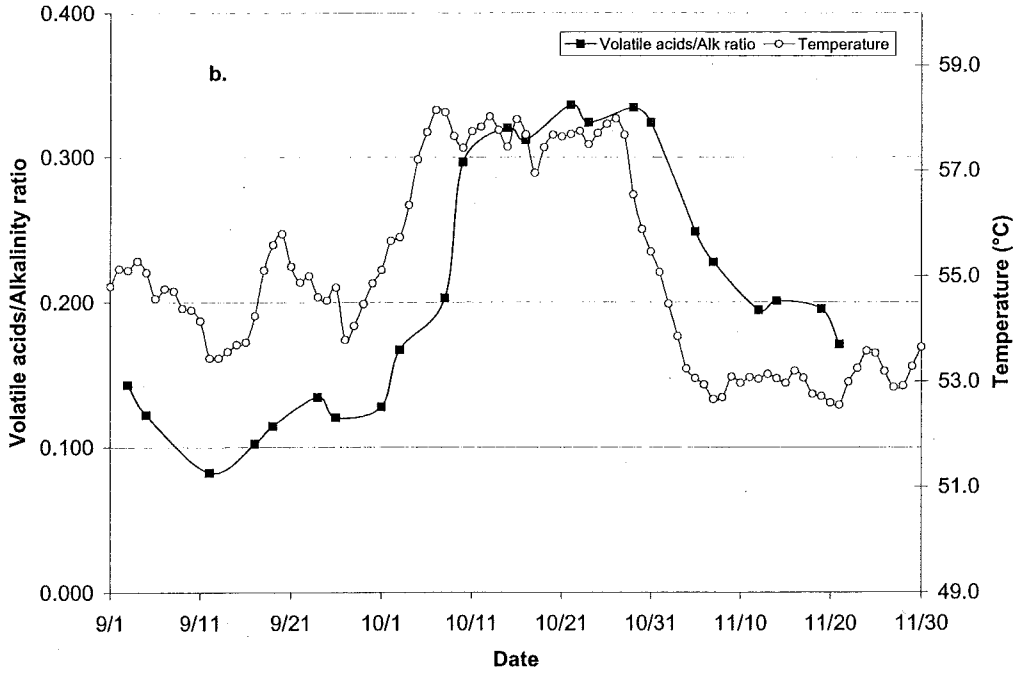


Figure 6. Transient – Composition of digester gas.

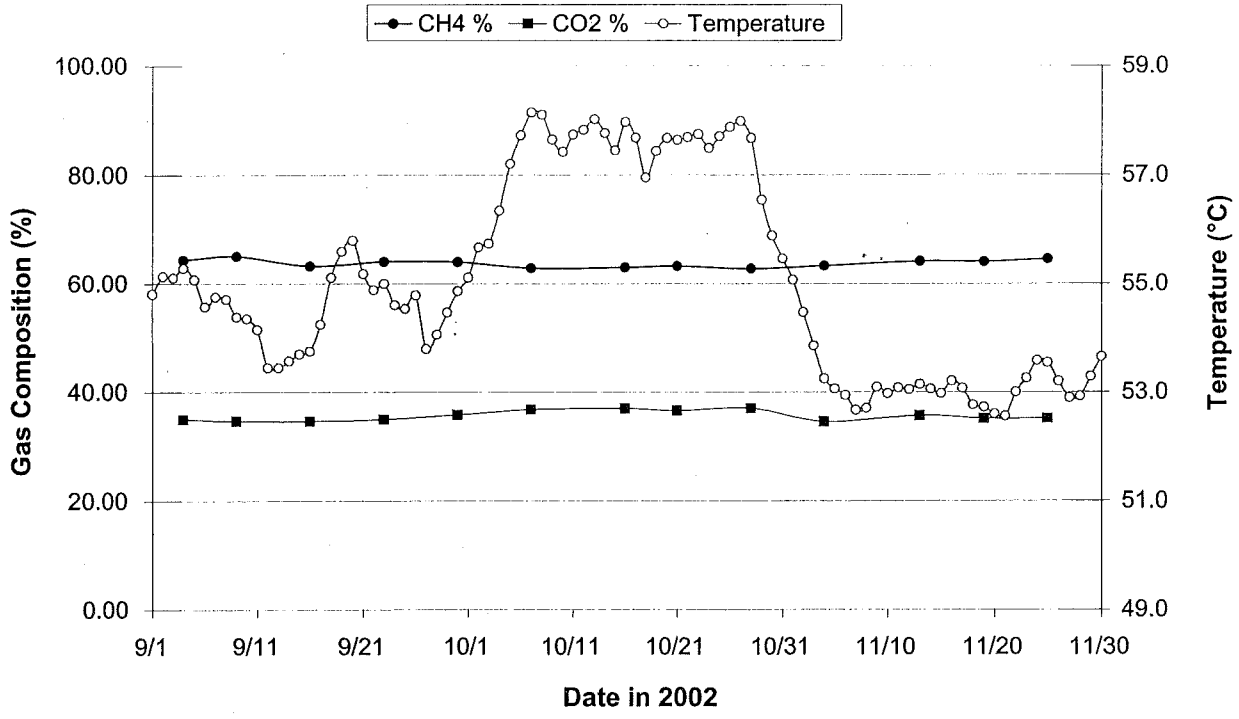


Figure 7. Transient - Volatile solids destruction versus digester temperature.

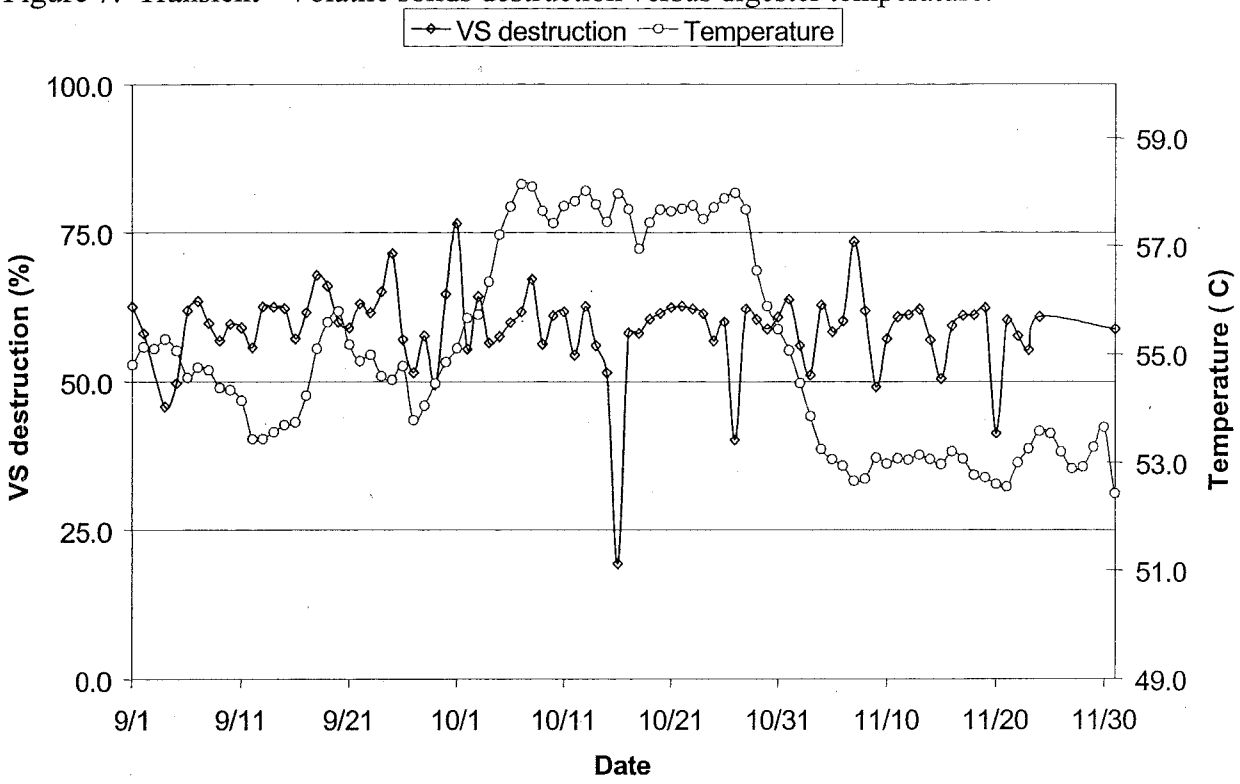


Figure 8. Steady-state – Volatile sulfur compounds in digester gas of digester 1D1.

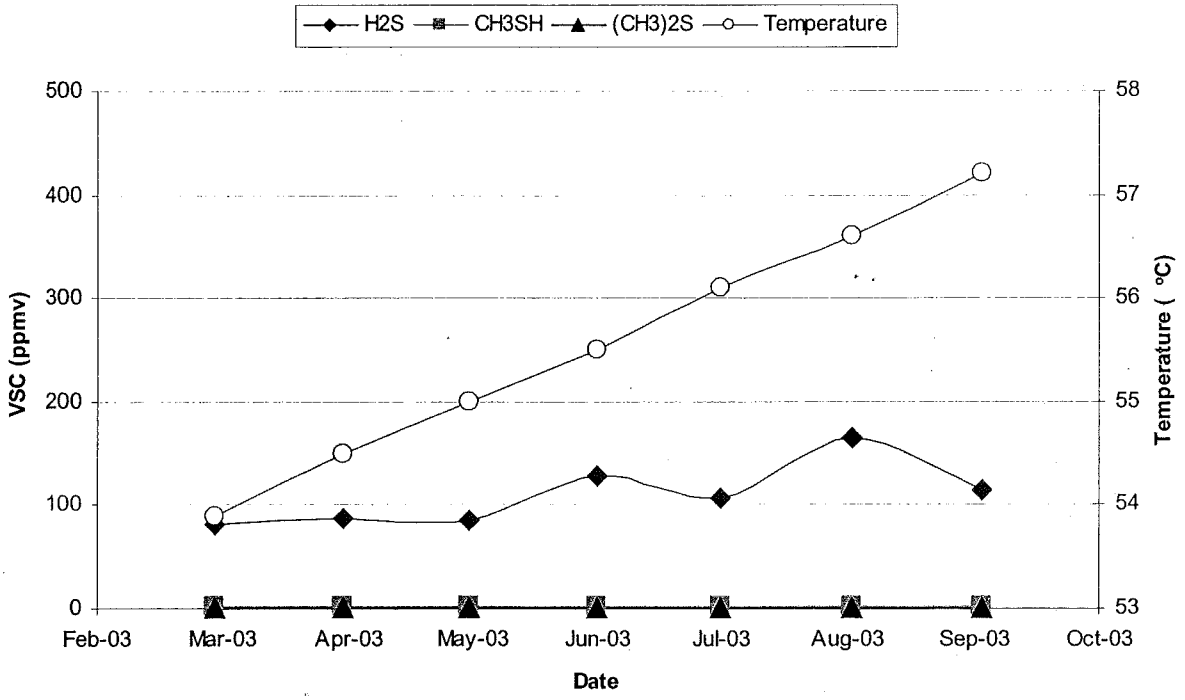


Table 3. Operation parameters during steady-state test (Digester 1D1).

Parameter[a]	**Temperature**						
	53.9 ± 0.09	54.5 ± 0.27	55 ± 0.12	55.5 ± 0.11	56.1 ± 0.09	56.6 ± 0.08	57.2 ± 0.13
PS feed rate (m^3/d)	657 ± 4	661 ± 11	661 ± 13	653 ± 42	662 ± 14	659 ± 15	643 ± 76
TS in PS (%)	4.0 ± 0.5	3.8 ± 0.3	4.1 ± 0.6	3.9 ± 0.3	3.8 ± 0.2	3.3 ± 0.34	3.1 ± 0.3
VS in PS (% of TS)	78.5 ± 2.6	78.7 ± 2.7	79.1 ± 1.1	79.8 ± 1.3	79.4 ± 0.69	78.6 ± 1.1	78.2 ± 1.0
TWAS feed rate (m^3/d)	159 ± 12	167 ± 9	169 ± 14	169 ± 9	170 ± 11	167 ± 17	171 ± 9
TS in TWAS (%)	5.6 ± 0.7	6.0 ± 0.7	6.3 ± 1.0	6.6 ± 0.8	6.0 ± 0.6	6.2 ± 0.6	5.6 ± 0.7
VS in TWAS (% of TS)	82.8 ± 1.6	82.8 ± 2.7	83.3 ± 1.5	84.0 ± 1.1	83.4 ± 0.9	82.4 ± 0.5	81.5 ± 1.0
First-stage HRT (d)	11.4 ± 0.2	11.2 ± 0.3	11.2 ± 0.3	11.4 ± 0.9	11.1 ± 0.22	11.2 ± 0.3	11.6 ± 1.7
Period (in 2004)	2/10 – 3/14	3/15 - 4/16	4/17 – 5/19	5/20 – 6/21	6/22- 7/24	7/25 – 8/26	8/27 – 9/28

[a] Average ± standard deviation. Abbreviations as in Table 2.

Trace amounts of methyl mercaptan ($\leq$2.5 ppm_v) were only observed at a digester temperature of 57.2^{0}C. This was the reason to limit the steady-state test to a maximum temperature of 57.2^{0}C.

Biochemical stability

The average VFA concentration in the biosolids of digester 1D1 was between 246 and 368 mg/L (as acetic acid) without a clear correlation with the temperature (Figure 9). VFA concentrations were well below the levels that were observed during the transient test. The alkalinity remained relatively constant in the range of 3750 to 4170 mg/L (as $CaCO_3$) at all temperatures. The VFA to alkalinity ratio, shown in Figure 10, was always less than 0.089 and never reached the high levels of the transient test.

Digestion parameters

The digester gas composition is shown in Figure 11. The methane content was always in the range of 61.8 to 63%, which was the same as during the transient test. The VSD showed a slightly declining trend from 62% at 53.9^{0}C to 58% at 57.2^{0}C (Figure 12).

DISCUSSION

As the hydrogen sulfide concentration remained relatively constant in either test, the increase in odor nuisance during the transient test can be probably be attributed to elevated production of methyl mercaptan. Odor abatement at wastewater treatment plants has traditionally been focused on the capture and removal of hydrogen sulfide,[18] however, the present results emphasize also the importance of methyl mercaptan, which as hydrogen sulfide has an odor threshold in the lower ppb range. Another factor that may have contributed to the increased perception of odor nuisance during the transient test could have been the elevated production of VFA. Although VFA were only analyzed in biosolids, it may be assumed that they partly volatize to air and, depending on their odor thresholds, may have increased the odor intensity.

Whereas the VFA to alkalinity ratio during the steady-state test remained well below 0.1, an increase beyond 0.3 occurred during the transient test. As a rule of thumb, a ratio exceeding a value of 0.3 is an indication of biochemical instability, elevated VFA production and a potential for digester souring and declining performance. Likewise, it may be postulated that the production of methyl mercaptan is a symptom of biochemical instability or microbial imbalance. Recent studies have shown that methanogens are involved in the biodegradation of methylated VSC such as methyl mercaptan. Hence, inhibition of methanogenic activity would result in the accumulation of methyl mercaptan and other methylated VSC. A similarity may exist with the studies of Speece[21] and Yerkes,[22] who have suggested that an elevated VSC production may be a result of toxicity in anaerobic processes. For instance, the concentrations of methyl mercaptan and dimethyl sulfide increased when toxic compounds such as chloroform or tetrachloro ethylene were added to an anaerobic sludge digester.[22] Thus, a rapidly increasing

Figure 9. Steady-state – VFA in digested biosolids of digester 1D1.

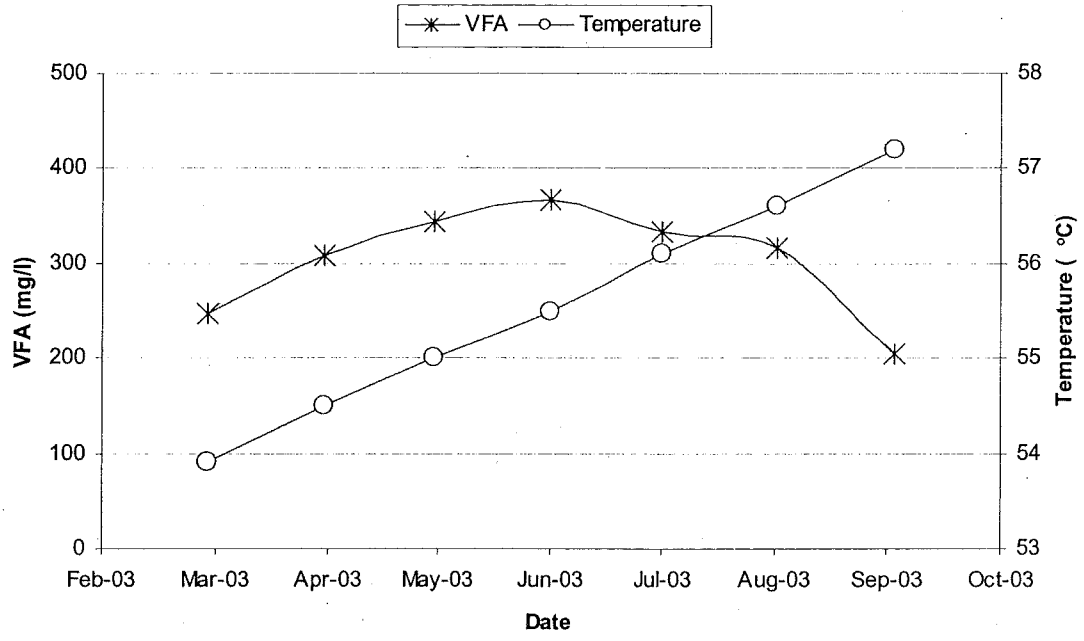


Figure 10. Steady-state – VFA to total alkalinity ratio in digester 1D1.

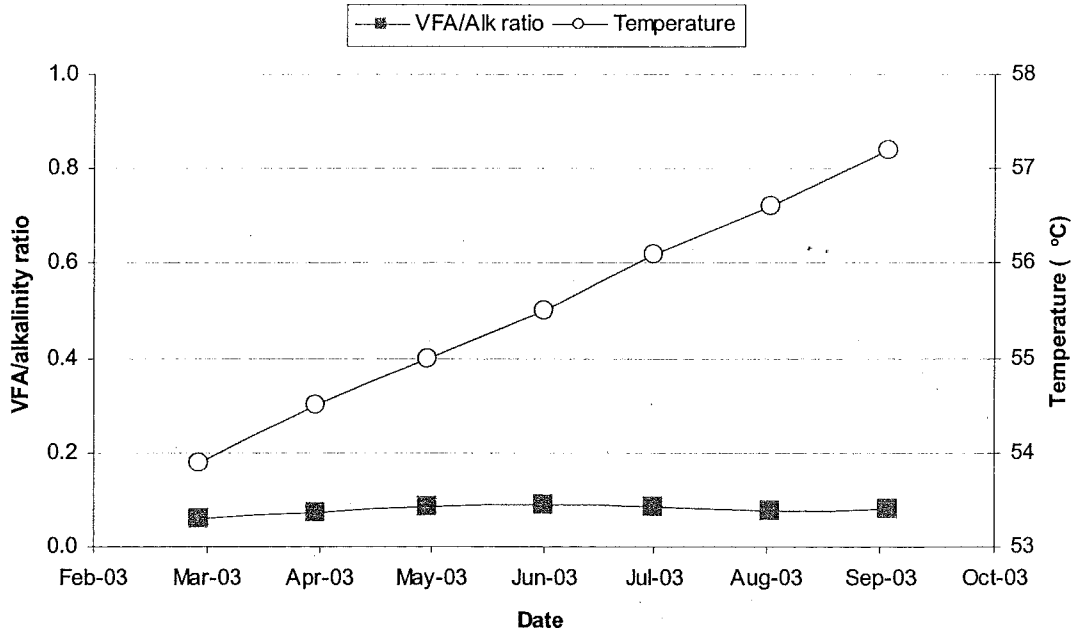


Figure 11. Steady-state – Composition of digester gas of digester 1D1.

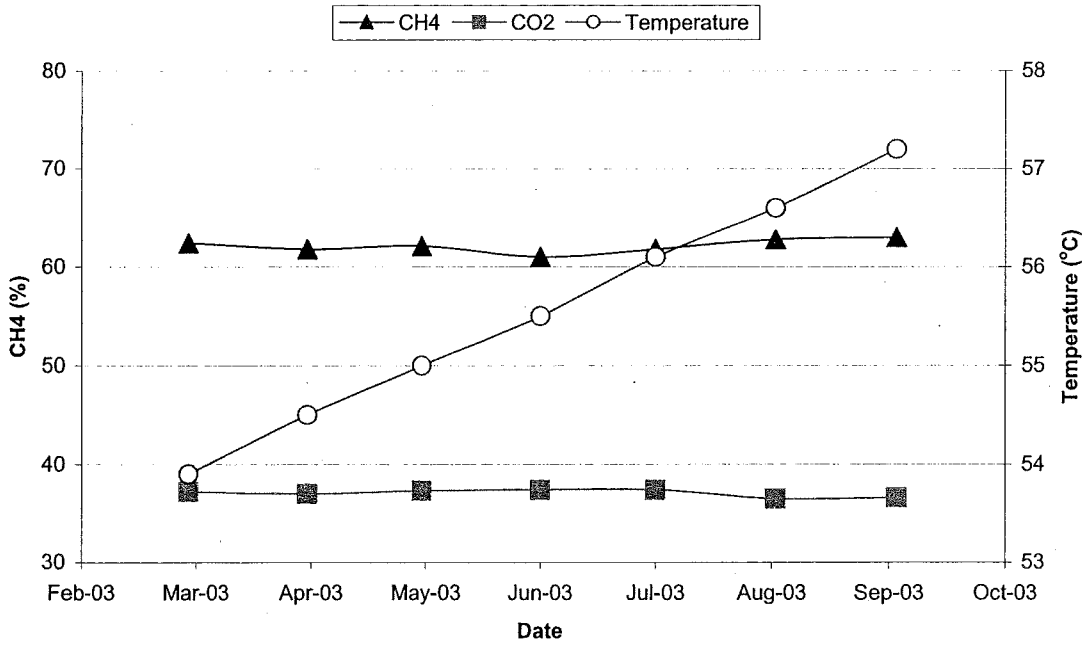
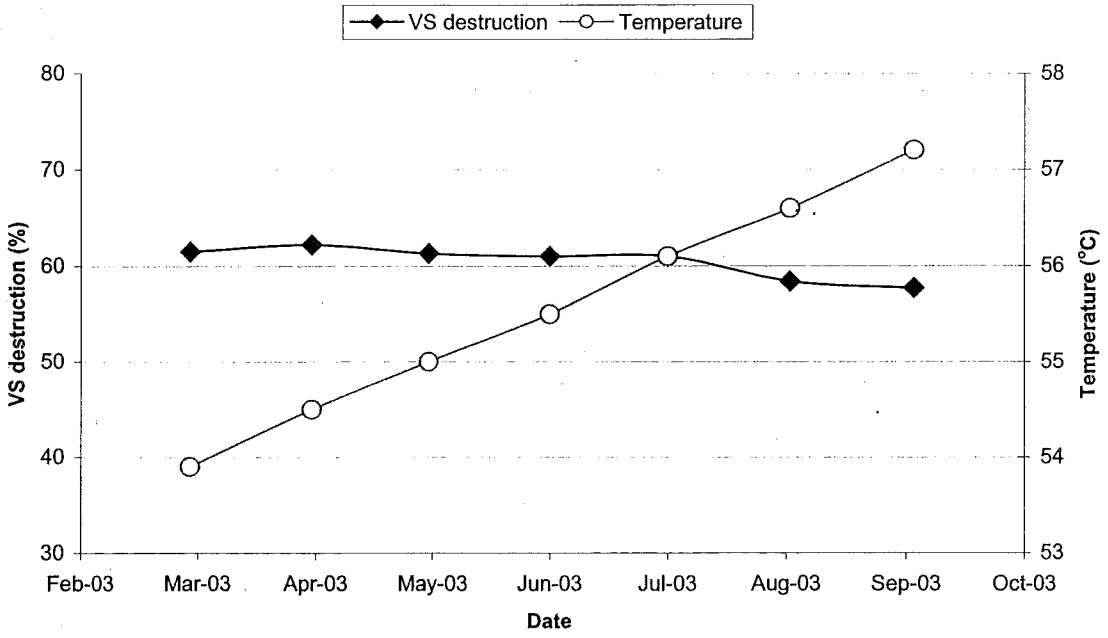


Figure 12. Steady-state – Volatile solids destruction in digester 1D1.



temperature and the presence of toxic compounds may cause the similar effect of methyl mercaptan accumulation, mediated by a microbial imbalance of methanogenic activity being inhibited. Whereas a rapid increase of the digester temperature within the thermophilic range should be avoided, it is interesting to note that a rapid temperature increase is favorable when converting mesophilic digesters to thermophilic operation. This is to establish a microbial population of truly thermophiles instead of thermotolerant species.[23]

Although the increase of the VFA to alkalinity ratio during the transient test indicated that the rapid and short-term increase in temperature caused biochemical instability of the digesters, a significant effect on the methane production and volatile solids destruction was not observed. It could have been that the transient test was too short and the temperature increase too little to cause a significant deterioration of digestion parameters. During another test at Terminal Island Treatment Plant where the temperature was rapidly increased to 65^0C, methane production and solids destruction sharply declined.[14]

Wastewater treatment plants that seek compliance with the time-temperature requirement for batch disinfection in Alternative 1 of 40 CFR 503.32 may need to operate the digesters at a relatively high thermophilic temperature if the batch digester holding capacity is limited. The present results show that the digester temperature can be increased to at least 57^0C without an effect on digester performance, provided that the temperature increase is gradual to allow sufficient time for microbial populations to adapt.[24] Recent laboratory studies on the anaerobic digestion of manures have demonstrated biochemical instability and poor digester performance at temperatures over 60 ^{0}C.[1,3,4] For the thermophilic anaerobic digestion of wastewater sludge, further research with full-scale digesters is warranted to determine whether a similar temperature maximum exists.

REFERENCES

1. Varel, V.H.; Hashimoto, A.G.; Chen, Y.R. *Appl. Environ. Microbiol.* **1980**, *40*, 217.

2. Nozhevnikova, A.N.; Kotsyurbenko, O.R.; Parshina, S.N. *Wat. Sci. Tech.* **1999**, *40 (1)*, 215.

3. Gabb, D.M.D.; Jenkins, D.; Gosh, S.; Hake, J.; De Leon, C.; Williams, D. In *Proceedings of the 14th Annual Residuals and Biosolids Management Conference*, Boston, Massachusetts, Feb 27 – Mar 1, 2000; Water Environment Federation: Alexandria, Virginia [CD-ROM].

4. Ahring, B.K.; Ibrahim, A.A.; Mladenovska, Z. *Wat. Res.* **2001**, *35*, 2446.

5. Van Lier, J.B. *Antonie van Leeuwenhoek* 1996, *69*, 1.

6. Iranpour, R.; Cox, H.H.J.; Oh, S.; Starr, M.A.; Fan, S.; Minamide, T.; Mundine, J.E. In *Proceedings Disinfection 2005*, Mesa, Arizona, Feb 6 – 9, 2005; Water Environment Federation: Alexandria, Virginia.

7. Iranpour, R.; Cox, H.H.J.; Alatriste-Mondragon, F.; Starr, M. In *Proceedings 10th World Congress on Anaerobic Digestion*, Montreal, Canada, Aug 29 – Sep 2, 2004; International Water Association: London, UK; pp 2047-2050.

8. Iranpour, R.; Cox, H.H.J.; Fan, S.; Abkian, V.; Haug, R.T. *Water Sci. Tech.* **2005** (in press).

9. Iranpour, R.; Alatriste-Mondragon, F.; Cox, H.H.J.; Kearney, R.J. *J. Res. Sci. Technol.* 2004, *1 (4)*, 253.

10. Iranpour, R.; Cox, H.H.J.; Kearney, R.J.; Clark, J.H.; Pincince, A.B.; Daigger, G.T. *J. Res. Sci. Technol.* 2004, *1 (4)*, 209.

11. Iranpour, R.; Cox, H.H.J.; Kearney, R.J.; Haug, R.T. *Water Environ. Res.* **2005** (accepted).

12. Iranpour, R.; Cox, H.H.J.; Oh, S.; Fan, S.; Kearney, R.J.; Mundine, J.E.; Haug, R.T. *Water Environ. Res.* **2005** (in press).

13. U.S. EPA *Federal Register* **1993**, *58*, 9248.

14. Iranpour, R.; Alatriste-Mondragon, F.; Cox, H.H.J.; Hernandez, G.; Haug, R.T.; Kearney, R.T. In *Proceedings WEF/WEAU Residuals and Biosolids Management Conference & Exhibition 2004*, Salt Lake City, Utah, Feb 22 – 25, 2004; Water Environment Federation: Alexandria, Virginia [CD-ROM].

15. Haug, R.T.; Hartnett, W.J.; Ohanian, E.B.; Hernandez, G.L.; Abkian, V.S.; Mundine, J.E. In *Proceedings of the 16th Annual Residuals and Biosolids Management Conference*, Austin, Texas, Mar 3 – 6, 2002; Water Environment Federation: Alexandria, Virginia [CD-ROM].

16. Wilson, T.E.; Iranpour, R.; Windau, T.D. In *Proceedings 9th European Biosolids and Biowaste Conference*, Wakefield, UK, Nov 14 – 17, 2004 [CD-ROM].

17. *Method 18. Standard Operating Procedure for Analysis of Fixed Gases in Air and Gaseous Samples by Gas Chromatography* (SOP-AIR-010-4), U.S. Environmental protection Agency, 1992.

18. *Standard Methods for the Examination of Water and Wastewater,* 18th edition, American Public Health Association; American Water Works Association; Water Environment Federation: Washington, D.C, 1992.

19. *Laboratory Methods of Analysis for Enforcement Samples*, Revised June 26, 1998, South Coast Air Quality Management District, 1998.

20. Water Environment Research Foundation, *Identifying and Controlling Municipal Wastewater Odor Phase 1: Literature Search and Review*, Project 00-HHE-5A, 2003.

21. *Anaerobic Biotechnology for Industrial Wastewaters*, Speece, Archae Press: Nashville, Tennessee, 1996.

22. Yerkes, D.W.; Zitomer, D.H.; Owens, D.; Speece, R.E. In *Proceedings of the 73rd Annual Water Environment Federation Technical and Exposition Conference*, Anaheim, California, Sep 28 – Oct 14, 2002; Water Environment Federation: Alexandria, Virginia [CD-ROM].

23. Shao, Y.J., Kim, H.S., Oh, S., Iranpour, R., Jenkins, D. In *Proceedings Water Environment federation 75th Annual Technical Exhibition and Conference*, Sep 28-Oct 2, 2002 Chicago, Illinois, Sep 28 – Oct 2, 2002; Water Environment Federation: Alexandria, Virginia [CD-ROM].

24. Iranpour, R.; Cox, H.H.J.; Fan, S.; Abkian, V.; Haug, R.T.; Kearney, R.J. *Biotechnol. Bioeng.* **2005** (in press).