Anaerobic Digester Hydrogen Sulfide Removal at the Manatee County, FL Southwest Water Reclamation Facility

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ABSTRACT

The results of a full-scale trial initiated in May 2006 by the Manatee County Southwest Water Reclamation Facility are presented, and the impacts of peroxide regeneration of spent iron salts on the removal of hydrogen sulfide (H_2S) from anaerobic digesters at the SWWRF are examined. Treatment with hydrogen peroxide was initiated in a thickened primary sludge line containing an average 300 Lbs/day Fe (primarily as FeS) and 80 mg/L dissolved sulfide. Prior to treatment, dissolved sulfide levels in the primary digester averaged 20 mg/L and were found to drop to < 0.1 mg/L throughout the course of the trial. The vents of the primary digesters exhausted biogas containing an average 200 ppm H_2S. After treatment, biogas H_2S concentration reduced to 20 ppm on average. Within two sludge ages, similar effects were noted in the secondary digester. Additional positive changes were noted in the volume and quality of biogas produced, and in finished biosolids quality.

KEYWORDS

Anaerobic digestion, odor control, corrosion control, hydrogen sulfide, hydrogen peroxide, iron salts, mercaptan, peroxide regenerated iron.

INTRODUCTION

Manatee County's Southwest Water Reclamation Facility (SWWRF) is a 22 MGD conventional activated sludge plant that has faced H_2S odor issues for some time. The construction of new commercial and residential developments, recently begun to the south and west of the plant, combined with increasing pressure from existing residential neighborhoods to the north and east has further hastened the plant's need for improved hydrogen sulfide odor control. In February of 2006, the SWWRF approached Siemens Water Technologies and US Peroxide seeking cost effective solutions to the various pressing odor issues at the treatment plant.

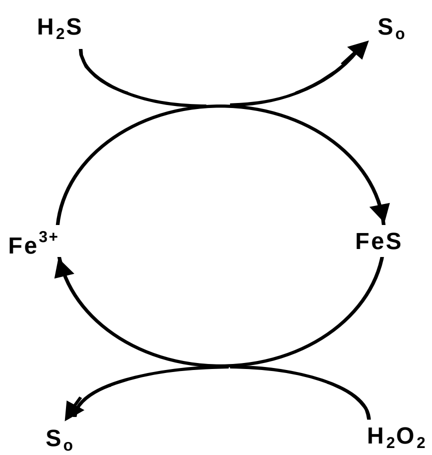
In April 2006, after investigating potential odor sources at the plant, officials at the Manatee SWWRF decided that one of the most pressing issues was the odor of the sludgeworks, specifically the vents of the anaerobic digesters. H_2S concentrations at these vents averaged 200 ppm with peak levels regularly above 400 ppm. Recent work at San Antonio Water Systems (SAWS) (Winters, et al.) had shown H_2O_2 to be effective for controlling sulfide in a DAF unit containing a mixed FeS-laden sludge, while it also had the beneficial side effect of improving methane generation and limiting biogas H_2S accumulation in the anaerobic digesters a considerable distance downstream. Given the positive results at SAWS, and the fact that iron was currently being added in the collection system for odor control, a similar treatment approach of beneficially reusing spent iron was chosen.

Because the Manatee SWWRF had a considerably different sludge handling process than SAWS, it was decided that the key analog between these two odor control projects would be the removal of sulfide by the regeneration of the spent iron salts in the sludge by treatment with hydrogen peroxide (here forward referred to as "peroxide regenerated iron").

Treatment Process Design

Manatee County utilizes approximately 300 pounds per day of iron (via $FeSO_4$) for odor control in the plant's collection system, most of which terminates in the primary sludge as FeS. It was also noted that nearly the entire dissolved sulfide load entering the digesters resided in the primary sludge, with typical values of 60-100 mg/L. Given these observations, it was determined that utilizing peroxide regenerated iron technology on the thickened primary sludge (TPS) line would give the best overall sulfide control in the primary digesters by targeting a location where the loadings of both sulfide and FeS were the greatest. Peroxide regenerated iron technology combines the use of iron salts with hydrogen peroxide in a unique fashion, whereby the iron salt is added as the primary sulfide control agent in the collection system, and hydrogen peroxide is added at specific points downstream to regenerate the spent iron (FeS) (Walton, et al.). The key to the technology is the regeneration step, which oxidizes the sulfide to elemental sulfur and in the process "frees up" the iron making it reusable for subsequent downstream sulfide control (Figure 1), in this case, odor control in the primary digesters. Thus the ability for peroxide regenerated iron to control sulfide is two-fold: iron catalyzed removal of sulfide in the short term, and regeneration of iron for the removal of sulfides that are generated downstream in the process. It is common practice to add iron salts into a digester for H_2S control (and struvite control) so in essence the peroxide regenerated iron technology is a novel enhancement of an existing industry practice (Mamais, et al.).

Figure 1 - Representation of the catalytic regeneration cycle (Walton, et al.)



Inputs: Hydrogen sulfide
Hydrogen peroxide

Catalyst: Ferrous / Ferric iron

Outputs: Elemental sulfur

In the case of thickened primary sludge, it was assumed that the process would become considerably more complex than had been previously observed in domestic wastewater, due to the vastly differentiated organic and biological content of the TPS. It was first assumed that a large portion of the H_2O_2 would be lost to decomposition, and much of the remaining hydrogen peroxide would be utilized for iron catalyzed removal of the abundant sulfides in the sludge. Consequently, regenerating enough iron to establish long term odor control required adding H_2O_2 at a treatment level still greater than the amount required to remove most of the sulfides from the TPS.

Based on the results of a dose-response study of "peak purgeable" H_2S and H_2O_2, shown in Figure 2, and taking into consideration known process parameters (Table 1), a treatment level of 1500 mg/L H_2O_2 was chosen for the trial. With typical flow rates on the TPS line of 10 – 20 gallons/minute, this resulted in an average theoretical usage of 90 gallons/day 50% H_2O_2 (w/w).

Figure 2 - Purgeable H_2S v. Treatment Level. >95% removal of H_2S with treatment of 1000 mg/L H_2O_2.

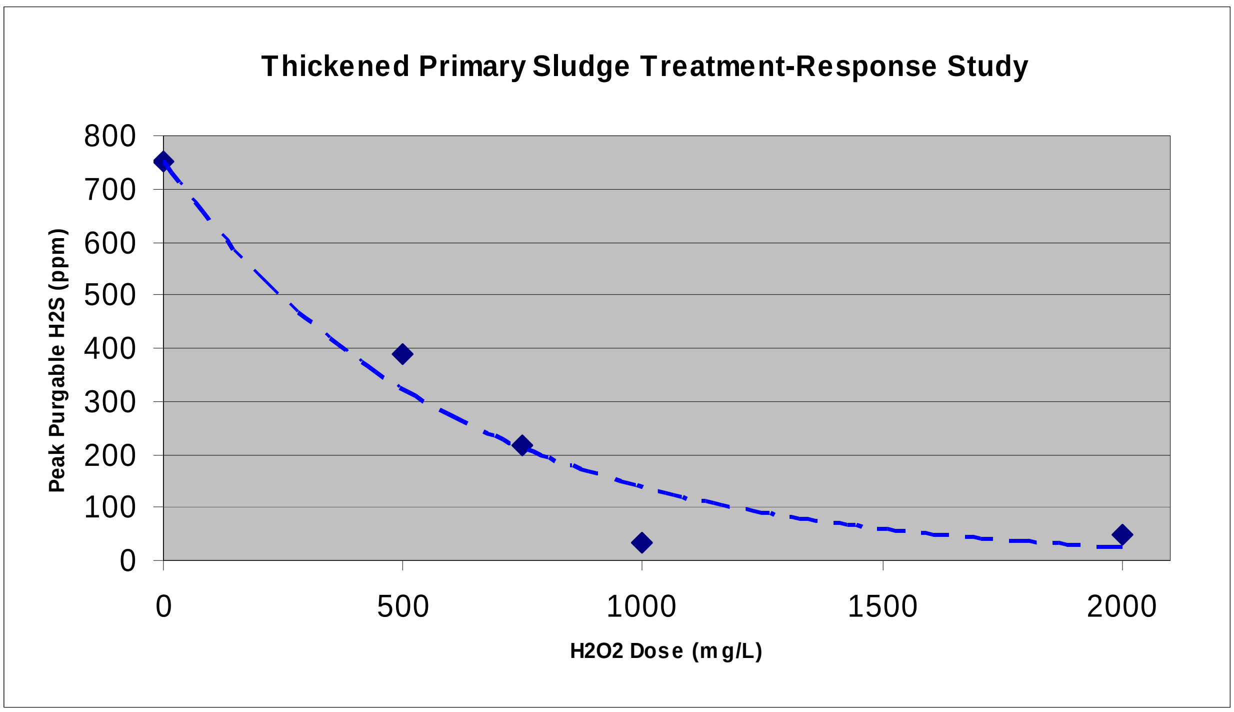


Table 1 – Manatee SWWRF Digester Process Parameters.

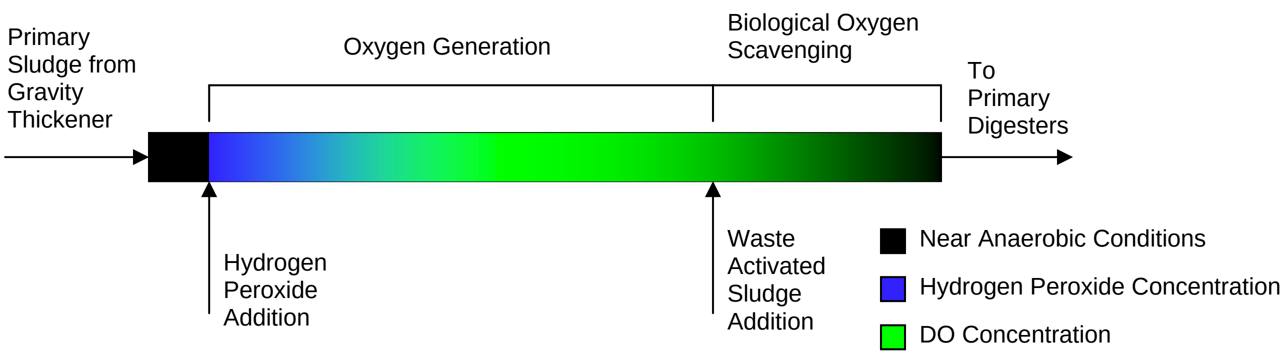
Digester Stage	Quantity	Capacity (gal)	Description
Primary	3	800,000	Anaerobic, Single Stage, Floating Cover, Semi-Continuous Feed
Secondary	1	1,000,000	Anaerobic, Single Stage, Floating Cover, Semi-Continuous Feed

Digester Inputs	Flow Rate (gal/min)	Dissolved Sulfide (mg/L)	Est. Fe Load (Lbs/day)
Thickened Primary Sludge	10 - 20	40 - 100	~300
Waste Activated Sludge	15 - 30	< 0.1	unknown

Treatment Process Implementation

Bench scale tests showed that H_2O_2 residuals in TPS dropped to < 0.5 mg/L within 3 minutes of treatment. The average available retention time between H_2O_2 treatment and TPS/WAS mixing was determined to be 8-10 minutes. This provided assurance that mixing with WAS would occur under conditions with no residual H_2O_2, creating the optimal conditions for scavenging any remaining DO in the subsequent 2 – 4 minutes between WAS mixing and digester addition. This concept is depicted in the concentration profile of Figure 4.

Figure 3 – Theoretical treatment process profile: conversion of excess H_2O_2 to DO and subsequent biological depletion of DO.

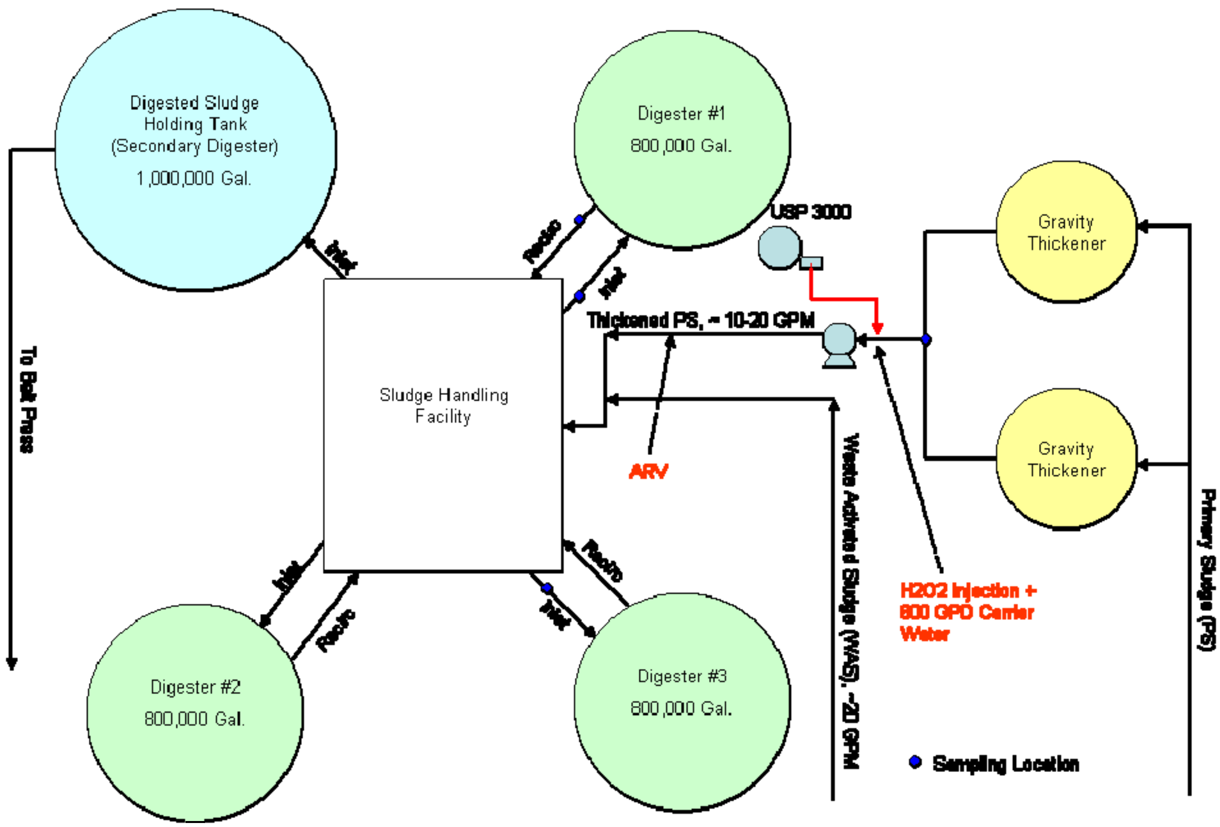


Due to the expected decomposition of a portion of the H_2O_2 to oxygen gas, it was assumed that pressure within the pipeline would increase. This required that the design include an air-relief valve on the TPS line downstream of peroxide treatment. At Manatee, the ARV was an existing feature and no modifications were necessary. Both the regulation of pressure and the assurance of available treatment retention time were considered primary design parameters in order to insure that H_2O_2 and evolved oxygen would not enter the digester and negatively impact the anaerobic digestion process. Current evaluation is centered on better understanding the mechanism by which peroxide evolves oxygen in iron-laden sludge and should identify the optimal design parameters that balance iron regeneration and oxygen evolution.

Several design features were included to minimize the potential for oxygen to evolve and enter the digesters. Although the theoretical treatment design targeted an average dose of 90 GPD of H_2O_2 (50% w/w), actual dosages were feedback-controlled by thickened primary sludge flow demand. This allowed treatment to continuously approximate the desired 1500 mg H_2O_2/L TPS. Additionally, the feedback control allowed for peroxide treatment to halt if the TPS line ever became stagnant (< 2 GPM). Finally, carrier water was added to the hydrogen peroxide just before treatment such that the concentration of the H_2O_2 solution was strictly < 8% w/w, and typically 4% - 6% w/w. The dilute peroxide would react more efficiently, with less peroxide decomposing to oxygen and better mixing resulting (improving FeS conversion efficiency). As the trial proceeded, a faster than expected system response, coupled with seasonally reduced sludge flows, required that the level of treatment be adjusted occasionally, first to 750 mg/L to moderate the pace of sulfide removal in the digester, then finally to 1250 mg/L, which became the final dosage target.

Figure 4 shows the finished design of the treatment process in the context of the Manatee SWWRF sludgeworks and includes detail of treatment and monitoring locations.

Figure 4 – Process flow diagram of the Manatee County SWWRF sludgeworks.



METHODOLOGY

To assess the progress of treatment, multiple odor parameters were tracked. For this trial the process metrics of importance were the sulfide levels within the primary digesters, in both the solution and gaseous phases, with the H_2S output of the digester vents having the most bearing on the outcome of the trial. Additionally, "purgeable" mercaptans were monitored to see if sludge pretreatment could achieve significant removal, but were a secondary issue in the overall success of the trial. The variables monitored, as well as the methods used, are listed in Table 2.

Hydrogen sulfide levels were monitored continuously at the vents of both primary digester #1 and the secondary digester utilizing an H_2S data logger (Detection Instruments 0 – 1000 ppm "Odalog"). The data logger was fixed horizontally underneath the vent cover such that the gas exiting the vent was allowed to passively enter the sensor without corrupting it. It was necessary for the Odalog to be located in fresh air to prevent sensor damage and ensure accurate data. Although this allowed for continuous monitoring, it subjected the data logger to variable weather and digester operating conditions that created significant noise in the resulting data. Daily H_2S averages and peak levels were used to minimize noise and attain a more representative trend.

Table 2: Parameters monitored throughout the trial.

Sample Location	Parameter	Method	Collection Interval
Primary Digester #1 Contents	Dissolved Sulfide (mg/L)	Filtration + Gastec #211 or #211LL Tubes	Weekly
Primary Digester #1 Contents	Peak Purgable Hydrogen Sulfide (ppm)	Purgables Method + H2S Monitor Peak	Weekly
Primary Digester #1 Contents	Purgable Mercaptans (ppm)	Purgables Method + Gastec #70L Tube	Weekly
Primary Digester #1 Vent	H2S Gas Content (ppm)	H2S Data Logger	1 minute
Secondary Digester Vent	H2S Gas Content (ppm)	H2S Data Logger	1 minute

Liquid phase variables were monitored either by disposable colorimetric tubes (cf. table 2) or by one of two "purgeable gas" methods. Although useful only in a comparative sense, purgeable sulfide and mercaptan levels were utilized throughout the trial to monitor the change in the potential for the contents of the digester to off-gas these odorous compounds. This method was a fast and straightforward means of determining the progress of treatment. The procedure for this test, as it was conducted during this trial, follows:

1) 100 mL of sample sludge is added to a 1 L clear plastic flip-top bottle.
2) The air space in the bottle is sparged by gently blowing air over the top of the bottle for 10 seconds. The bottle was then capped.
3) The bottle is shaken vigorously for 10 seconds. Depending on the variable to be measured, either step 4a or 4b is to be followed.

4a) As the flip-top cap is opened, an H_2S gas monitor (Odalog) is placed so that it covers the entire opening. The bottle is then squeezed at approximately two second intervals until the maximum reading can be recorded from the monitor.

4b) An appropriate mercaptan disposable gas colorimetric tube is placed through a one-holed stopper and inserted into a metered hand pump (Gastec GV-100 pump and #70L tubes were used in this trial). This entire assembly is into the opening of the bottle as the flip-top is removed, and the appropriate volume of headspace gas is pulled through the tube with the pump

The method for measuring sulfide ion in solution utilized disposable colorimetric tubes (Gastec #211H, #211M, #211, #211LL depending on expected sulfide concentration). Sample modification by filtration of the sludge sample through a coarse filter (25-75 µm pore size) was necessary to obtain a solution clear enough to use these tubes successfully. Determining the concentration of sulfide ion in the primary digester contents was critical in assessing the progress of the trial, and was the only empirical metric available during the study.

RESULTS

Within 40 days of treatment initiation, approximately 1 digester age, dissolved sulfide levels in the primary digester dropped from an average 20 mg/L to approximately 1 mg/L. After continued treatment through a second digester age, these levels remained < 0.1 mg/L.

Figure 5: Purgeable and dissolved sulfides content in primary digester #1.

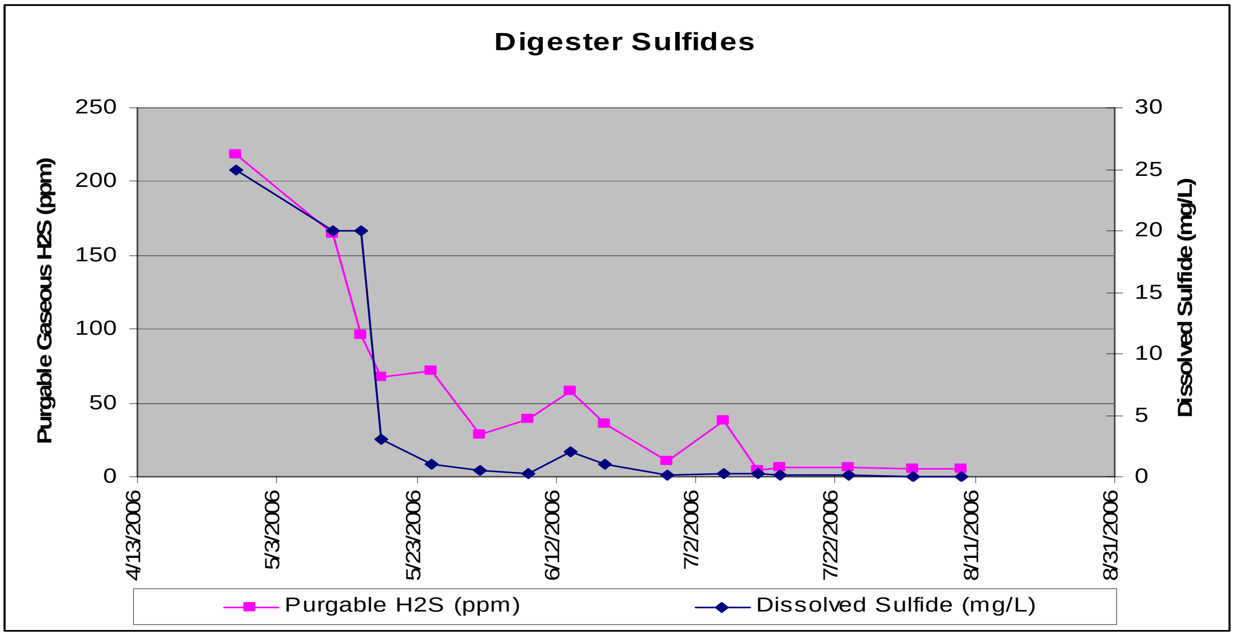
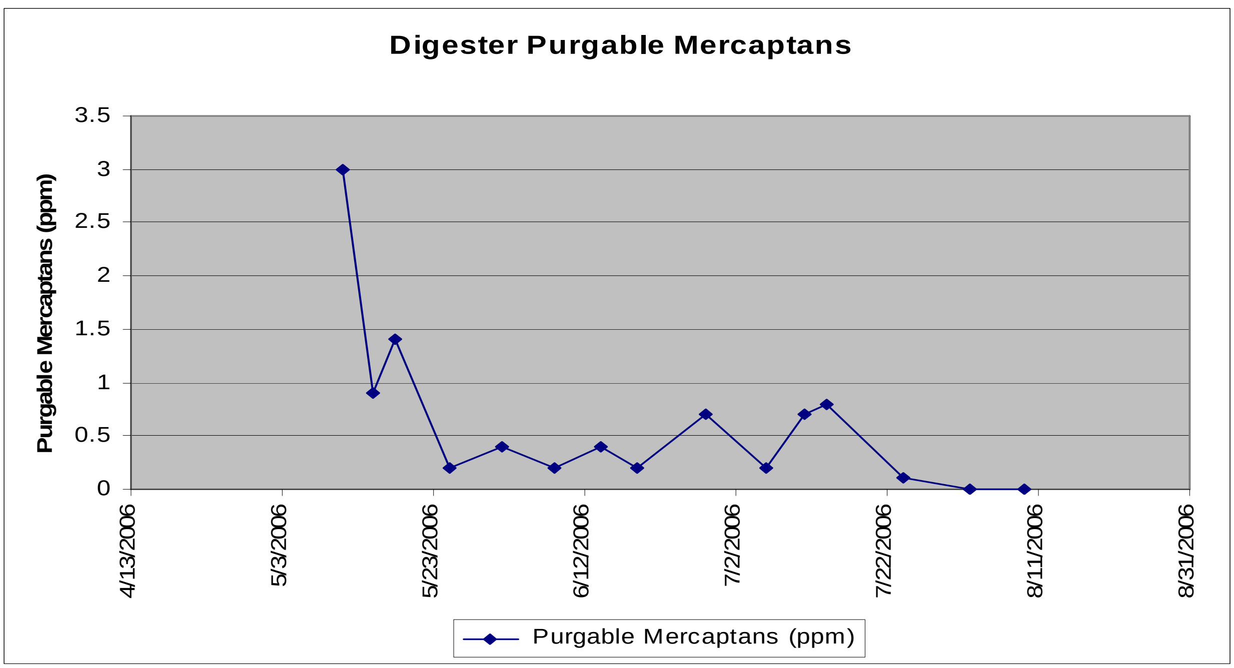


Figure 6: Total mercaptans purgeable from the primary digester sludge.



A correlative effect was also observed in purgeable H_2S measurements, where average levels dropped from 200 ppm to 50 ppm after the first sludge age, and further reduced to 20 ppm by the end of the second sludge age. Figure 5 above establishes this acute reduction in sulfide levels, as well as the correlation between the two measurements.

Purgeable mercaptans dropped from 1-3 ppm to non-detectable levels (< 0.01 ppm) (Figure 6). Mercaptan levels were not initially considered within the treatment specifications and therefore monitoring did not begin until approximately one week before the start of treatment, creating some uncertainty about the true pre-treatment values.

Improvements were also noted in H_2S gas levels at the vent of primary digester #1, falling from 200 to 20 ppm on average, with peak H_2S levels dropping from approximately 400 ppm to 100 ppm over the course of the trial (Figure 7). After considerable time, similar reductions in H_2S occurred at the vent of the secondary digester (Figure 8). It is important to note that this dataset could be significantly affected by extended wind events, with two notable events occurring on 4/28/06 through 5/1/06 and 6/11/06 through 6/13/06 (Tropical Storm Alberto).

Figure 7: Daily average and maximum hydrogen sulfide levels at the vent of primary digester #1. Recorded H_2S levels were susceptible to interference from wind conditions.

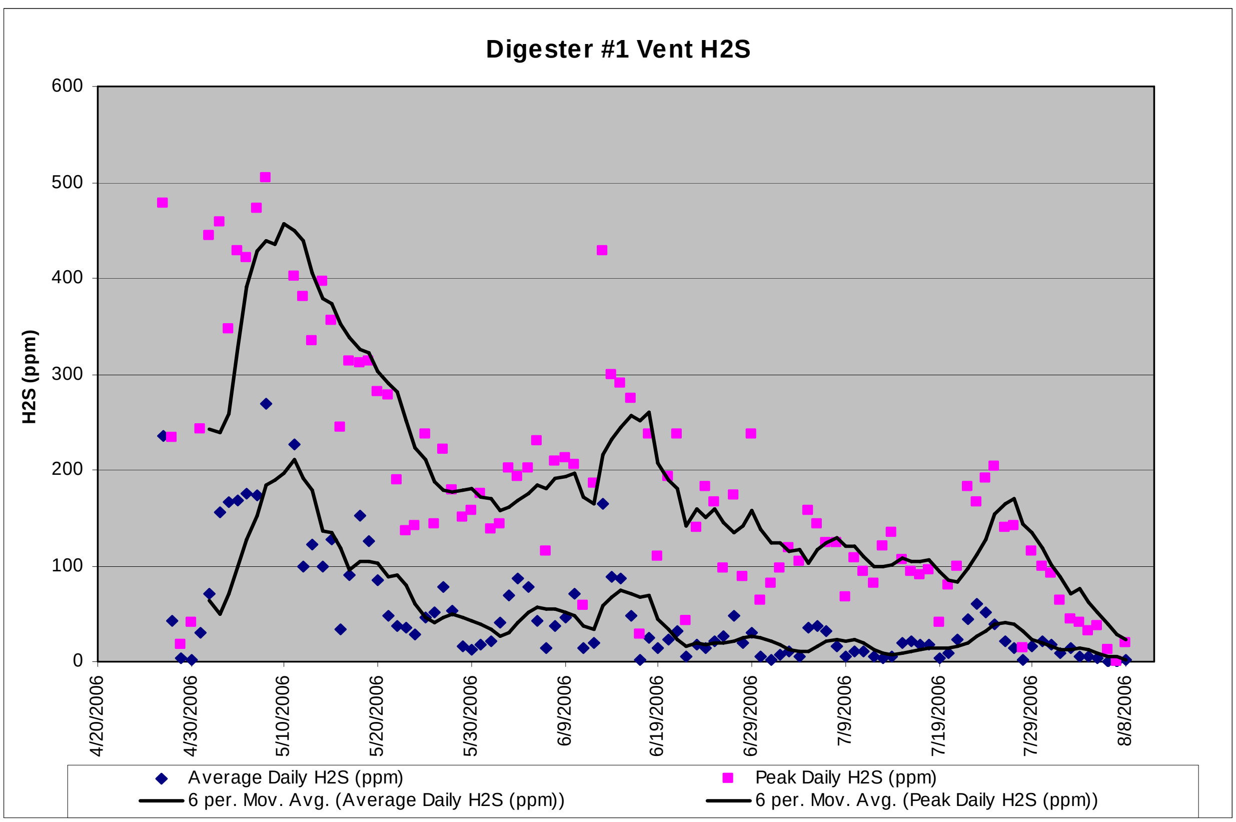
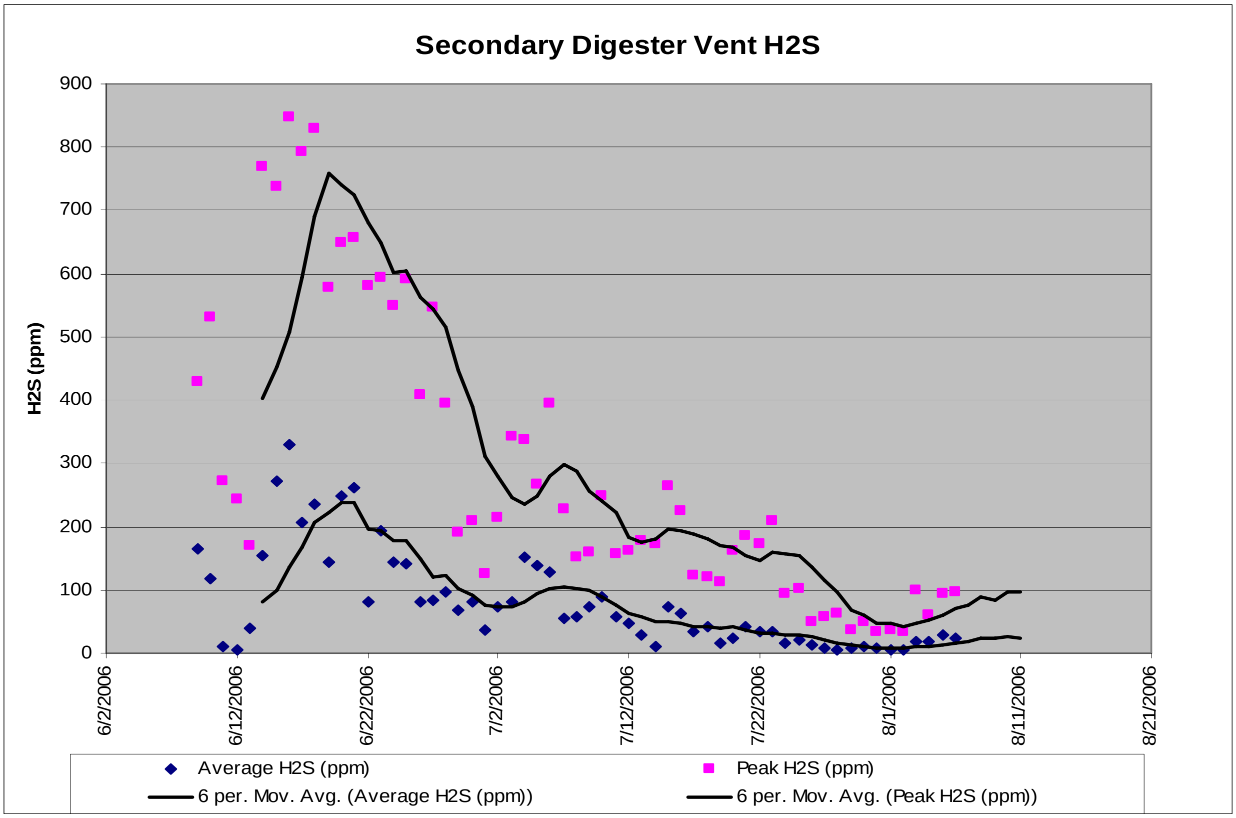


Figure 8: Daily average and maximum hydrogen sulfide levels at the vent of the secondary digester. Recorded H_2S levels were susceptible to interference from wind conditions.



In addition to the results collected from the digester odor study, several ancillary benefits of the treatment process were noted by subjective observation:

- Improved quality of digester gas and increased digester biogas production were evident after about 60 days (ca. 1.5 sludge ages), eliminating the need for the SWWRF to purchase supplemental natural gas to operate the digester heat exchangers, and making cogeneration of electricity economically viable again.
- A visual improvement in finished solids quality was noted suggesting solids dewatering benefits (an area for further study).
- Elimination of sulfides in the belt filter press effluent resulted in a 2 – 4 mg/L reduction in dissolved sulfide at the headworks of the treatment plant. Consequently, improved solids settling and reduced odors could be noted throughout the entire plant.

DISCUSSION

In practice, the reduction in hydrogen sulfide within the digesters occurred in a more dramatic fashion than had originally been anticipated. Given that the most significant improvements at SAWS were noted after two digester ages (Winters, et al.), an approximately 75% reduction in sulfide/H_2S after one digester age at Manatee, combined with a seasonal decrease in sludge flow rates prompted reevaluation of the H_2O_2 dose levels going forward. Consequently, it was decided to modify the level of peroxide dosage occasionally during the trial in order to certify that the H_2O_2 was acting mainly to oxidize sulfides and regenerate iron with minimal O_2 evolution. Nevertheless, it is important to note that the results showed the effect of treatment to be additive. One could postulate that the long term outcome of treatment at any reasonable dose level (above an unknown critical minimum) would have the net result of sulfide elimination within the digester, with only the rate of sulfide decrease affected.

The high level of reduction in sulfides noted in the secondary digester was also unexpected, but the context of the chemistry behind peroxide regenerated iron technology causes this reduction to make sense in retrospect. The continuous treatment and subsequent conversion of FeS to unbound Fe^{+2} eliminated sulfide entering the primary digester while binding sulfide that was generated thereafter. This created a continuous feed of sulfide free sludge from the primary digester, potentially containing residual free ferrous iron to the secondary digester. After considerable time, older sulfide laden sludge would be replaced with treated sludge, and residual Fe^{+2} would potentially be available to bind any additional sulfide generated by digestion. A comparison of Figures 7 and 8 provides significant support for this conjecture. The final result was nearly complete destruction of sulfides throughout the entire sludgeworks and, as noted under the subjective results, a reduction of sulfides at the headworks of the Manatee SWWRF. It has been hypothesized that the lack of a seasonal turn-down in sulfides at the plant (due mostly to the lack of significant cool weather in Florida) created an inventory of sulfides that was continuously recirculated through the sludgeworks and back to the headworks and primary clarifier of the plant, and returned again to the sludgeworks. Given that there were relatively few release points for H_2S, combined with significant generation of sulfide as a normal result of the anaerobic conditions in the primary clarifier and sludgeworks, a large inventory of sulfides was maintained. Treatment with peroxide regenerated iron effectively “broke the cycle” by creating a means to eliminate the inventory and prevent the sulfide inventory from building again.

Although not quantitatively monitored during the trial, significant improvements were noted in both biogas volume and quality. The previous study at SAWS (Winters, et al.) demonstrated that these improvements were likely, but the lack of sufficient process monitoring equipment at Manatee prevented the specific collection of data on either of these subjects. Other studies have described methane inhibition due to sulfide scavenging of essential metal micronutrients (Bretler, et al, Speece, and Gonzales-Gil et al). Nevertheless, several observations made during the trial support this conjecture effectively. With respect to biogas quality, the reduction in H_2S alone is sufficient to make this claim, but the change in waste gas burner flame color from yellow-orange to nearly colorless provides further support. Additionally, the plant has historically needed to supplement biogas in previous summers by purchasing natural gas. Necessary to achieve the minimal energy value and volume of gas required to run the digester heat exchangers, natural gas expenses were ~$25,000 over six weeks in 2005 – an expense not incurred during the summer of this trial. Further evidence for the generation of additional biogas volume was noted by the tendency, beginning at approximately 1.5 digester ages, for the floating cover on the secondary digester to remain at its maximum height for extended periods of time. Although knowledge about the improvements in biogas output was limited, the benefits were nevertheless realized by plant management, prompting the repair and reinstatement of biogas cogeneration at the plant. Further study would be required to be able to make more concrete statements about the effect of H_2O_2 treatment on digester biogas generation.

An existing observation was made in the biogas ductworks at Manatee SWWRF. A crystalline formation within the biogas ductwork was found and could possibly be evidence that oxygen in some form entered the digesters, but it is unclear whether this layer of yellow crystal is a result of deposition or, more concernedly, corrosion. Because the examined ductwork was most likely severely corroded before the trial began, it is difficult to determine whether this finding represents a corrosion threat, or merely a change in operating conditions. Studies are underway to characterize the process factors that will ensure failsafe operation of the peroxide regenerated iron process as it regards to oxygen carryover.

CONCLUSIONS

By the end of the trial, it was evident that the long term results of digester sulfide treatment were more far reaching than originally expected. While it was initially unknown whether the positive impacts of peroxide regenerated iron would depress sulfides low enough to warrant continued treatment, in actuality, sulfide ion (S^{-2}) and H_2S were reduced to better than expected levels. The added benefits of mercaptan reduction and improved solids and biogas quality further support the overall value of the process. By comparison to previous work that examined peroxide treatment of a mixed sludge in a DAF unit (Winters et al.), it is also clear that treating sulfide in thickened primary sludge prior to anaerobic digestion is a more direct means of odor control. Although treating it with hydrogen peroxide requires specific process safeguards, thickened primary sludge, in the case of Manatee SWWRF, contained the majority of iron and sulfide feed to the digester and therefore appears to be the most efficient means to sulfide control. Nevertheless, the process as designed for the Manatee County SWWRF is certainly not the only means for digester odor control, and other municipalities that add iron to their collection systems or headworks may also find that regenerating iron with hydrogen peroxide prior to anaerobic digestion provides a superior alternative to simply adding more iron.

ACKNOWLEDGMENTS

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REFERENCES

Winter, F.J. et al., "Bio-Solids Process Enhancements From the Use of Hydrogen Peroxide for Hydrogen Sulfide Odor Control – The San Antonio Experience", (2006) Proceedings of Water Environment Federation Conference and Expo, 2006.

Walton, J.R. et al., "Peroxide Regenerated Iron-Sulfide Control (PRI-SC)™: Integrating Collection System Sulfide Control with Enhanced Primary Clarification by Adding Iron Salts and Hydrogen Peroxide", (2003) Proceedings of Water Environment Federation Conference and Expo, 2003.

Mamais, D. et al., “Determination of Ferric Chloride Dose to Control Struvite Precipitation in Anaerobic Sludge Digesters”, *Water Environment Research*, Vol. 66, No. 7, pp. 912-018 (1994).

Bretler, G. and Marison, I.W. “A Medium Optimization Strategy for Improvement of Growth and Methane Production by *Methanobacterium thermoautotrophicum*”, *J. Biotechnol.* Vol. 50, Issues 2-3, pp. 201-212 (Oct 1, 1996).

Speece, R.E. “Survey of Municipal Anaerobic Sludge Digesters”, *Water Research*, Vol. 22, No. 3, pp 365-372 (Mar 1988).

Gonzales-Gil, G. et al., “Effects of Nickel and Cobalt on Kinetics of Methanol Conversion by Methanogenic Sludge as Assessed by On-Line CH4 Monitoring”, Appl. Environ. Microbiol., Vol. 65, No. 4, pp 1789-1793 (Apr 1999).