Bio-Solids Process Enhancements Resulting From the Use of Hydrogen Peroxide for Hydrogen Sulfide Odor Control - The San Antonio Experience

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ABSTRACT

The paper will present results of a trial initiated in February 2004 by the San Antonio Water System (SAWS) to quantify the impacts of hydrogen peroxide injection prior to dissolved air flotation thickening of wastewater sludges.

Since February 2000, the San Antonio Water System has successfully used iron salts ($FeSO_4$) for odor and corrosion control in the Dos Rios Water Recycling Center (WRC) collection system. In May of 2003, the Dos Rios WRC began receiving about 300,000 gallons per day of a mixture of primary and waste activated sludges from SAWS' Leon Creek WRC. When the Dos Rios WRC facility started receiving sludge from Leon Creek, several negative impacts were observed. Operators immediately noticed a significant increase in sulfide odors from the DAF units treating the Leon Creek sludge. In addition, a 2-3% decrease in percent solids of combined Leon Creek/Dos Rios belt filter press dewatered sludge was observed. In addition, volatile solids reduction through the anaerobic digestion process decreased dramatically. Finally, an expected increase in methane production due to increased sludge volume was not realized.

In order to investigate the efficacy of hydrogen peroxide (H_2O_2) towards resolving these negative impacts, SAWS initiated a trial involving injection of H_2O_2 into the Leon Creek sludge line several minutes ahead of the DAF units. Impacts to be quantified were H_2S odors, polymer usage, volatile solids destruction, methane production, and dewatering efficiency. Past experience had suggested that hydrogen peroxide may enhance the performance of flotation thickening and sludge dewatering, and may result in a reduction of polymer use. It had also been suggested that hydrogen peroxide (in the presence of iron salts) could potentially increase methane production through partial oxidation of organic compounds (e.g. lignins) in the sludge, which may be recalcitrant to anaerobic digestion. Finally, it was thought that the hydrogen peroxide residuals in the Leon Creek sludge would also react to regenerate the iron salts from the Dos Rios sludges and achieve additional odor control in a blend tank where Leon Creek and Dos Rios sludges are mixed.

KEYWORDS

San Antonio Water System, Lignin, Hydrogen Peroxide, Hydrogen Sulfide, Odor Control, Gas Sampling, Flotation Thickening.

INTRODUCTION

History of the San Antonio Water System

SAWS was created through the consolidation of three predecessor agencies on May 19, 1992: the City Water Board (the previous city-owned water supply utility); the City Wastewater Department (a department of the city government responsible for sewage collection and treatment); and the Alamo Water Conservation and Reuse District (an independent city agency created to develop a system for reuse of the city's treated wastewater).

SAWS currently operates four major Water Recycling Centers (WRCs) with a combined capacity of 225.5 MGD. The largest and most modern is the Dos Rios WRC with a rated capacity of 125 MGD; the Salado Creek and Leon Creek WRCs are SAWS' oldest plants and are rated at 46 MGD each. These three facilities operate as conventional activated sludge plants. The smallest of SAWS' facilities is the Medio Creek WRC, a carrousel plant, with a capacity of 8.5 MGD.

Leon Creek WRC

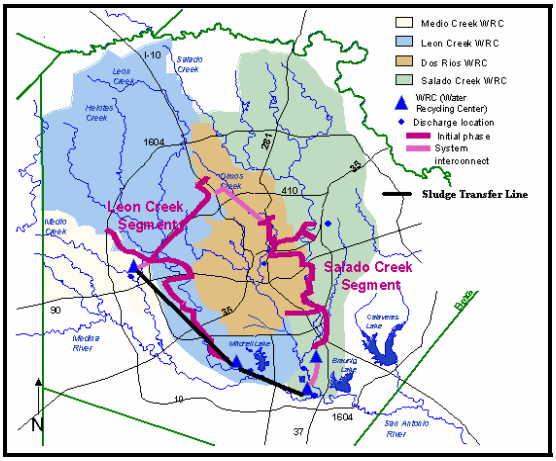
Salado Creek WRC

Dos Rios WRC

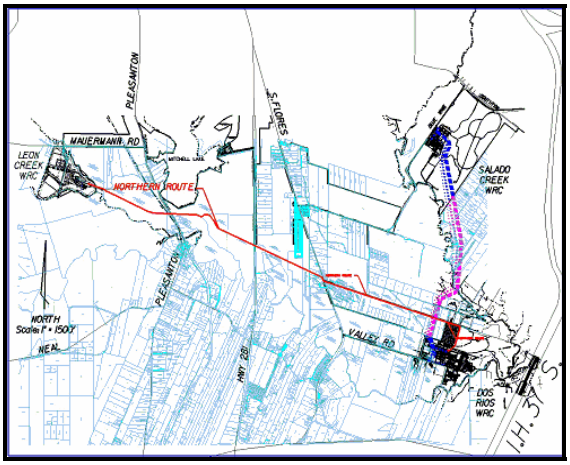
Medio Creek WRC

Sludge Consolidation Process

Through various studies, SAWS had shown that consolidation and centralization of all sludge dewatering activities at the Dos Rios WRC would be the most efficient and economical method for the future treatment and utilization of its biosolids. Construction of a series of force mains from the Medio Creek and Leon Creek WRCs to transfer sludges produced at these facilities was begun. Waste sludge from the Medio Creek WRC is transferred via a force main to a major trunk line on the Leon Creek collection system where it is transported and mixed with raw sewage. This mixture arrives at the headworks of the Leon Creek facility for additional treatment. Leon Creek WRC produces both primary and waste activated sludges. These are then blended together in an 800,000-gallon blend/holding tank. The blended sludge at a concentration of about 1.0 to 1.5 % solids is then pumped through a seven-mile force main to the Dos Rios facility for thickening, digestion and dewatering. This force main was completed and in full operation by April 2003.



SAWS Sewersheds



Leon Creek Force Main

Existing Odor Control and Issues

Since February 2000, the San Antonio Water System has successfully used iron salts ($FeSO_4$) for odor and corrosion control in the Dos Rios Water Recycling Center (WRC) collection system. In April of 2003, the Dos Rios WRC began receiving about 300,000 - 400,000 gallons per day of a mixture of primary and waste activated sludges from SAWS' Leon Creek WRC. While the Dos Rios WRC collection system has the benefit of iron salt addition for odor control, the Leon Creek WRC collection system does not. SAWS has not considered the addition of iron salts on the Leon leg as odors in this collection system are not considered to be a problem of the same magnitude as on the Dos Rios system.

When the Dos Rios WRC facility started receiving sludge from Leon Creek, several negative impacts were observed. Operators at Dos Rios immediately noticed a significant increase in sulfide odors from the DAFT units treating the Leon Creek sludge. The units treating Leon Creek WRC sludges are fed directly from a seven-mile force main directly into the DAFT units on the north side of the sludge thickening processes area at the Dos Rios facility. This configuration was found to be a perfect source for odor generation.

An additional unexpected problem occurred when an expected increase in methane production due to increased sludge volume was not realized. This loss of gas production would have a very negative affect on SAWS intention to utilize digester gas in an up coming project for electrical generation. These issues, especially the decrease in gas production sent SAWS' staff into a high level of activity searching to identify the reasons for the loss of gas productivity and odor generation.

Leon Creek Blend Tank

Leon Creek Pumping Station

From operational experiences at the Leon Creek facility, the problem was theorized to be due to the higher amounts of paper waste discharged in the Leon Creek collection system. Paper wastes contain lignin, celluloses and other poorly biodegradable organics. In addition, operational experience had shown that this facility needed long detention times in its digesters for good gas productivity. These hydraulic detention times (HRTs) were on the order of 40 days.

With this information, a possible problem for the poor gas production was identified. The issue of odor production was thought to be due to the detention time of the sludge within the force main. It should be noted that sulfide odors are not present at the Leon Creek WRC sludge blending tank; hence, the production of sulfide could only be coming from the sludge traveling the force main.

Hydrogen peroxide (50%), a known and effective oxidizing agent, was chosen to address this problem. SAWS' staff felt comfortable with the use of hydrogen peroxide for odor control, as there was a long history of peroxide use at the Dos Rios facility. Since the chemical of choice was going to be fed directly to the DAFT units, peroxide was considered a better choice than iron salts as it would not generate the additional solids, and the contact time of only a few minutes would not allow the iron reaction to go to completion for optimum odor control. Peroxide was also very easy to install at other locations as SAWS current contract allowed these additions at current pricing. SAWS staff felt that peroxide would better address these two problems and that other operational issues may be corrected.

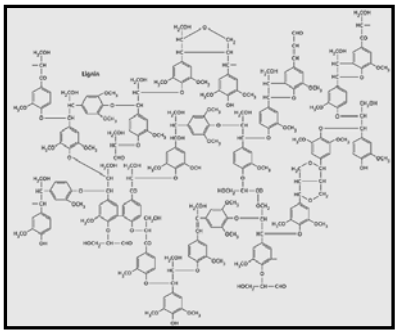
METHODOLOGY

In order to investigate the efficacy of hydrogen peroxide (H_2O_2) towards resolving these negative impacts, SAWS initiated a trial involving injection of 50% H_2O_2 into the Leon Creek sludge line several minutes ahead of the DAF units used for thickening at the Dos Rios WRC. Impacts to be quantified were liquid and vapor phase H_2S concentrations at the DAF units for odor control. It had also been suggested that hydrogen peroxide could potentially increase methane production through oxidation/modification of large organic compounds such as lignin, known to be in paper fibers.

After some discussion, possible mechanisms were suggested by which hydrogen peroxide could positively impact methane production. One mechanism involves the breakdown or modification of residual lignin on the paper fibers in the sludge. Another mechanism involves the breakdown

or modification of biopolymers, which may inhibit the sludge digestion process. This "pre-digestion" step might allow the microorganisms in the methane production process to do a better job of digesting the sludge. Potentially, this would lead to higher production of methane. Therefore, methane production in the digesters during the trial was to be also monitored.

Experience had suggested that hydrogen peroxide might also enhance the performance of flotation thickening and sludge dewatering and that peroxide may have additional benefits in the reduction of polymer use. Since there was a potential benefit in these areas, staff also decided to monitor DAF polymer usage, volatile solids destruction, and dewatering efficiency (% solids) for any possible confirmation of these effects. Finally, it was thought that the hydrogen peroxide residuals in the Leon Creek sludge would also react to regenerate the iron salts from the Dos Rios sludges and achieve additional odor control in a blend tank at Dos Rios where Leon Creek and Dos Rios sludges are mixed prior to digestion.



Typical Lignin Structure

Peroxide Injection System

The trial was begun on February 20, 2004 with the goal of eliminating H_2S and odors around the DAF units treating the Leon Creek sludge and the sludge-blending tank. The trial was initially set to run 60 to 90 days, as SAWS staff felt that this would be sufficient time (about 2-3 Sludge ages) for the digesters to recover gas productivity and a long enough time period to observe any decrease in odors in the area.

RESULTS AND DISCUSSION

Odor Control

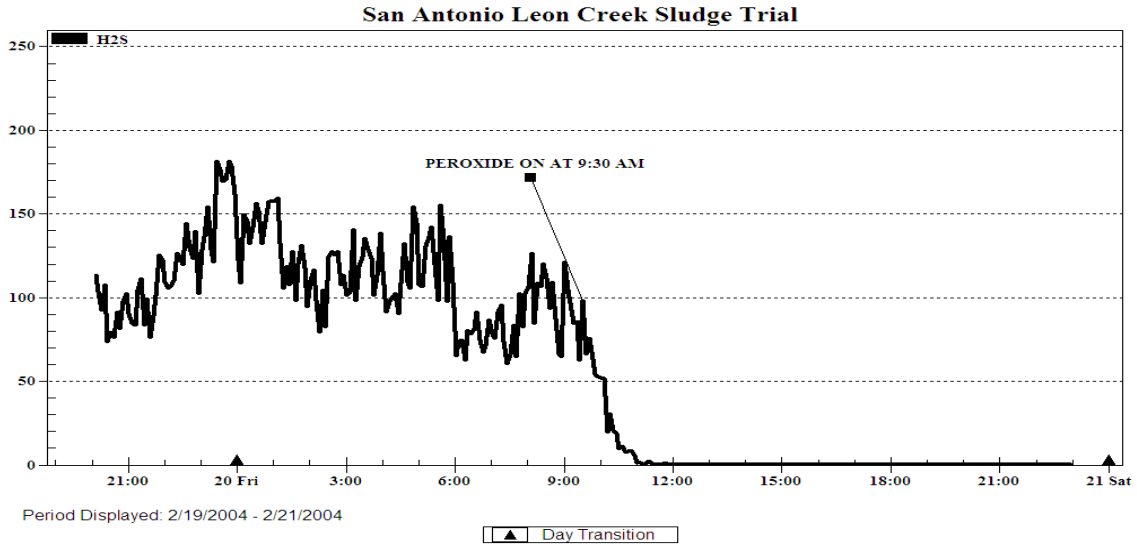
The following data tables and charts summarize and demonstrate the effectiveness of hydrogen peroxide for the control of hydrogen sulfide at the Dos Rios DAFT Units used for thickening of the Leon Creek sludge. Of further significance, the data collected also documents improved digester gas (methane) production. SAWS' staff expected these effects and improvements from the peroxide additions. Peroxide treatment of the Leon Creek sludge has also shown a marked contribution to recovery of the sludge dewatering efficiency (% belt press cake solids) as seen prior to Leon Creek sludge introduction. Reduced DAFT polymer consumption had also been

seen initially, but longer-term polymer usage levels have not confirmed this trend. Further studies that will be conducted under tighter process control will be required to document this fourth possible benefit.

Gaseous sampling was performed using an Odalog hydrogen sulfide data logger (See Figure 1). The Odalog data logger was placed next to the underflow weir (the most turbulent area) of the #3 DAFT unit. Liquid sulfide (soluble sulfide) measurements were also taken from five separate sample points within the DAFT treatment process. These points were: 1) the Leon Creek sludge transfer line before the DAF units; 2) & 3) In front of the weirs of DAFT units #2 and #3; 4) & 5) The DAFT underflows of DAFT #2 and #3 (See Table 1 and Table 2).

The data demonstrated that elimination of hydrogen sulfide to levels below 1 ppm from the most turbulent area of the process within the system could be achieved within 90 minutes of starting peroxide flow. The peroxide dosage to achieve this elimination was about 88 GPD or a dose rate of about 150 mg/l. At this dose rate, the expected daily cost would be around $210.00/day which was acceptable to SAWS. This dose rate has become the target rate for all future activities.

Figure 1



Additional testing of the gas phase on DAFT #3 was performed to verify the long term suppression of hydrogen sulfide generation during the period of February 21 through February 27 (Figure 2). All results with the exception of two periods when the feed system was shut off showed below detectable levels.

Figure 2

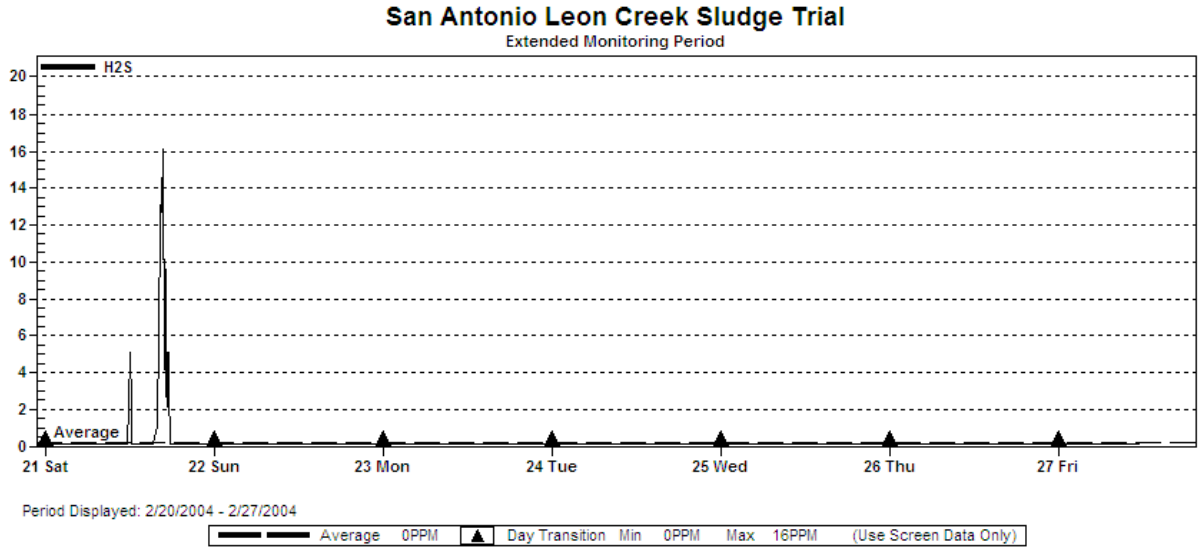


Table 1

Liquid Sulfide (mg/L) @ Leon Creek DAF Sample						
Date	Time	Leon	#2 Underflow	#3 Underflow	#2 Overflow	#3 Overflow
2/19/2004	9:50			1.0		
2/19/2004	10:05		0.3			
2/19/2004	10:20	3.3				
2/19/2004	11:00		0.3			
2/19/2004	11:20			0.9		
2/19/2004	11:40		0.2			
2/19/2004	12:00			1.0		
2/19/2004	13:00		0.4			
2/19/2004	13:30			1.2		
2/19/2004	15:00	3.1				
2/19/2004	15:30			1.2		
2/19/2004	15:50			1.1		
2/19/2004	16:30					1.1
2/19/2004	15:50		0.4			
2/19/2004	16:30				0.3	

Table 2

Liquid Sulfide (mg/L) @ Leon Creek DAF Sample Points								
	Date	Time	Leon Sludge	#2 Underflow	#3 Underflow	#2 Overflow	#3 Overflow	#3 Gas H_2S
Peroxide	2/20/2004	8:10						172 ppm
Off	2/20/2004	8:20			1.8			
I	2/20/2004	8:30		0.6				
V	2/20/2004	9:00	3.6					
On	2/20/2004	9:15						
88 GPD	2/20/2004	9:30						68 ppm
V	2/20/2004	9:35		0.8				
I	2/20/2004	9:40			1.6			
I	2/20/2004	10:05		0.1				30 ppm
I	2/20/2004	10:10			0.8			
I	2/20/2004	10:30						10 ppm
I	2/20/2004	10:35		0				
I	2/20/2004	10:40			0.1			
I	2/20/2004	11:00						0 ppm
I	2/20/2004	12:15						0 ppm
I	2/20/2004	12:20		0				0 ppm
I	2/20/2004	12:25			0			0 ppm
I	2/20/2004	12:40	3					0 ppm
I	2/20/2004	14:20		0				0 ppm
I	2/20/2004	14:25			0			0 ppm
I	2/20/2004	15:00		0				0 ppm
105 GPD	2/20/2004	15:05			0			0 ppm
I	2/20/2004	16:00		0				0 ppm
I	2/20/2004	16:05			0			0 ppm
I	2/21/2004	9:30		0				0 ppm
I	2/21/2004	9:35			0			0 ppm
I	2/21/2004	10:30		0				0 ppm
V	2/21/2004	10:35			0			0 ppm

Peroxide Impact on Polymer Usage

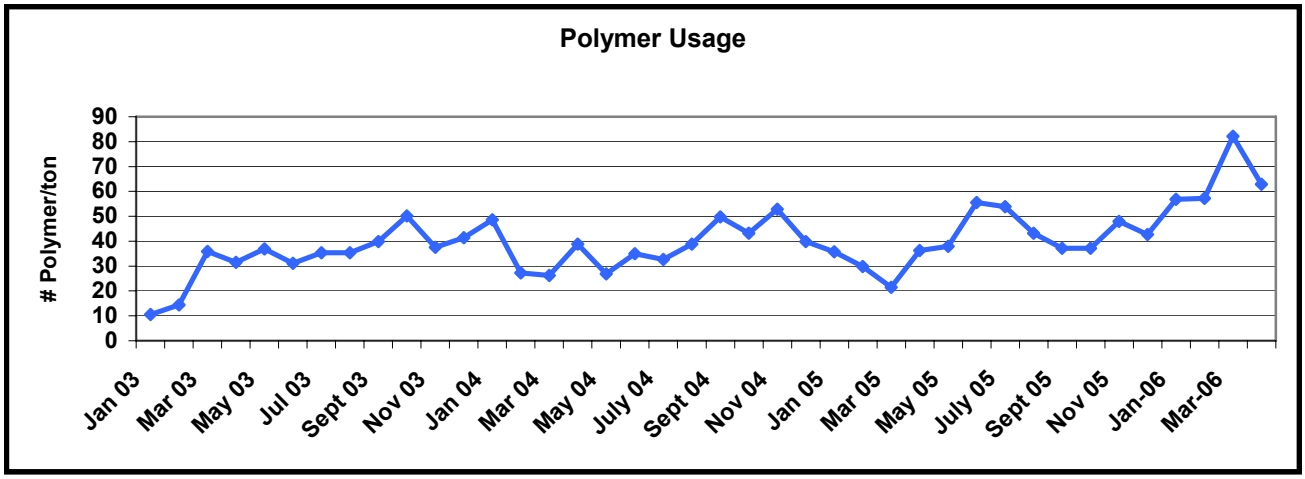
The data contained in the following table (Table 3) initially seemed to provide supporting evidence that peroxide was having an effect on reducing polymer usage at the Dos Rios DAFT units. After peroxide addition was begun on February 20, 2004, polymer costs compared to the previous three months appeared to be decreased by about $4000/month. While this decrease did not recover all the costs associated with peroxide treatment, a sufficient offset to operating costs appeared possible. Operator interviews also provided supporting evidence, confirming that the Leon Creek polymer pump rates were reduced once peroxide treatment was started. Table 3 shows that between the months of February through June polymer rates and the costs associated were reduced, but by July 2004, rates have increased to pre-peroxide levels. The polymer feed system employed at the Dos Rios facility causes the Dos Rios DAFT polymer pump rates to increase or decrease at the same rate as that used on the DAFT's treating the Leon sludges, this may be a plausible explanation for the increased usage of polymer after the July time period. SAWS has begun tracking historical and ongoing data in an effort to elucidate the precise impact of peroxide on polymer usage. Additional data and further work at the DAFT units is required to evaluate the full peroxide impact on polymer usage (Figure 3).

Table 3

Month	# Poly/ton	Daily Cost	Total Month
Jan 03	10.49	$149.00	$4,617
Feb 03	14.45	$205.24	$5,747
Mar 03	35.89	$560.73	$17,383
Apr 03	31.55	$544.42	$16,333
May 03	36.85	$505.72	$15,677
Jun 03	31.14	$387.69	$11,631
Jul 03	35.33	$489.79	$15,183
Aug 03	35.35	$442.92	$13,731
Sept 03	39.83	$477.13	$14,314
Oct 03	50.18	$549.69	$16,491
Nov 03	37.50	$473.68	$14,216
Dec 03	41.46	$504.03	$15,625
Jan 04	48.65	$582.54	$18,059
Feb 04	27.28	$370.24	$10,737
Mar 04	26.25	$398.10	$12,341
Apr 04	38.83	$397.97	$11,939
May 04	26.82	$466.02	$13,980
June 04	34.95	$467.26	$14,017
July 04	32.72	$476.96	$14,785
Aug 04	38.82	$519.33	$16,099

Month	# Poly/ton	Daily Cost	Total Month
Sept 04	49.78	$397.37	$11,921
Oct 04	43.14	$516.04	$15,997
Nov 04	52.82	$553.46	$16,604
Dec 04	39.88	$564.48	$17,499
Jan 05	35.74	$502.98	$15,592
Feb 05	29.82	$449.12	$12,575
Mar 05	21.53	$423.59	$13,131
Apr 05	36.30	$549.24	$16,477
May 05	37.98	$555.56	$17,222
June 05	55.51	$666.04	$19,981
July 05	53.82	$544.71	$16,886
Aug 05	43.22	$480.30	$14,889
Sept 05	37.10	$465.63	$13,969
Oct 05	37.15	$449.79	$13,944
Nov 05	47.97	$507.27	$15,218
Dec 05	42.68	$517.48	$16,042
Jan-06	56.81	$557.20	$16,716
Feb-06	57.17	$601.71	$16,848
Mar-06	82.11	$669.01	$20,739
Apr-06	62.89	$631.39	$18,311

Figure 3



Peroxide Impact on Dewatering Efficiency

Based on available information and historical data, the Dos Rios facility appears to have realized a recovery of about 2% TS in its belt filter press sludges after the addition of peroxide. The data used for comparison purposes was from May and June of each year as noted in Table 4 below. The months of May and June were used as a typical months for these comparisons. Initial year

data after peroxide addition proved promising, however the trend in the following year did not confirm initial results. SAWS will continue to monitor these levels for future planning.

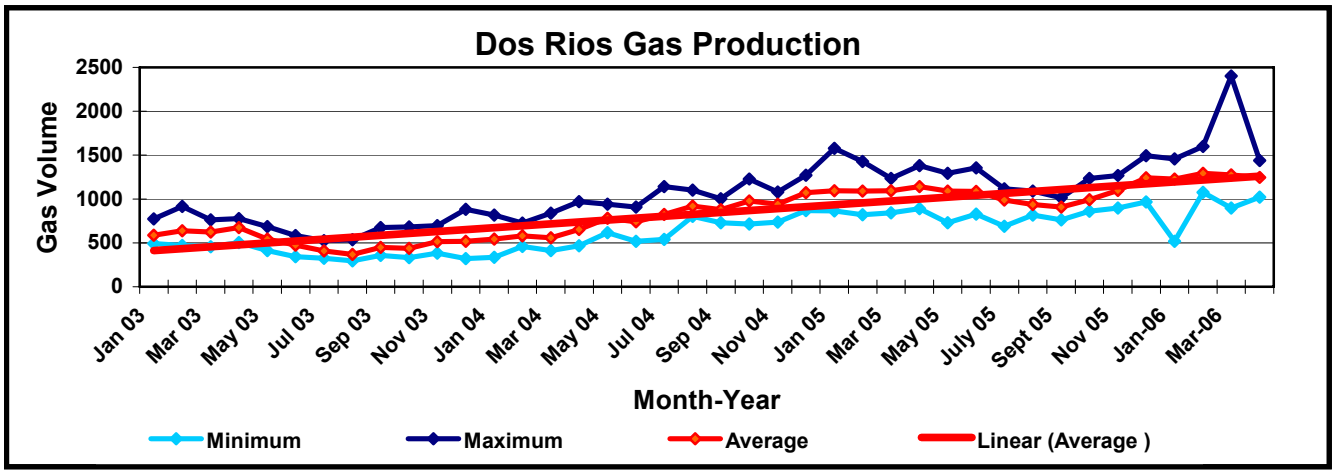
Table 4

Month-	%	Month-	%	Note
May-01	21.8	Jun-01	21.35	% cake solids prior to processing Leon Creek Sludge at Dos Rios
May-02	22.0	Jun-02	21.6	% cake solids prior to processing Leon Creek Sludge at Dos Rios
May-03	19.9	Jun-03	19.8	% cake solids with Leon Creek Sludge being processed at Dos Rios (no H_2O_2)
May-04	21.7	Jun-04	21.6	% cake solids with Leon Creek sludge processed at Dos Rios (with H_2O_2)
May-05	20.4	Jun-05	19.8	% cake solids with Leon Creek sludge processed at Dos Rios (with H_2O_2)

Peroxide Impact on Digester Gas Production

Digester gas production has shown significant increases over the past year since peroxide was first introduced into the DAFTs treating the Leon Creek sludge. This increase was first noted after about three sludge ages (Digester HRT of ~21 days) from peroxide additions. The amount of time required to measure significant improvements in methane production (about 3 sludge ages) as a result of pre-oxidation of Leon Creek sludge with peroxide, was consistent with predictions by SAWS staff. Operational data shows a continuous improvement in gas production since beginning peroxide addition on February 20, 2004 (Figure 4). Since about January 2005, gas production has leveled off around the theoretical volume expected for the sludge production levels at the Dos Rios facility. With the current gas volumes being generated, methane utilization is plausible and might result in a real cost advantage in the future in either SAWS gas to energy project or possible purification and sale of the methane produced at open market pricing.

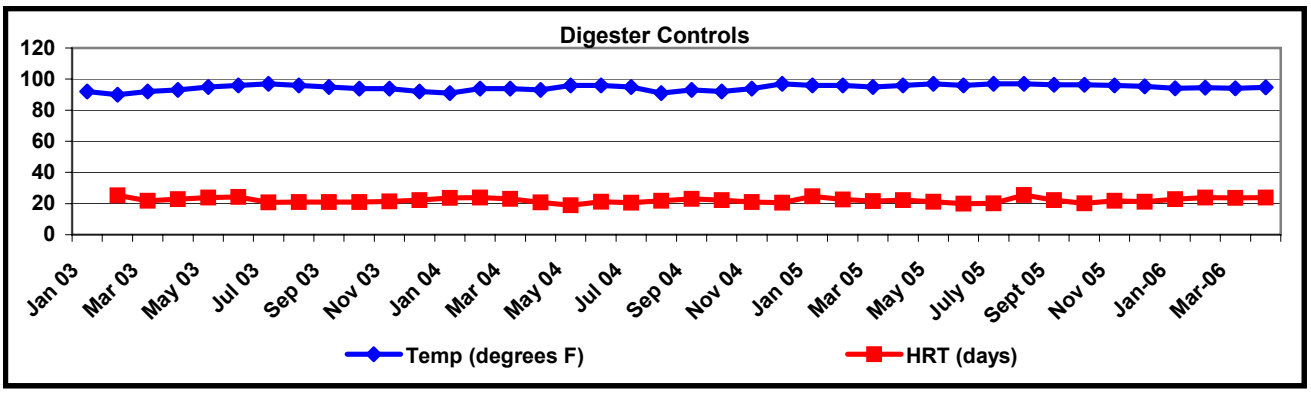
Figure 4



Peroxide Impact on Other Operational Measures

While increased gas production was expected, the magnitude of increase has exceeded SAWS expectations. Historic experience with Leon Creek sludge has demonstrated that high HRTs are required for optimum Leon sludge digestion. The HRTs required are about double that of the HRTs required at the Dos Rios facility. Data gathered has shown that over the testing period HRTs have not varied significantly and have occurred around historical values or have decreased slightly as expected. Temperatures observed in the Dos Rios digesters have also shown no real additional variability over historical levels (See Figure 5).

Figure 5



CONCLUSIONS

The use of hydrogen peroxide at Dos Rios WRC has clearly gone beyond SAWS staff's expectations since its introduction for odor control of the Leon Creek WRC sludge transferred to the Dos Rios facility. The hydrogen peroxide dosage of about 150 mg/l into the Leon Creek sludge are consistently eliminating hydrogen sulfide to below 1 ppm levels in and around the Dos Rios DAFT units and blend tank. Additionally, plant operators have reported that odors perceivable to them in the area have disappeared in totality. Peroxide, while having the expected effect on hydrogen sulfide removal, has also resulted in additional benefits. These include significant increases in digester gas production, and some improvements in sludge dewaterability. At present, SAWS does not recover digester gas for beneficial usage but the additional 500,000 cubic feet per day of digester gas production could have a potential value of $2000 - $4000 per day at current gas pricing based on the 650 BTU/CF heat value of the digester gas or current gas pricing delivered in Texas. From the odor control trial, odor removal has been achieved and the future gas to energy project of SAWS may have been saved.

ACKNOWLEDGEMENTS

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