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September 2004

Environmental Technology Verification Report

NATCO Group, Inc. – Paques
THIOPAQ Gas Purification Technology

Prepared by:



**Greenhouse Gas Technology Center
Southern Research Institute**



Under a Cooperative Agreement With
U.S. Environmental Protection Agency

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THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM



ETV Joint Verification Statement

TECHNOLOGY TYPE:	Sour Gas Processing System
APPLICATION:	Biogas Purification
TECHNOLOGY NAME:	Paques THIOPAQ
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The U.S. Environmental Protection Agency (EPA) has created the Environmental Technology Verification (ETV) program to facilitate the deployment of innovative or improved environmental technologies through performance verification and dissemination of information. The goal of the ETV program is to further environmental protection by accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the purchase, design, distribution, financing, permitting, and use of environmental technologies.

ETV works in partnership with recognized standards and testing organizations, stakeholder groups that consist of buyers, vendor organizations, and permittees, and with the full participation of individual technology developers. The program evaluates the performance of technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests, collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The Greenhouse Gas Technology Center (GHG Center), one of six verification organizations under the ETV program, is operated by Southern Research Institute in cooperation with EPA's National Risk Management Research Laboratory. A technology area of interest to some GHG Center stakeholders is reliable renewable energy sources. The generation of heat and power at industrial, petrochemical, agricultural, and waste-handling facilities with renewable energy sources such as anaerobic digester gas (biogas) or landfill gas is a particular interest. Removal of the harmful components of biogases (primarily

hydrogen sulfide and other sulfurous compounds) while minimizing the creation of secondary waste streams and effluents is essential to development of these renewable energy sources. NATCO Group, Inc. (NATCO), located in Houston, Texas, has requested that the GHG Center perform an independent performance verification of the Paques THIOPAQ technology – a gas purification system.

TECHNOLOGY DESCRIPTION

The following technology description is based on information provided by NATCO and Paques and does not represent verified information. This technology, developed in The Netherlands by Paques BioSystems, is designed to safely and efficiently remove hydrogen sulfide (H₂S) from biogas and other sour gases while minimizing the generation of harmful emissions or effluents. The process is suitable to applications where the processed biogas can be utilized as fuel. The system also allows the production of elemental sulfur for subsequent sale or use. A variation of this technology is the Shell-Paques system, which operates on the same principles as THIOPAQ, but includes system components that can process low-, medium-, and high-pressure natural gas as well as acid gas and Claus tail gas.

The Paques desulfurization technology is a caustic scrubber-based system designed to maintain a high level of H₂S removal while addressing several shortcomings of conventional technologies. This technology is designed by Paques Biosystems to: (1) reduce hazardous effluents from the scrubber by aerobically digesting the waste into a more benign sulfurous product, and (2) regenerate and recycle sodium hydroxide (NaOH) needed in the scrubber. The THIOPAQ system is specifically designed for low-pressure biogas streams.

The THIOPAQ process begins with the input of biogas or sour gas into an absorber unit (or scrubber) at ambient pressure. Scrubber design is site-specific in regards to vessel size, construction specifications, and gas and solution flow capacities. System pH ranges from 8.2 to 9. The counter-current scrubber design washes the sour gas or biogas with caustic solution in a packed bed or packed beds containing 2-inch Pall rings. Treated gas (sweet gas) exits the scrubber top, enters a knockout drum, and is routed for on-site use or to a sales gas stream.

The liquid stream is then sent to the bioreactor (ambient pressure) where caustic solution is regenerated through a series of chemical reactions and biological oxidation of dissolved sulfide. A blower supplies air to a distribution header in the bottom section of the reactor to enhance mixing. Some of the oxygen is consumed in reactions with sulfide to produce sulfur by the actions of the Thiobacillus bacteria. The bacteria are maintained using a continuous feed of proprietary nutrients supplied by Paques. These nutrients are pumped into the bioreactor with a small metering pump. Regenerated solvent from the bioreactor is pumped back to the scrubber for reuse.

VERIFICATION DESCRIPTION

The GHG Center tested a THIOPAQ system installed and operating at a 40 million gallons per day (MGD) water pollution control facility (WPCF) designed to process industrial wastewater streams from numerous local companies including grain and food processing plants and a paper mill. Approximately three MGD of flow coming from the paper mill is pretreated in three upflow anaerobic sludge blankets (UASBs). Each UASB generates around 100 to 200 cubic feet per minute (cfm) of biogas (generally 60 percent CH₄, 38 percent CO₂, and 1 to 2 percent H₂S). The gas generated in each UASB is collected and used to fuel a sludge incinerator within the plant that is capable of consuming all of the biogas generated on-site under normal plant operations. The biogas is flared during rare occurrences when the incinerator is not operating or is being fueled with natural gas.

Field tests were performed on June 29 through July 1, 2004 on the THIOPAQ system to independently verify the performance of this technology. One-month (June 1 through July 1, 2004) of process monitoring data was provided by the facility to allow the GHG Center to evaluate system operations over a longer term. The verification included evaluation of both environmental and operational performance of the system.

Environmental Performance

- Air Emissions
- Liquid Effluent

Operational Performance

- H₂S Removal Efficiency
- Gas Composition and Quality
- NaOH Consumption
- Sulfur Product Purity

Nine grab samples were collected during the verification period to directly measure the concentrations of H₂S and other sulfur compounds emitted to the atmosphere from the bioreactor vent. Vent gas flow rates were not determined due to difficulties with cyclonic and highly variable flow. Therefore, vent gas emissions are reported as estimates only. Seven bioreactor slurry samples were collected to determine the sulfates, sulfides, and total suspended solids (TSS) content of liquids disposed from the system as wastewater.

For verification of operational performance, nine corresponding biogas grab samples were collected on both the upstream and downstream sides of the THIOPAQ system and submitted for analysis. Results of the analyses were used with biogas flow rates through the system to evaluate system removal efficiency for H₂S and other sulfur compounds. The results also allowed the center to evaluate the effects of the system on biogas composition and heating value. NaOH consumption rates were monitored and reported, and composite solid waste samples from the system were collected for determination of elemental sulfur content. Plans to measure the amount of solids produced by the system were abandoned during field testing. The facility only wastes solids every three weeks or so on an as-needed basis. The frequency and amount of solids removed varies widely depending on the amount of solids removed through the liquid effluent. Removal of solids cake at this facility was operator specific and infrequent, therefore, it was deemed too arbitrary for verification here. Because of this, a sulfur mass balance could not be completed for the system.

Quality assurance (QA) oversight of the verification testing was provided following specifications in the ETV Quality Management Plan (QMP). The GHG Center's quality manager conducted a technical systems audit (TSA) and an audit of data quality (ADQ) on at least 10 percent of the data generated during this verification. Two performance evaluation audits (PEAs) were also conducted. The GHG Center field team leader and project manager have reviewed the data from the verification testing and have concluded that the data quality objectives specified in the Test and Quality Assurance Plan were attained for the verification parameters that were evaluated (excluding vent gas emission rates and solids production rates).

VERIFICATION OF PERFORMANCE

Environmental Performance

- Concentrations of H₂S and total sulfur compounds in the air vented from the bioreactor were very low averaging 929 and 1,961 ppbv, respectively. H₂S typically comprised about half of the total sulfur compound concentrations, and methyl mercaptan, dimethyl sulfide, and dimethyl disulfide were the other prominent compounds.
- Vent gas flow rates were not determined due to difficulties with cyclonic and highly variable flow. Using air flow rates into the reactor logged by the facility, the estimated average reactor vent emission rates for H₂S and total sulfur compounds were 0.0012 and 0.0026 pounds per hour, respectively.
- The average sulfate, sulfide, and TSS concentrations in the bioreactor effluent were 3,480, 2,030, and 20,130 milligrams per liter, respectively.
- The average bioreactor effluent disposal rate during the 1-month monitoring period was 110 gallons per hour, or about 2,600 gallons per day. Resulting sulfate, sulfide, and TSS effluent disposal rates are 77, 45, and 444 pounds per day, respectively.

Operational Performance

- Biogas flow rates through the system during the three-day sampling period ranged from 119 to 504 standard cubic feet per minute (scfm) and averaged 322 scfm [or approximately 464 thousand cubic feet per day (10³ cfd)].
- Table S-1 summarizes the sour and processed gas average composition, H₂S content, and heat content for nine samples collected before and after the THIOPAQ system. The average H₂S removal efficiency on a mass basis was 99.8 percent. Biogas lower heating value (LHV) increased by approximately 8.6 percent due to changes in gas composition, specifically, removal of some of the CO₂ from the sour biogas.

Table S-1. Composition and Properties of Sour and Processed Biogas - Dry Basis

	Gas Composition					Higher and lower heating values (Btu/scf)		Relative Density	Compressibility
	CH ₄ (%)	CO ₂ (%)	N ₂ (%)	H ₂ S (ppm)	Total S (ppm)	HHV	LHV		
Avg. Sour Gas	62.44	33.75	1.89	19318	19336	633.9	568.6	0.8970	0.9970
Avg. Processed Gas	68.89	28.71	2.03	27.5	42.9	685.6	617.2	0.8454	0.9972

- During a continuous NaOH tank level monitoring period of 376 hours, a total of 947 gallons of 50-percent NaOH solution was consumed for an average consumption rate of 2.52 gal/hr (60.5 gal/day). The average sour biogas feed rate during that monitoring period was 355 scfm (or 511 x 10³ cfd) with an average 1.93 percent sulfur content. The average 50-percent NaOH consumption normalized to biogas feed rate was 0.12 gallons per thousand cubic foot of biogas processed, or 0.44 lb NaOH per lb sulfur.
- The average elemental sulfur content of the solids cake samples was 43.6 percent (wet basis). On a dry basis, elemental sulfur averaged 59.2 percent.

Details on the verification test design, measurement test procedures, and Quality Assurance/Quality Control (QA/QC) procedures can be found in the Test Plan titled *Test and Quality Assurance Plan – Paques THIOPAQ and Shell-Paques Gas Purification Technology* (SRI 2004). Detailed results of the verification are presented in the Final Report titled *Environmental Technology Verification Report for The Paques THIOPAQ Gas Purification Technology* (SRI 2004). Both can be downloaded from the GHG Center's web-site (www.sri-rtp.com) or the ETV Program web-site (www.epa.gov/etv).

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Greenhouse Gas Technology Center

A U.S. EPA Sponsored Environmental Technology Verification () Organization



Environmental Technology Verification Report

NATCO Group, Inc. – Paques THIOPAQ Gas Purification Technology

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ACRONYMS AND ABBREVIATIONS

ADQ	Audit of Data Quality
ASTM	American Society for Testing and Materials
Btu	British thermal units
Btu/scf	British thermal units per standard cubic foot
CAR	Corrective Action Report
cfm	cubic feet per minute
DQI	data quality indicator
DQO	data quality objective
EPA	Environmental Protection Agency
ETV	Environmental Technology Verification
gal	U.S. gallons
gal/day	gallons per day
gal/hr	gallons per hour
GHG Center	Greenhouse Gas Technology Center
lb	pound
lb/hr	pounds per hour
lb/day	pounds per day
LHV	lower heating value
mg/l	milligrams per liter
MGD	million gallons per day
NATCO	NATCO Group, Inc.
PEA	Performance Evaluation Audit
ppbv	parts per billion volume
ppmv	parts per million volume
QA/QC	Quality Assurance/Quality Control
QMP	Quality Management Plan
scfm	standard cubic feet per minute
TQAP	Test and Quality Assurance Plan
TSA	technical systems audit
10 ³ cf/d	thousand cubic feet per day
UASB	upflow anaerobic sludge blanket
WPCF	Water Pollution Control Facility

1.0 INTRODUCTION

1.1. BACKGROUND

The U.S. Environmental Protection Agency's Office of Research and Development operates the Environmental Technology Verification (ETV) program to facilitate the deployment of innovative technologies through performance verification and information dissemination. The goal of ETV is to further environmental protection by accelerating the acceptance and use of improved and innovative environmental technologies. Congress funds ETV in response to the belief that there are many viable environmental technologies that are not being used for the lack of credible third-party performance data. With performance data developed under this program, technology buyers, financiers, and permittees in the United States and abroad will be better equipped to make informed decisions regarding environmental technology purchase and use.

The Greenhouse Gas Technology Center (GHG Center) is one of six verification organizations operating under the ETV program. The GHG Center is managed by EPA's partner verification organization, Southern Research Institute (Southern), which conducts verification testing of promising greenhouse gas mitigation and monitoring technologies. The GHG Center's verification process consists of developing verification protocols, conducting field tests, collecting and interpreting field and other data, obtaining independent peer-reviewed input, and reporting findings. Performance evaluations are conducted according to externally reviewed verification Test and Quality Assurance Plans (TQAP) and established protocols for quality assurance.

The GHG Center is guided by volunteer groups of stakeholders. These stakeholders guide the GHG Center in selecting technologies that are most appropriate for testing, help to disseminate results, and review test plans and technology verification reports. A technology area of interest to some GHG Center stakeholders is reliable renewable energy sources. The generation of heat and power at industrial, petrochemical, agricultural, and waste-handling facilities with renewable energy sources such as anaerobic digester gas (biogas) or landfill gas is a particular interest. These gases, when released to the atmosphere, contribute millions of tons of methane emissions annually in the U.S. Cost-effective technologies are available that can curb these emissions by processing the gases to remove harmful constituents, recovering the methane, and using it as an energy source. Removal of the harmful components of biogases (primarily hydrogen sulfide and other sulfurous compounds) while minimizing the creation of secondary waste streams and effluents is essential to development of these renewable energy sources.

NATCO Group, Inc. (NATCO), located in Houston, Texas, requested that the GHG Center perform an independent performance verification of the Paques THIOPAQ technology – a gas purification system. This technology, developed in The Netherlands by Paques BioSystems, is designed to safely and efficiently remove hydrogen sulfide (H₂S) from biogas and other sour gases while minimizing the generation of harmful emissions or effluents. The process is suitable to applications where the processed biogas can be utilized as fuel. The system also allows the production of elemental sulfur for subsequent sale or use. A variation of this technology is the Shell-Paques system, which operates on the same principles as THIOPAQ, but includes system components that can process low-, medium-, and high-pressure natural gas, as well as acid gas and Claus tail gas. The Shell-Paques version is of particular interest to the natural gas, petrochemical, and refining industries. The two versions of the technology are similar in principle and operation, but this verification applies only to the Paques THIOPAQ version. A

THIOPAQ system installed and operating at a midwestern water pollution control facility (WPCF) was selected for this verification.

Field tests were performed on the Paques THIOPAQ system to independently verify the performance of this technology. The verification included evaluations of both environmental and operational performance of the system. Details of the verification test design, measurement test procedures, and Quality Assurance/Quality Control (QA/QC) procedures can be found in the Test and Quality Assurance Plan (TQAP) titled *Test and Quality Assurance Plan – Paques THIOPAQ and Shell-Paques Gas Purification Technology* [1]. The TQAP describes the rationale for the experimental design, the testing and instrument calibration procedures planned for use, and specific QA/QC goals and procedures. The TQAP was reviewed and revised based on comments received from industry experts and the EPA Quality Assurance Team. The TQAP meets the requirements of the GHG Center's Quality Management Plan (QMP) and satisfies the ETV QMP requirements.

The remainder of Section 1.0 describes the THIOPAQ system technology and test facility and outlines the performance verification procedures that were followed. Section 2.0 presents test results, and Section 3.0 assesses the quality of the data obtained. Section 4.0, submitted by NATCO, presents additional information regarding the THIOPAQ system. Information provided in Section 4.0 has not been independently verified by the GHG Center.

1.2. PAQUES THIOPAQ TECHNOLOGY DESCRIPTION

Renewable biogas produced from the management of municipal and farm waste is a potentially viable energy source. Operational performance data is needed to verify the ability of technologies to remove contaminants in biologically generated gas streams. Biogas can be made more usable and environmentally benign if contaminants (primarily H₂S) are removed prior to their use as an energy source. Conventional H₂S removal technologies such as caustic scrubbers are available, but these systems may be costly to operate and produce hazardous effluents. Redox processes are also available, but these require use of chelating agents and generate potentially hazardous effluents.

1.2.1. THIOPAQ Process

THIOPAQ is a biotechnological process for removing H₂S from gaseous streams by absorption into a mild alkaline solution followed by the oxidation of the absorbed sulfide to elemental sulfur by naturally occurring microorganisms. THIOPAQ is licensed by Paques for biogas applications. The Shell- Paques version of the technology is used for refinery gas and other high pressure applications.

The Paques desulfurization technology is a caustic scrubber-based system designed to maintain a high level of H₂S removal while addressing several shortcomings of conventional technologies. According to NATCO, this technology is designed to: (1) reduce hazardous effluents from the scrubber by aerobically digesting the waste into a more benign sulfurous product, and (2) regenerate and recycle sodium hydroxide (NaOH) needed in the scrubber. The THIOPAQ system is specifically designed for low-pressure biogas streams. NATCO states that H₂S to sulfur conversion efficiency is expected to be between 95 to 99 percent.

The THIOPAQ process begins with the input of biogas or sour gas into an absorber unit (or scrubber) at ambient pressure. Scrubber design is site-specific in regards to vessel size, construction specifications, and gas and solution flow capacities. System pH ranges from 8.2 to 9. The counter-current scrubber design washes the sour gas (or biogas) in a packed bed or packed beds containing 2-inch Pall rings. A total draw-off tray combined with a liquid redistribution tray in-between the packed beds ensures proper

liquid redistribution. Treated gas (sweet gas) exits the scrubber top, enters a knockout drum, and is routed to the sales gas stream.

The liquid stream is then sent to the bioreactor (ambient pressure). A blower supplies air to a distribution header in the bottom section of the reactor, enhancing mixing. Some of the oxygen is consumed in reactions with sulfide to produce sulfur by the actions of the Thiobacillus bacteria. The bacteria are maintained using a continuous feed of proprietary nutrients supplied by Paques. These nutrients are pumped into the bioreactor with a small metering pump.

Regenerated solvent from the bioreactor is pumped back to the scrubber for reuse. A portion of the solvent from the bioreactor is also pumped to a settling tank where solids are separated from the solution and collected gravimetrically. NATCO estimates a potential elemental sulfur purity of 95 percent in the sludge cake from the vacuum filter press. The solution is then recycled back to the bioreactor for reuse. A general process flow diagram of the THIOPAQ process is shown in Figure 1-1.

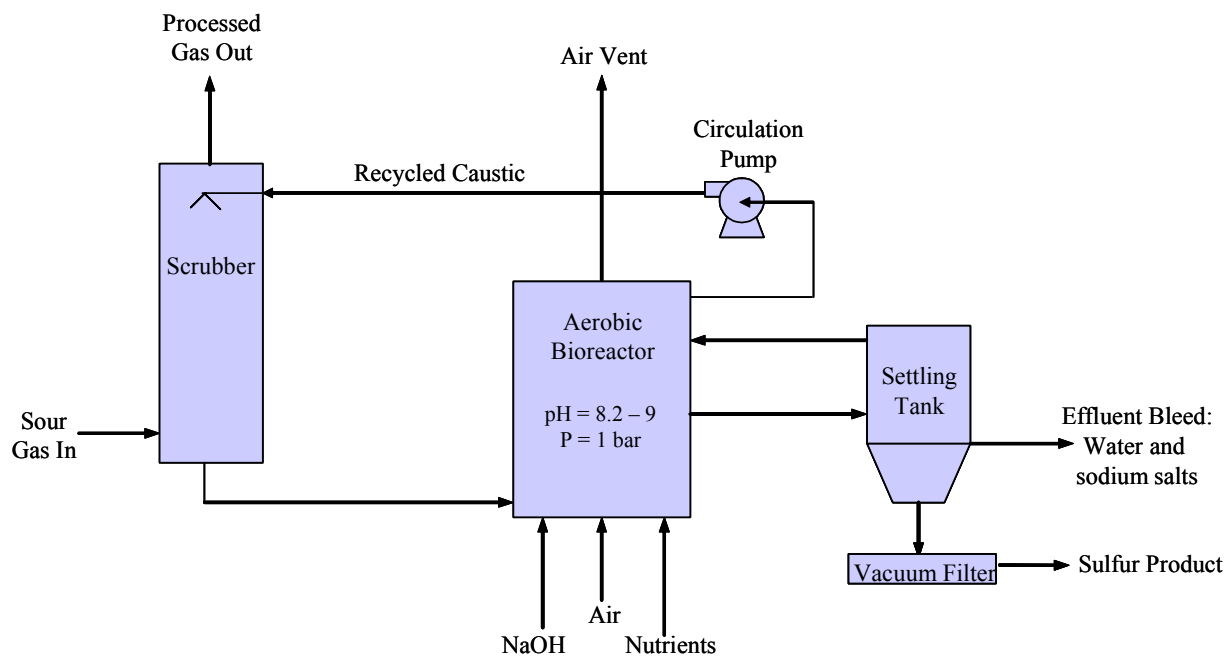
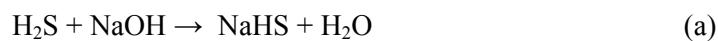


Figure 1-1. Simplified THIOPAQ System Schematic

1.2.2. Process Chemistry

The reactions that drive these processes occur primarily in the scrubber and the bioreactor. The first main reaction in the scrubber (at feed gas pressure) is H₂S absorption. The H₂S is absorbed by the dilute caustic scrubber solution (NaOH) in the scrubber according to the following chemical reaction:

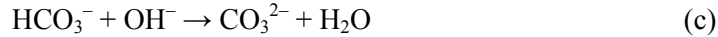


Reaction (a) shows that solution alkalinity is consumed during this process. The solution leaving the scrubber (NaHS + H₂O) is directed to the bioreactor.

Hydroxide ions are also consumed in the scrubber during a CO₂ absorption step:



and a carbonate formation step:

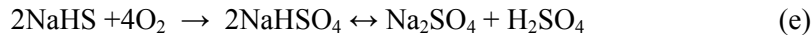


Note: According to NATCO, the actual amount of CO₂ removed from the sour gas generally is small. The carbonate / bicarbonate buffer moderates the solution pH to the appropriate range, providing hydroxide ions for H₂S removal and allowing for the selective removal of H₂S and the slip of CO₂.

The liquid stream loses the OH⁻ ion in the scrubber and gains the OH⁻ ion back in the bioreactor. The bioreactor operates near atmospheric pressure and is aerated (constant mix) with a controlled inflow of ambient air. The bacteria react with the spent scrubber solution and convert the dissolved sulfide to solid elemental sulfur as follows:



This step relies on the biological oxidation of the dissolved sulfide into elemental sulfur using aerobic bacteria (Thiobacillus). A small portion of the dissolved sulfide (less than 5 percent) is completely oxidized to sulfate as follows:



Solution alkalinity is partially regenerated in the bioreactor via the reactions in equation (d). Caustic solution regeneration eliminates the need for a large supply of NaOH to maintain pH above 8.2. Solution regeneration is not 100 percent as shown in equation (e), so additional make-up NaOH is required. A controlled amount of 50-percent NaOH is added to the system continuously using a small metering pump. An automated level sensor detects when bioreactor solution level is high, and a controlled amount of system effluent is bled to the wastewater treatment plant influent stream, restoring proper solution level. This bleed stream also prevents the accumulation of sulfate ions. Air leaving the bioreactor is vented to atmosphere.

According to NATCO, the sulfur produced has a hydrophilic nature, which significantly reduces the chance of equipment fouling or blocking. This characteristic also makes the product suitable for agricultural use as fertilizer. Alternatively, the sulfur can be melted to yield a high-purity product which meets international Claus sulfur specifications.

1.2.3. Host Facility Description and THIOPAQ Integration

The WPCF that hosted the THIOPAQ verification is a 40-million gallon per day (MGD) wastewater treatment facility specifically designed to process industrial wastewater streams from numerous local industries including grain and food processing plants and a paper mill. Approximately three MGD of flow coming from the paper mill is characterized as low-flow, high biological oxygen demand-type waste. The facility uses three Biothane upflow anaerobic sludge blankets (UASBs) to pre-treat this wastewater stream. The system was designed to handle an average of 818 and a maximum 1184 cubic feet per minute (cfm) and was built in anticipation of future plant expansion. Currently, the three UASBs generate around 300 to 600 cfm of biogas [or around 432 to 864 thousand cubic feet per day (10³ cfd)].

Biogas composition can vary but is generally 60 percent CH₄, 38 percent CO₂, and 1 to 1.5 percent H₂S. The gas generated in each UASB is collected, combined, compressed, and used to fuel a sludge incinerator within the plant. The sludge incinerator will consume all of the biogas generated on-site under normal plant operations. The biogas is flared during rare occurrences when the incinerator is not operating or is being fueled with natural gas.

The facility installed a THIOPAQ system in 2001 to efficiently scrub H₂S from the biogas prior to its use as fuel or incineration in the flares (Figure 1-2).



Figure 1-2. THIOPAQ System Tested

The THIOPAQ system tested here has a biogas treatment capacity of 1000 cubic feet per minute, is largely automated and PLC-controlled, and includes numerous monitoring devices to record the system parameters shown in Figure 1-1. Table 1-1 summarizes some of the monitoring instrumentation used at the plant.

The system at this facility decants a liquid effluent batch only about once per week. Solids are removed by a vacuum filter press (made by Straight-Line Filter Press) approximately once every three weeks. The facility has not yet found a buyer or user of the solid waste containing sulfur, so the solids are collected in a large bin and disposed of in a landfill. The bioreactor vent is a two-foot diameter rain-capped vent emitting directly to atmosphere.

Table 1-1. Host Site THIOPAQ Monitoring Instrumentation

Parameter	Typical Range	Instrumentation	Location
Biogas flow (generation) rate	100 - 200 acfm per each UASB	Fluid Components International, Model ST98 thermal mass flow meters (three total)	One on the outlet of each UASB
Scrubber solution flow rate	800 to 1,000 gpm	Promag 50/53W electromagnetic flow monitor	Scrubber pump discharge
NaOH consumption rate	Approximately 1,500 lb/day	Milltronics level sensor	NaOH holding tank

1.3. PERFORMANCE VERIFICATION OVERVIEW

Field tests were performed on a Paques THIOPAQ system to independently verify the performance of this technology. Field testing by the GHG Center was conducted over a three-day period at the facility. A one-month period of process monitoring data including biogas flow rate, NaOH consumption, bioreactor tank level, and air flow rates into the bioreactor was provided by the facility. These data allowed the GHG Center to evaluate these system operations over a longer term. The verification included evaluation of both environmental and operational performance of the system.

Environmental Performance

- Air Emissions
- Liquid Effluent

Operational Performance

- H₂S Removal Efficiency
- Gas Composition and Quality
- NaOH Consumption
- Sulfur Purity

Sections 1.3.1 and 1.3.2 briefly describe the sampling and analytical procedures. Detailed descriptions of the sample collection, handling, custody, and analytical procedures that were followed during this verification can be found in the TQAP. Several modifications to the sampling and analytical procedures specified in the TQAP were implemented during field testing. These changes in test procedures are discussed in Section 1.3.3.

1.3.1. Environmental Performance Parameters

Air Emissions. The bioreactor vent continuously releases vent gases to the atmosphere. The GHG Center conducted measurements on this vent to independently verify concentrations H₂S and other sulfur compounds, if any, that are liberated from the vent. GHG Center personnel collected three vent air samples in Tedlar bags on each of three consecutive days for analysis. Collected samples were express shipped to Air Toxics, Ltd. in Folsom, California for next day analysis. Concentrations of H₂S and other sulfur compounds were quantified following ASTM Method D5504 [2] and reported in units of parts per billion by volume (ppbv). Vent gas flow rates were not independently verified (see Section 1.3.3). However, the plant continuously monitors the amount of air injected into the bioreactor. These data were

provided to the GHG Center for use here as a surrogate for the vent air release rate since the maximum vent volumetric flow rate should be equivalent to or less than the volumetric air input.

Liquid Effluent. The THIOPAQ system includes only one liquid effluent point – the effluent bleed stream used to regulate solution conductivity. The THIOPAQ system reduces the volume of hazardous liquid effluent associated with conventional wet scrubbers, but small amounts of effluent must be bled from the system intermittently to maintain proper system pH and conductivity. This effluent, consisting mainly of water and small amounts of sulfate and sulfides, is directed back to the wastewater treatment facility. Under normal plant operations, it is only necessary to remove liquid effluent from the system every week or so. Rather than attempt to capture these events and measure the volume of effluent removed, the facility provided tank level data for a one-month period. These data allowed the GHG Center to calculate the amount of liquid removed from the system and then determine an average weekly effluent rate.

A total of seven liquid effluent samples were collected during the verification period and analyzed for total sulfates (EPA Method 300.0), total sulfides (EPA Method 376.1), and total suspended solids (EPA Method 160.2) by CT Laboratories of Baraboo, Wisconsin.

1.3.2. Operational Performance Parameters

H₂S Removal Efficiency. The Center conducted three tests per day to determine the system's H₂S removal efficiency. This was done in conjunction with the environmental testing outlined above. Time-integrated biogas samples were collected in Tedlar bags simultaneously at the inlet and outlet of the scrubber during each test. Collected samples were express-shipped to Empact Analytical in Brighton, Colorado for determination of H₂S and 17 other sulfur-based compounds by ASTM Method 5504. Results of each species in each sample were standardized and reported in units of parts per million by volume (ppmv). Removal efficiency was calculated based on the measured inlet and outlet concentrations and the biogas throughput values provided by facility instrumentation.

Gas Composition and Quality. Gas processing by the THIOPAQ system is not expected to significantly impact gas composition or quality other than removal of H₂S. The center examined gas quality before and after treatment in the THIOPAQ to verify that gas quality was not significantly affected by treatment. The same sets of integrated biogas samples used to determine H₂S removal were analyzed by Empact to determine gas composition according to ASTM Method D1945 [3] and lower heating value using ASTM D3588 [4]. Results of the analysis were examined to determine if the composition and lower heating value (LHV) of the gas are significantly changed by THIOPAQ processing.

NaOH Consumption Rate. The THIOPAQ system reduces NaOH consumption through NaOH regeneration in the bioreactor. The host facility uses a metering pump to add NaOH to the process and a NaOH tank level sensor to continuously monitor consumption. The center evaluated the NaOH tank level data for a one-month period to report the NaOH consumption rate at this facility.

Sulfur Production and Purity. The sulfur containing solids cake generated by the THIOPAQ system represents a potentially salable product. The center collected a total of five solids cake samples from the vacuum press for determination of moisture content and to estimate elemental sulfur content. Samples were submitted to Core Laboratories of Houston, Texas for analysis.

Process Operations. Several key operational parameters that are logged by the facility were provided to the GHG Center to aid in post-testing data analysis. These included biogas flow rate through the system, scrubber water flow rate, bioreactor level, NaOH tank level, and air flow rate to the bioreactor. These

data, all collected by site metering equipment (Table 1-1), are not used as primary verification parameters but are included in this report to document system operations during testing. They also allowed the center to evaluate operational stability or variation during the verification test periods.

1.3.3. Modifications to TQAP

The procedures and protocols described in the TQAP were selected prior to visiting the WPCF. When the testing began at the site, several changes were necessary for successful implementation. These changes were needed to adapt the procedures to site-specific operating practices and the characteristics of the process streams that were measured. The changes to the verification protocol are described in Corrective Action Reports that were submitted to the GHG Center QA Manager and filed at the GHG Center. A summary of the changes that were adopted is presented here.

Upon arrival at the test site it was noted that the settling tank described in the system design documentation was no longer an active component of the process. Consequently, suspended solids in the bioreactor were higher than anticipated in the test plan. It was also noted that solids removal did not occur daily, but rather every three weeks or so after manual measurements of suspended solids passed a threshold value. These operations were highly operator dependant and were not conducted on a regular basis. Some operators would instead route the solids slurry back to the plant and not to the filter press for recovery. Therefore, regular, meaningful measurements of solids recovery were not possible. Liquid bleed for pH and conductivity control was still triggered by the bioreactor tank level and was roughly a fixed volume (approximately 6 inches in tank level or 1,590 gallons per event). This revision of the discharge schedule prevented the planned measurement of smaller flows as presented in the TQAP. These process modifications and other corrections of the initial information from the plant required changes in verification parameters and test methods. In each case the proposed changes were reviewed by the project QA Manager and approved upon his recommendation by GHG Center management.

These configuration and operational changes in the THIOPAQ process were addressed by the following changes in experimental design and methods:

- Elimination of direct measurement of solids production rate as non-meaningful.
- Use of plant measurements for bioreactor vent flow rate, with spot verification using vane anemometer.
- Change in procedure for effluent disposal rate using non-verified plant data. The planned gravimetric measurement was deleted as unworkable and replaced with data from the plant process instruments to detect bleed event, record the level change and to quantify the resulting volume that was removed from the reactor (a 6-inch drop equals 1,590 gallons).
- Addition of total suspended solids measurement to liquid sample analysis, and change of sample schedule.
- Addition of extended data period (one month of hourly averages) for plant process measurements.

Other changes in the sampling and measurements approach were implemented in the field and are described below. Documentation and QC checks were followed as outlined in the TQAP for setup and measurement procedures for sample acquisition and sample handling.

Vent Flow Measurement: The field team leader attempted measurements and found that a standard pitot traverse was impractical due to cyclonic flow, duct configuration, wind, and low flow rate. The

measurement plan was changed to use plant process data with confirmatory check runs using vane anemometer.

Collection of Vent Gas: Integrated 1-liter bag samples were collected over a 3- to 4- minute period rather than the one-hour sample specified in the TQAP.

Collection of sour and processed biogas samples: In consultation with the analytical laboratory, cylinder samples for gas quality were eliminated and the analyses were performed on bag samples used for sulfur species (ASTM 5504) analysis. Use of Tedlar bags minimizes H₂S sample deterioration. In addition, the 24-30 hour hold time limit was exceeded. Due to logistical issues such as sample packaging and shipping, samples were held for up to 48 hours before analysis. This extended holding time may have caused sample degradation or losses of H₂S in the bags. Although the extent of the degradation, if any, cannot be quantified, it is expected to be minimal. This is because results reported here are consistent with sour and processed biogas H₂S concentrations measured at the facility which are analyzed within an hour of collection.

Liquid NaOH Solution Flow Measurement: The QC check was changed to use an onsite volume check device (graduated sight glass).

2.0 VERIFICATION RESULTS

The verification period was June 1 through July 1, 2004. Field testing was conducted by GHG Center personnel over a 3-day test period from June 29 through July 1, 2004. Bioreactor vent gas, sour biogas, processed biogas, liquid effluent, and solids samples collected during this 3-day test period are summarized in Table 2-1. Follow-up effluent and solids samples were collected by facility personnel on July 14. Key THIOPAQ operational data including biogas throughput, reactor air flow, reactor level, and NaOH tank level were logged by the facility over the entire one-month verification period and provided to the GHG Center. Results of the verification of THIOPAQ environmental and operational performance are presented in Sections 2.1 and 2.2. The laboratory reports detailing sample analyses are on file at the GHG Center and available on request, but too voluminous for inclusion here. A sulfur mass balance for the technology could not be calculated because operational procedures at the facility were not appropriate for measuring the sulfur solids production rate.

Table 2-1. Sampling Matrix

Date	Sample Type (Sample ID and time collected)				
	Bioreactor Vent Gas	Sour Biogas	Processed Biogas	Liquid Effluent	Solids Cake
6/29/04	Vent 1 (0920)	Sour gas 1 (0945)	P gas 1 (0945)	Effluent 1 (1000)	
	Vent 2 (1115)	Sour gas 2 (1125)	P gas 2 (1120)		
	Vent 3 (1315)	Sour gas 3 (1325)	P gas 3 (1320)		
6/30/04	Vent 4 (1030)	Sour gas 4 (1055)	P gas 4 (1050)	Effluent 2 (1030)	
	Vent 5 (1130)	Sour gas 5 (1200)	P gas 5 (1155)		
	Vent 6 (1320)	Sour gas 6 (1330)	P gas 6 (1325)	Effluent 3 (1315)	
7/1/04	Vent 7 (0840)	Sour gas 7 (0850)	P gas 7 (0845)		Solids 1 (0900)
	Vent 8 (0950)	Sour gas 8 (1000)	P gas 8 (0955)	Effluent 4 (1100)	Solids 2 (1000)
	Vent 9 (1120)	Sour gas 9 (1135)	P gas 9 (1130)	Effluent 5 (1130)	Solids 3 (1100)
7/14/04 ^a				Effluent 6	Solids 4
				Effluent 7	Solids 5

^a Samples were collected by facility personnel on 7/14/04. Collection times were not recorded.

2.1. ENVIRONMENTAL PERFORMANCE

2.1.1. Air Emissions

Three vent gas samples were collected from the bioreactor on each of the three test days of the technology verification. The schedule of vent gas sampling is included in Table 2-1. The results of the analyses of these samples are summarized in Table 2-2. Full documentation of the laboratory analyses are maintained in the GHG Center files. As shown in Table 2-2, concentrations of H₂S and total sulfur compounds were very low, averaging 929 and 1,961 ppbv, respectively. H₂S typically comprised about half of the total sulfur compound concentrations. Methyl mercaptan, dimethyl sulfide, and dimethyl disulfide were the other prominent sulfur compounds.

Table 2-2. Summary of Sulfur Compounds in Vent Gas Samples

Date	Time	H₂S ppbv	Total S Compounds ppbv
6/29/04	0920	990	2154
	1115	95	1235
	1315	7.2	903
6/30/04	1030	240	1105
	1130	200	738
	1320	1300	2523
7/1/04	0840	3900	5120
	0950	430	1494
	1120	1200	2381
Average		929	1961

Difficulties with direct vent gas flow rate measurement forced the Center to use plant process data for the air blower flow rates as a surrogate for the vent gas flow. After analyzing these data, it is apparent that the air flow through the reactor is highly variable. The flow rates logged during the 3-day sampling period are plotted as Figure 2-1 and summarized as follows:

Bioreactor Vent Gas Flow Rate Statistics

<u>Statistic</u>	<u>Value (scfm)</u>
Average	246.3
Maximum	432.0
Minimum	91.0
Standard Deviation	56.5

This level of variability was evident over the entire 1-month verification period and is reported by the facility to be typical for this gas stream. The variable speed air blower is regulated by the THIOPAQ control system to respond to changes in biogas throughput. Biogas flow rates through the system, also plotted in Figure 2-1, are also highly variable. These variabilities complicated evaluation of vent gas flow rates. GHG Center personnel also obtained vane anemometer readings in the vent as an independent check on the air blower process data. The agreement between the two data sets is poor, further complicating this measurement. Since the flow rate data is poor, only the concentrations of sulfur compounds in the vent gas are summarized in Table 2-2.

To provide potential THIOPAQ system users with an estimate of potential bioreactor emissions, the average concentrations shown in table 2-2, and the average vent gas flow rate for the 3-day test period were used to calculate estimated average emission rates in units of pounds per hour (lb/hr). The average estimated H₂S and total sulfur (quantified as H₂S) emission rates for the bioreactor vent were 0.0012 and 0.0026 lb/hr, respectively.

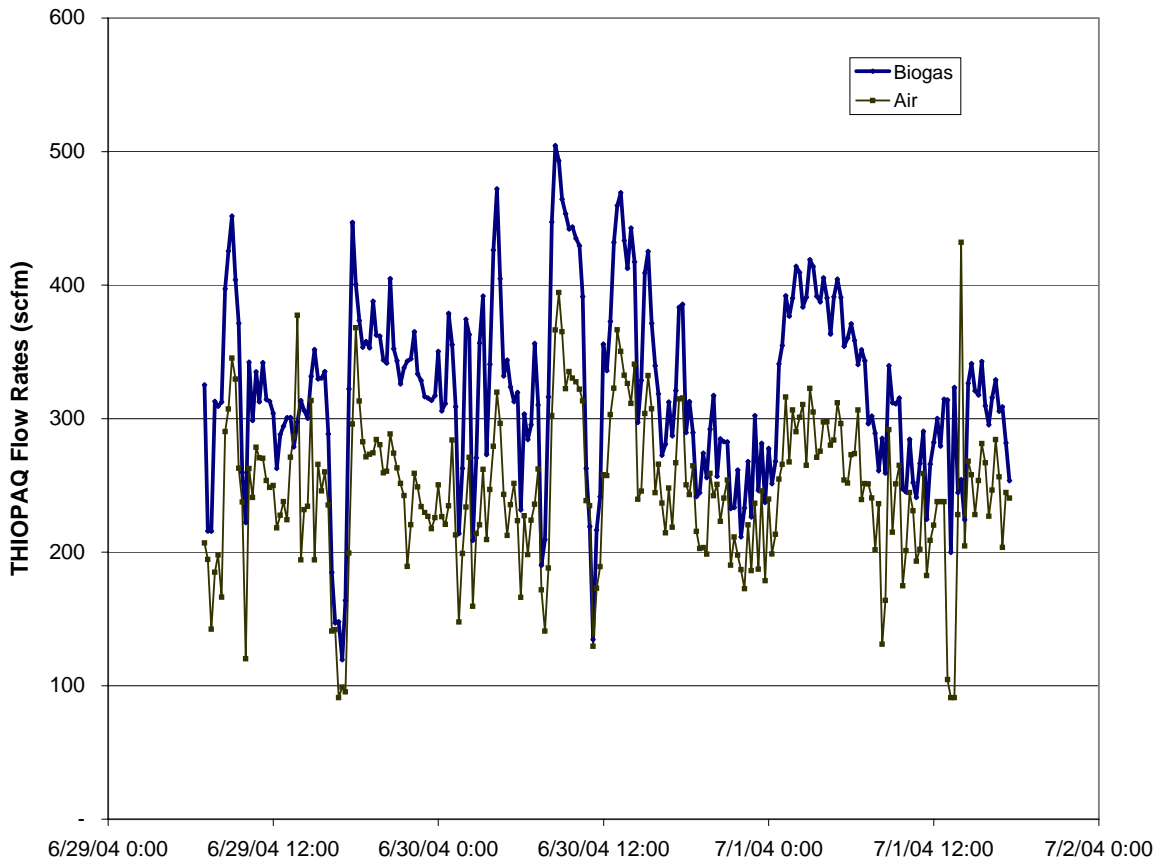


Figure 2-1. Biogas and Reactor Air Flow Rates During Testing

2.1.2. Liquid Effluent

A total of seven samples of THIOPAQ effluent (reactor slurry) were collected during the verification for determination of total sulfides, total sulfates, and total suspended solids. Results are summarized in Table 2-3.

Results of the sulfide analyses were much higher than expected and, after investigation of ion chromatographs run by the laboratory, it is evident that thiosulfate was present in the samples. Thiosulfate is a potential interference for the analytical method used here, so results presented here are possibly biased high by the presence of thiosulfate.

One hour average tank levels were provided by the facility over the entire 1-month verification period. A total of 81,600 gallons of effluent were released during the verification period. Based on these data, the average effluent rate was approximately 110 gallons per hour (gal/hr), or about 2,600 gallons per day (gal/day). These values were not independently verified by the GHG Center, but are used to estimate mass emissions of sulfate, sulfide, and solids during the period.

The average sulfate, sulfide, and TSS concentrations shown in Table 2-3 and the average effluent rate of 2,600 gal/day during the period were then used to estimate discharge rates. The estimated liquid disposal rates for sulfate, sulfide, and solids during the verification period are 77, 45, and 444 lb/day, respectively.

Table 2-3. Total Sulfate, Total Suspended Solids and Total Sulfide in Reactor Slurry

Date	Sample	Total Sulfate mg/l	Total Suspended Solids mg/l	Total Sulfide^a mg/l
6/29/04	Effluent #1	3740	22150	1680
6/30/04	Effluent #2	3710	20940	1770
	Effluent # 3	3730	21180	2000
7/1/04	Effluent # 4	4020	21560	1820
	Effluent # 5	3610	20730	1880
7/14/04	Effluent # 6	2850	16800	2470
	Effluent # 7	2690	17560	2560
	Average	3480	20130	2030

^a Potential thiosulfate interference causing high bias in total sulfide test results.

2.2. OPERATIONAL PERFORMANCE

2.2.1. Gas Composition, Gas Quality, and H₂S Removal Efficiency

The primary purpose of the THIOPAQ technology is to safely and efficiently remove H₂S from sour gas. A total of nine sour and processed biogas samples were collected by GHG Center personnel during the 3-day verification period and analyzed for H₂S content. Biogas flow rate through the system during the test period ranged from 119 to 504 scfm and averaged 322 scfm (or 464 x 10³ cfd). The average throughput was approximately 39 percent of design average capacity.

Average H₂S removal efficiency (mass %) is calculated based on the average measured concentrations of H₂S in the sour biogas and the treated biogas as well as the average measured flow rate of biogas into the scrubber and an estimated flow rate out of the scrubber. Changes in gas flow rate into and out of the scrubber were expected to be negligible. Therefore, an equivalent biogas input and output flow rate was assumed in the TQAP for determining the mass flows of H₂S in and out of the scrubber, and the resulting mass removal efficiency for the system. However, the biogas flow rate out of the scrubber is slightly less than the input flow rate due to the removal of H₂S and a portion of the CO₂ in the scrubber. The biogas flow rate out of the scrubber was estimated based on a material balance for the components of the biogas (N₂ and CH₄) that were not impacted by the scrubber. Material balance calculations yield a maximum change in biogas flow rate of 9.7 %.

Although significant changes were observed in biogas flow rate due to the scrubbing of the H₂S and CO₂, a sensitivity analysis indicates that the maximum impact of the reduced biogas flow rate on the H₂S removal efficiency calculation is 0.01% because of the large change in H₂S concentration. Therefore, the assumption of equivalent flow rates in calculation of the H₂S removal efficiency does not significantly

impact the data quality, and is used in this report. H₂S removal efficiency is then calculated as the change in concentration of H₂S across the scrubber.

The same samples were analyzed for basic gas composition and heating value to evaluate if gas treatment by THIOPAQ impacted the quality of the gas. Results are summarized in Table 2-4. Figure 2-2 illustrates the gas composition before and after the treatment.

Table 2-4. Composition and Properties of Sour and Processed Biogas - Dry Basis

Sample ID	Gas Composition					Heat Content (Btu/scf)		Relative Density	Compressibility
	CH ₄ (%)	CO ₂ (%)	N ₂ (%)	H ₂ S (ppm)	Total S (ppm)	HHV	LHV		
Sour Gas 1	61.84	35.28	1.62	12603	12619	620.8	558.8	0.9088	0.9970
Processed Gas 1	67.51	30.71	1.42	37.6	53.8	671.9	604.8	0.8604	0.9971
Sour Gas 2	62.23	34.6	1.80	13869	13885	625.0	562.6	0.9032	0.9970
Processed Gas 2	67.59	30.57	1.47	36.1	51.9	672.7	605.5	0.8592	0.9971
Sour Gas 3	62.73	34.57	1.06	16489	16503	633.4	570.1	0.9005	0.9970
Processed Gas 3	70.00	28.70	1.08	21.2	35.0	696.7	627.1	0.8385	0.9972
Sour Gas 4	61.8	34.66	1.83	17156	17170	625.1	562.7	0.9045	0.9970
Processed Gas 4	69.12	28.83	1.85	26.0	39.8	687.9	619.2	0.8430	0.9972
Sour Gas 5	60.85	34.51	2.97	16781	16792	614.7	553.3	0.9078	0.9970
Processed Gas 5	68.75	28.02	2.94	16.4	32.8	684.2	615.9	0.8400	0.9973
Sour Gas 6	62.13	34.69	1.27	19180	19199	629.2	566.4	0.9033	0.9970
Processed Gas 6	66.76	31.71	1.28	31.7	47.4	664.5	598.1	0.8690	0.9971
Sour Gas 7	63.57	31.42	2.58	24352	24369	664.7	580.3	0.8794	0.9971
Processed Gas 7	69.14	28.18	2.21	28.2	44.3	688.1	619.3	0.8397	0.9972
Sour Gas 8	63.52	32.06	1.82	25957	25987	646.9	582.3	0.8824	0.9971
Processed Gas 8	70.81	26.39	2.36	31.5	48.6	704.7	634.3	0.8227	0.9973
Sour Gas 9	63.25	31.95	2.07	27472	27497	645.0	580.5	0.8827	0.9971
Processed Gas 9	70.32	25.27	3.69	19.1	32.5	699.7	629.8	0.8188	0.9974
Avg. Sour Gas	62.44	33.75	1.89	19318	19336	633.9	568.6	0.8970	0.9970
Avg. Processed Gas	68.89	28.71	2.03	27.5	42.9	685.6	617.2	0.8454	0.9972

H₂S concentrations in the sour biogas averaged 1.93 percent. Processed gas contained an average 27.5 ppm H₂S. Based on these average concentrations, average H₂S removal efficiency was 99.8 percent. Analysis of the gas compositional data also indicates that the THIOPAQ system reduces the CO₂ concentration of the biogas by an average 15 percent. This change in gas composition creates an increase in methane concentration and heating value. The average LHV of the processed biogas was approximately 8.6 percent higher than the sour gas.

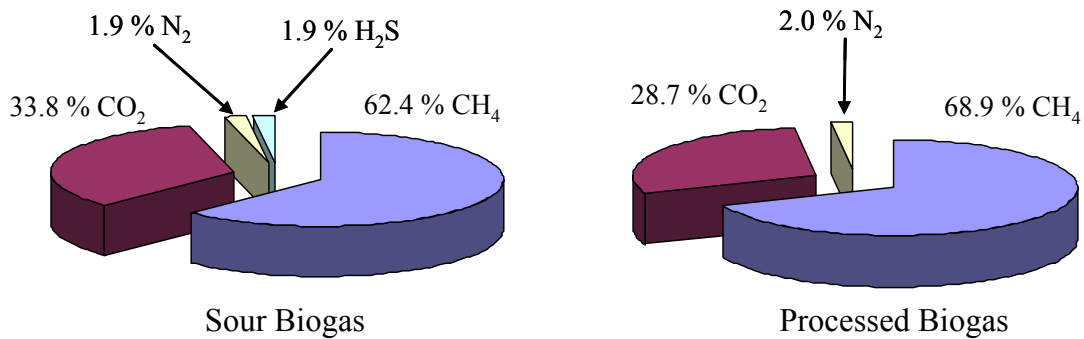


Figure 2-2. Biogas Composition Before and After THIOPAQ

2.2.2. NaOH Consumption

A primary benefit of THIOPAQ is the potential reduction in NaOH consumption, and subsequent operating costs. NaOH consumption rates are site specific and will vary depending on the gas processing rate, sour gas H₂S concentrations, and the desired removal efficiency. Data presented here are representative of the conditions experienced at this facility during the verification period.

Final adjustments to the NaOH feed rate were made by the facility engineer on June 16, 2004. One-hour average tank level data collected from that point in time to the end of the verification period are plotted in Figure 2-3 and are used to report NaOH consumption during the verification. Unless additional adjustments are made to system operations, the NaOH feed rate is constant as illustrated in the figure. During the 376-hour period shown, a total of 947 gallons of 50-percent NaOH solution were consumed for an average consumption rate of 2.52 gal/hr (60.5 gal/day). This rate was field verified by GHG Center personnel (see Section 3.3.2). The average sour biogas feed rate during the monitoring period was 355 scfm (511 x 10³ cfd), or about 39 percent of design capacity. The sour gas was an average 1.93 percent sulfur. The average 50-percent NaOH consumption normalized to biogas feed rate was 0.12 gallons per thousand cubic feet of biogas processed, or 0.44 lb NaOH per lb sulfur.

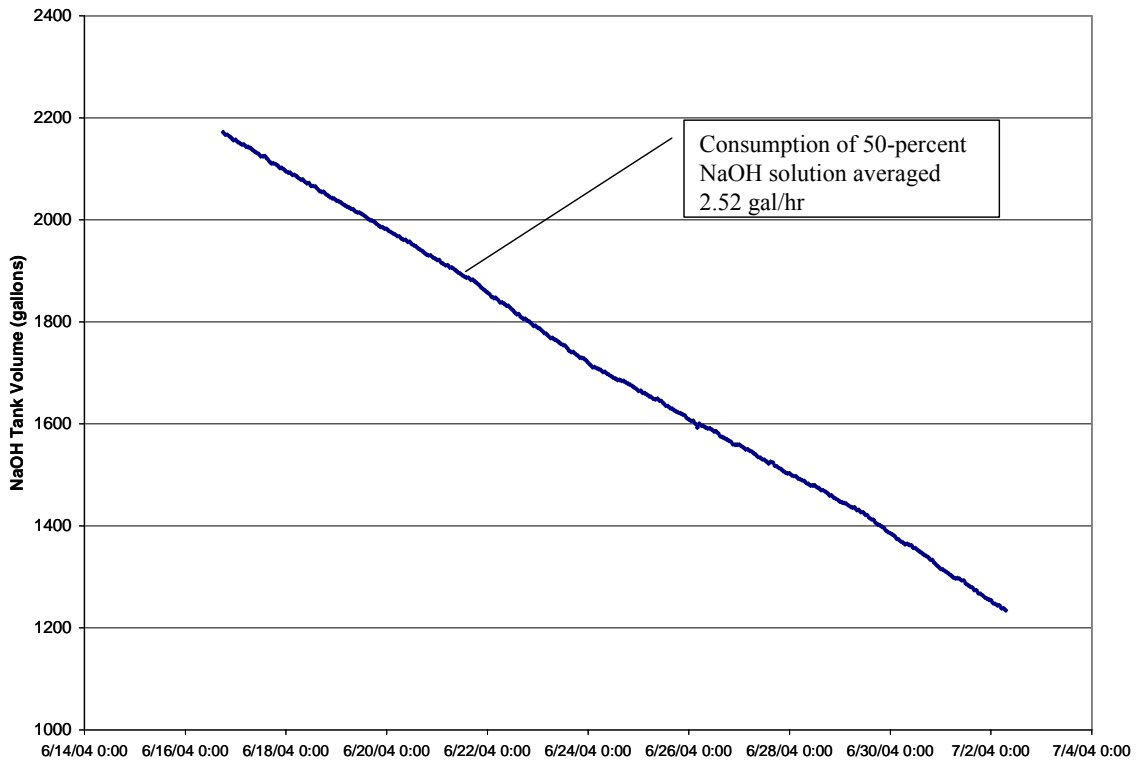


Figure 2-3. NaOH Tank Volume During Verification Period.

2.2.3. Sulfur Production and Purity

A total of five samples of THIOPAQ solids cake were collected during the verification for estimation of elemental sulfur and moisture content. The remaining solids were not identified. Results are ± 10 percent and are summarized in Table 2-5.

Table 2-5. Composition of the Solids Removed From the THIOPAQ Process.

Date	Time	Sulfur %	Other Solids %	Water %
7/1/04	1000	58	22	20
	1030	53	19	27
	1100	53	18	29
7/14/04	1000	26	48	26
	1030	28	44	27
Average		44	30	26

The average elemental sulfur content of the samples as collected was 44 percent. On a dry basis, elemental sulfur averaged 59 percent of the solids collected.

Plans to measure the amount of solids produced by the system were abandoned during field testing. The facility only removes solids every three weeks or so on an as-needed basis. The frequency and amount of solids removed varies widely depending on the amount of solids removed through the liquid effluent (the amount of liquids bled and the total suspended solids content of the liquid). Removal of solids cake at this facility was so operator specific and infrequent that it was deemed too arbitrary for verification here. Because of this, a sulfur mass balance could not be completed for the system.

Analysis of the liquid effluent composition and disposal rate indicated that the average total suspended solids disposal rate via the effluent is 444 lb/day. These solids are the same material that is collected on as solids cake on the vacuum press, so it is estimated that 59.2 percent of the solids disposed of as effluent (or 263 lbs) is recoverable elemental sulfur. Since the THIOPAQ system tested here is not configured to maximize solids recovery rate, the GHG Center could not determine how much of that sulfur is recoverable for subsequent use.

3.0 DATA QUALITY ASSESSMENT

3.1. DATA QUALITY OBJECTIVES

The GHG Center selects methodologies and instruments for all verifications to ensure that the desired level of data quality in the final results is obtained. The GHG Center specifies DQOs for each verification parameter before testing starts and uses these goals as a statement of data quality. Ideally, quantitative DQOs are established based on the level of confidence in results needed by stakeholders or potential users of a technology. In some cases, such as this verification, quantitative DQOs are not well defined and therefore, qualitative DQOs are established.

During this verification, determination of each of the primary verification parameters was conducted based on published reference methods. The methods used are summarized in Table 3-1.

Table 3-1. Verification Reference Methods

Verification Parameter	Required Measurements	Applicable Reference Methods
H ₂ S air emissions (vent)	H ₂ S Concentrations	Modified ASTM D5504
Sulfate emissions	Sulfates in water	EPA Method 300.0
Sulfide emissions	Sulfides in water	EPA Methods 376.1
Total suspended solids	TSS in water	EPA Method 160.2
H ₂ S removal efficiency	Sour gas H ₂ S content	ASTM D5504
	Processed gas H ₂ S content	
Gas Quality	Gas composition	ASTM D1945
	Gas heating value	ASTM D3588
NaOH consumption rate	NaOH consumption rate	None, see Section 3.3.2
Sulfur production	Solids moisture content	Internal laboratory procedures
	Solids sulfur content	

The qualitative DQOs for this verification, then, are to meet all of the QA/QC requirements of each method. In some cases, the laboratory conducting the analyses has internal QA/QC checks that are performed in addition to the method requirements. The analytical methods used here were introduced in Section 1.3. Additional details regarding these methods can be found in the TQAP. A summary of the QA/QC requirements and results for each method are provided in the following sections.

3.2. ENVIRONMENTAL PERFORMANCE PARAMETERS

The primary verification parameters for environmental performance were concentrations of H₂S in the vent gas and sulfate and sulfide concentrations in the effluent. QA/QC requirements for the methods used to verify these two parameters are discussed below.

3.2.1 H₂S Concentrations in Vent Gas

Vent gas sample collection date, time, run number, and bag IDs were logged and laboratory chain of custody forms were completed and shipped with the samples. Copies of the chain of custody forms and results of the analyses are stored in the GHG Center project files. Collected samples were express shipped to Air Toxics, Ltd., on each of the three days of sampling for next day analysis. A coordinated effort minimized sample holding times, which ranged from 22 to 33 hours. Air Toxics analyzed collected samples in accordance with a modified version of ASTM Method 5504. The QA/QC procedures specified in the method were followed, and are summarized in Table 3-2.

Table 3-2. Summary of Vent Gas Analytical QA/QC Checks

QC Check	Minimum Frequency	Acceptance Criteria	Results Achieved
Five point instrument calibration (ICAL)	Prior to sample analysis	Relative standard deviation \leq 30%	Results acceptable
Laboratory control sample (LCS)	After each ICAL	90 percent of the compounds quantified must be within 70 – 130% of expected values	H ₂ S within the range of 90 to 120% of expected values
Laboratory blank	After the ICAL	Results lower than reporting limit	All compounds below reporting limit
Duplicate analyses	10% of the samples	Relative percent difference of \leq 25% for compounds detected 5 times higher than reporting limits	Relative difference \leq 25% for compounds detected

As an additional QC check, the GHG Center supplied one blind/audit air sample to the laboratory for analysis. The audit gas was an independent Reference Standard of H₂S in air manufactured by Scott Specialty Gases with a certified analytical accuracy of 25 ppm \pm 5 percent. The audit sample was collected, handled, and analyzed using the same procedures and equipment as the vent gas samples. The laboratory result was 21 ppm, or approximately \pm 16 percent of the certified concentration. This QC check served as a performance evaluation audit (PEA) for this verification, and was reported to the Southern QA manager for inclusion in the audit report.

3.2.2 Sulfate and Sulfide Effluent Emissions

Concentrations of sulfates and sulfides in the liquid effluent samples were determined by CT Laboratories using the methods identified in Table 3-1. The QA/QC procedures specified in the methods were followed and are summarized in Table 3-3. Documentation from CT Laboratories that each of these QC checks were conducted indicates that the qualitative DQO was met.

Table 3-3. Summary of Effluent Sulfate and Sulfide Analytical QA/QC Checks

QC Check	Minimum Frequency	Acceptance Criteria	Results Achieved
Three-point instrument calibration	Before analyses	None—establishes instrument calibration curve	Calibration conducted
Daily single-point calibration	Daily, prior to sample analyses	Result within 10% of expected values	Result within 10%
Duplicate analysis	Two samples	Not specified	Repeatability within 2%
Daily single-point calibration reanalysis	Daily, after sample analyses	Result within 5% of initial response	Result within 5%

3.3. OPERATIONAL PERFORMANCE PARAMETERS

The primary verification parameters for operational performance were concentrations of H₂S in the sour and processed biogas, the biogas compositional analyses, and the NaOH consumption determination. QA/QC requirements for the methods used to verify these two parameters are discussed below.

3.3.1 Biogas H₂S, Composition, and Heating Value

For all biogas samples collected (Table 2-1), sample collection date, time, run number, and canister ID were logged and laboratory chain of custody forms were completed and shipped with the samples. Copies of the chain of custody forms and results of the analyses are stored in the GHG Center project files. Collected samples were shipped to Empact for compositional analysis and determination of LHV per ASTM Methods D1945 and D3588, as well as H₂S analyses according to Method D5504. All samples were analyzed within 48 hours of collection, which exceeds the 24 hour method recommendation. Empact maintains strict continuous calibration criteria on the instrumentation used for the sulfur and compositional analyses using certified reference standards. Copies of these calibration data are stored in the GHG Center project files. As independent calibration checks, blind audits were submitted to Empact on two similar verifications within the past year to evaluate analytical accuracy on the methane analyses [5, 6]. These audits qualified as PEAs as required by the ETV QMP. Both audits indicated analytical accuracy within 3.0. Since the same sampling and analytical procedures were used here by the same laboratory analyst, the audit was not repeated a third time.

In addition to the blind audit samples, duplicate analyses were conducted on two of the sour biogas samples and two of the processed biogas samples. Duplicate analysis is defined as the analysis performed by the same operating procedure and using the same instrument for a given sample volume. Results of the duplicate analyses showed an average analytical repeatability of 0.03 percent for both methane and LHV. Duplicate analyses were also conducted on the sour gas samples to demonstrate H₂S repeatability. Average repeatability was approximately 4 percent.

3.3.2 NaOH Consumption

NaOH consumption rates were determined using data provided by the facility. GHG Center personnel conducted a field check to verify the accuracy of the tank level sensor used to log NaOH consumption. The NaOH tank is equipped with a graduated sight glass. Two sets of manual sight glass readings were recorded along with the elapsed time of a given change in level. Calculated NaOH consumption rate based on the manual readings averaged 2.62 gal/hr. The average rate reported by the facility (Section 2.2.2) was 2.52 gal/hr, a difference of approximately 4 percent.

3.4. VERIFICATION AUDITS

In addition to the QA/QC activities discussed here, several audit activities were conducted in support of this verification. Southern's QA manager conducted an on-site technical systems audit (TSA) of the measurement equipment, techniques, and methods to ensure compliance with the requirements of the TQAP. During the TSA, the QA manager and GHG Center field technician noted and documented all of the changes in the TQAP procedures due to site operational differences on corrective action reports. These reports are filed at the GHG Center.

Southern's QA manager also conducted an audit of data quality (ADQ) for this verification. The ADQ is an evaluation of the measurement, processing, and data evaluation steps to determine if systematic errors have been introduced. The QA manager randomly selected approximately 10 percent of the data and followed through the analysis, processing, and reporting of the data to ensure accuracy. The ADQ also included review of any problems, changes, or corrective actions documented during the test program to verify that their impact on data quality has been assessed and documented.

Finally, the PEAs described in Sections 3.2.1 and 3.3.1 satisfied the PEA requirement from the GHG Center's QMP.

4.0 TECHNICAL AND PERFORMANCE DATA SUPPLIED BY NATCO GROUP

Note: This section provides an opportunity for NATCO and Paques to provide additional comments concerning the THIOPAQ System and its features not addressed elsewhere in the Report. The GHG Center has not independently verified the statements made in this section.

In anticipation of future plant expansion, the THIOPAQ system tested here was designed for higher biogas throughputs than currently available. This means that the unit is currently operating at just 30 to 50 percent of capacity (50 to 70 percent turndown). According to NATCO and Paques, air blower control is less efficient at these capacities and the technology will likely operate more efficiently at throughputs closer to design capacity. It is expected that performance results presented here might further improve at sulfur loads closer to design capacity. System turndown can also have a negative impact on NaOH consumption rates. The rate verified here (0.36 lb NaOH per lb sulfur) may also improve at gas throughput rates closer to design capacity.

5.0 REFERENCES

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