THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM

U.S. Environmental Protection Agency

SOUTHERN RESEARCH INSTITUTE

ETV Joint Verification Statement

TECHNOLOGY TYPE:	Sour Gas Processing System
APPLICATION:	Biogas Purification
TECHNOLOGY NAME:	Paques THIOPAQ
COMPANY:	NATCO Group, Inc.
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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 permitters, 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 (H_2S) 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 H_2S 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 CH_4, 38 percent CO_2, and 1 to 2 percent H_2S). 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

- H_2S 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 H_2S 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 H_2S 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 H_2S and total sulfur compounds in the air vented from the bioreactor were very low averaging 929 and 1,961 ppbv, respectively. H_2S 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 H_2S 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 (10^3cfd)].

- Table S-1 summarizes the sour and processed gas average composition, H_2S content, and heat content for nine samples collected before and after the THIOPAQ system. The average H_2S 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 CO_2 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)			
	CH_4 (%)	CO_2 (%)	N_2 (%)	H_2S (ppm)	Total S (ppm)	HHV	LHV	Relative Density	Compres-sibility
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 10^3cfd) 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).

Signed Lawrence W. Reiter, Ph.D. 9/29/04

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