AN ABSTRACT OF THE THESIS OF

Hannah May Tuinstra for the degree of Honors Baccalaureate of Science in Chemical Engineering presented on June 1, 2006. Title: Feasibility Study for the Use of a Fuel Cell to Process Landfill Gas at Coffin Butte Landfill: Hydrogen Sulfide (H_2S) Detection and Removal.

Abstract approved: ______________________________

Skip Rochefort

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David Hackleman

Pacific Northwest Generating Cooperative (PNGC) operates the *Landfill Gas to Energy Facility* at Coffin Butte Landfill in Corvallis, OR. At this facility, three internal combustion engines use the landfill gas (predominantly methane and carbon dioxide) as fuel to turn generators that produce enough electricity to power 1,800 average sized homes. A possibility of a cleaner more efficient method for producing electric power from the landfill gas is fuel cell technology. One technological drawback is that all conventional fuel cells are poisoned to some extent by trace sulfur containing components in the landfill (e.g., PEM and solid oxide <1ppmv sulfur and phosphoric acid <50ppmv sulfur). Since hydrogen sulfide (H_2S) is the most prevalent sulfur compound in landfill gas, the focus of this thesis research was H_2S detection in, and removal from, the landfill gas. A gas chromatography method was developed to detect H_2S down to 1ppmv. Using this highly sensitive detection system, three additional sulfur containing compounds (thought to be mercaptans), were observed in the landfill gas. Two different methods for removing H_2S from landfill gas were investigated: silica gel and an H_2S

scavenger (SulfaTreat®, iron oxide encapsulated in a porous gel structure). A stream of landfill gas was diverted to a two bed testing system that was used to test silica gel and SulfaTreat®. SulfaTreat® was also tested in the laboratory with a controlled 1% H_2S in argon feed. Silica gel can be regenerated but the amount required and the size of the cylindrical bed needed to contain the materials (estimated size of 250,000 gallons) makes it an impractical method for sulfur removal from landfill gas. Since, SulfaTreat® is an iron oxide compound in a gel matrix; it can not be easily regenerated, which renders it to be a single use method. However, the expected sulfur removal rate with the SulfaTreat® material makes it a reasonable method to treat the landfill gas. PNGC is currently planning an expansion at Coffin Butte Landfill that will add two additional, higher efficiency, engines for power generation. Further studies should be performed with SulfaTreat® to determine optimal running conditions and removal rates. If this proves to be a satisfactory technology with reasonable economics, the next step would be to install a pilot scale fuel cell system at the landfill for testing. If successful, the fuel cell could be implemented to handle the excess landfill gas that is currently sent to a flare, as a means of doing long-term durability and stability testing.

Key Words: Fuel Cell, Landfill Gas Treatment, Hydrogen Sulfide Detection and Removal

Corresponding e-mail address: hannah.m.tuinstra@gmail.com

Feasibility Study for the Use of a Fuel Cell
to Process Landfill Gas at Coffin Butte Landfill:
Hydrogen Sulfide (H_2S) Detection and Removal

by

Hannah May Tuinstra

A PROJECT

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APPROVED:

Mentor, representing Chemical Engineering

Mentor, representing Chemical Engineering

Committee Member, representing Chemical Engineering

Head of the Department of Chemical Engineering

Dean, University Honors College

I understand that my project will become part of the permanent collection of Oregon State University, University Honors College. My signature below authorizes release of my project to any reader upon request.

Hannah May Tuinstra, Author

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PREFACE

In 2003, collaboration began between the Chemical Engineering Department at Oregon State University and the advanced science classes from Crescent Valley High School (CVHS in Corvallis, OR) to investigate the possibility of using fuel cell technology at Coffin Butte Landfill to produce electricity. Many different individuals have contributed to this project, including: OSU faculty (Dr. David Hackleman, Dr. Skip Rochefort, and Dr. Alex Yokochi), local industries (Bill Byers from CH_2M Hill and Chris Beatty from Hewlett Packard), CVHS teachers (Adam Kirsch and Tim Chambers), several high school classes, and three OSU senior chemical engineering lab groups. For many of the student researchers, this project was a first opportunity to attempt to solve an open-ended, long-term, significantly important “real-world” problem. Throughout this learning process a great deal of mentoring and guidance was necessary.

As the project coordinator for more than one year of this project, I had the privilege of interacting with many different contributors. The most memorable of these interactions were with high school students from Crescent Valley. We met weekly to plan and discuss our results, obstacles, and ideas. Some important skills were acquired, such as the ability to coordinate trips to the landfill for testing, becoming independent operators of analytical equipment, and interpreting unexpected results. Most importantly, researchers learned how to approach a problem that is not nicely packaged, waiting on a piece of paper or in a beaker on a classroom lab table. This experience, not routinely taught in high school lab classes, ignites a desire to research and explore solutions to real life problems.

FEASIBILITY STUDY FOR THE USE OF A FUEL CELL TO PROCESS LANDFILL GAS AT COFFIN BUTTE LANDFILL: HYDROGEN SULFIDE (H_2S) DETECTION AND REMOVAL

1. INTRODUCTION

Renewable energy from multiple sources is important to maintain and improve our quality of life. Keeping energy production and distribution localized to communities is also beneficial. One of these local, renewable energy sources is solid organic waste, which produces a methane rich gas when it decomposes. Municipal solid waste landfills are the largest source of anthropogenic methane emissions in the United States, accounting for about 34 percent of these emissions (Environmental Protection Agency). These methane emissions from landfills represent a lost opportunity to capture and use a significant energy resource. Instead of allowing landfill gas to escape into the air, it can be captured, converted, and used as an energy source. Using landfill gas prevents methane from migrating into the atmosphere. This reduces odors, local smog, and overall global climate change.

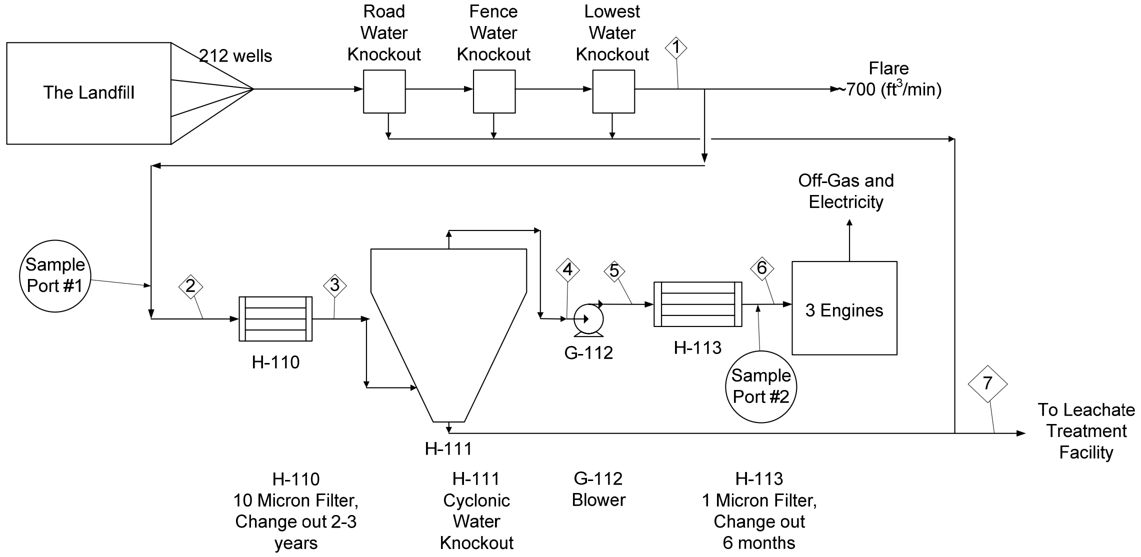
At Coffin Butte Landfill, located north of Corvallis in Benton County, Oregon internal combustion engines are used to combust the landfill gas and drive generators that produce enough electricity to power about 1,800 homes. This project examines another possibility for utilizing the landfill gas at Coffin Butte Landfill: fuel cell technology that would produce electricity at a higher efficiency and with a smaller impact on the environment.

2. COFFIN BUTTE LANDFILL

2.1 Current Operations

Five counties in Oregon contribute 550,000 tons of waste each year to Coffin Butte Landfill. Organic waste in the landfill decomposes to produce an off-gas, which is about 50% methane and 50% carbon dioxide (Gas Separations Technology). This off-gas is collected and converted into electric energy. Pacific Northwest Generating Cooperative (PNGC) operates the Gas Recovery Plant at Coffin Butte Landfill. Gas collection pipes are installed throughout the landfill, connected to 212 wellheads, and then to a blower. This gas is fed to three landfill gas fired internal combustion reciprocating engines, with a duty of 820 kW each, and converted into electric energy. A process flow diagram of the Gas Recovery Plant can be seen in Figure 2.1. The plant contributes 2.46 MW of power, serving approximately 1,800 averaged sized homes (PNGC).

The landfill produces about 1700 standard cubic feet per minute (SCFM) of off-gas, but the plant's current capacity is for only 1000 SCFM. The extra 700 SCFM cannot be utilized and is flared-off (burned in an open flame) to comply with EPA regulations. Waste collected at the landfill is expected to increase at an annual rate of 10% causing the difference between the landfill gas that is captured and the landfill gas that can be utilized for electrical production to increase. PNGC is planning to expand the capacity of the Gas Recovery Plant to accommodate this increase in landfill gas production. By the spring of 2007, PNGC plans to have completed the addition of two 1.6 MW reciprocating engines. These new engines will use a total of 950 SCFM and be 40% efficient, about twice the efficiency of the three existing engines.



Process flow streams							
	1	2	3	4	5	6	7
Flow Rate (SCFM)	1700	1000	1000	1000	1000	1000	
Temperature (^{o}F)	50	50	50	50	150	150	
Pressure (psig)				1.08	5.5	5.5	
H_2S (ppmv)	500 -1000	500 -1000	500 -1000	500 -1000	500 -1000	500 -1000	
CH_4 (vol%)	55	55	55	55	55	55	
O_2 (vol%)	0.5	0.5	0.5	0.5	0.5	0.5	
N_2 (vol%)	5	5	5	5	5	5	
CO_2 (vol%)	40	40	40	40	40	40	
H_2O (vol%)	0.5	<0.5	<0.5	<0.5	<0.5	<0.5	~100%

Current Coffin Butte
Landfill Gas Treatment
5/24/06
Hannah Tuinstra

Figure 2.1: Process Flow Diagram for the Gas Recovery Plant at Coffin Butte Landfill

2.2 Fuel Cell Technology

Although the benefits of the current combustion process greatly surpass just flaring the gas, it is inefficient and produces toxins such as NO_x, SO_x, and CO. For this reason, cleaner methods that are more efficient are being investigated. One of these alternative methods is fuel cell technology.

Coffin Butte Landfill continues to receive more waste increasing the amount of landfill gas produced. Ideally, PNGC would utilize all this gas, never using a flare. However, expansions in engine capacity are only economical about every three years when 1000 more SCFM of landfill gas is available for fuel. A possible solution to this waste of potential energy is a fuel cell. A correctly sized fuel cell could produce energy between expansion stages when the landfill is gradually generating more gas.

Fuel cell technology has already proven to be successful in this application and fuel cells are in service at over 150 landfills and wastewater treatment plants across the country. In 1992, Penrose Landfill in Sun Valley, California was one of the first of these facilities to successfully demonstrate fuel cell technology at a landfill. Connecticut's Groton Landfill has been producing 600,000 kWh of electricity a year, since 1996, with a continuous output of 140 kW (Fuel Cells 2000). A phosphoric acid fuel cell was installed at the Columbia Boulevard Wastewater Treatment Plant in Portland, Oregon in 1998. The fuel cell produces 1.5 million kWh of electricity per year from anaerobic digester gas, reducing the treatment plant's electricity bills by $102,000 annually (Northwest Regional Biomass Program). King County's South Wastewater Treatment Facility in Renton, Washington is currently sponsoring the world's largest demonstration project of a molten carbonate fuel cell using digester gas as fuel. The 1 MW fuel cell has been successfully producing enough power for 800 average sized homes since starting up in the summer of 2004 (Department of Natural Resources).

3. PREVIOUS WORK: OSU CHEMICAL ENGINEERING DEPARTMENT

In 2003, collaboration began between PNGC, advanced science classes from CVHS, and the OSU ChE Department to further investigate the possibility of implementing a fuel cell at Coffin Butte Landfill. Four basic types of fuel cells were considered: Proton Exchange Membrane, Phosphoric Acid, Molten Carbonate, and Solid Oxide. Considering fuel cell efficiency, cell material, and fuel reforming requirements, the research group from 2003 determined that the optimal type of fuel cell for Coffin Butte Landfill was a Solid Oxide Fuel Cell (SOFC) (Hinton). It was also determined that the average concentration of hydrogen sulfide (H_2S) in the landfill gas is sufficiently high to poison a SOFC. Less than 1 part per million by volume (ppmv) is necessary. In 2004, different H_2S removal methods were researched and recommendations for further investigation were made (Black, et al):

- Silica gel - further investigation recommended
- Claus Process - cannot remove H_2S to <1 ppmv
- Zinc Oxide - costly due to frequent regeneration requirements
- Biological System - not investigated due to lack of information and availability
- Sulfur-Rite® (commercial H_2S scavenger) - further investigation recommended

Based on the recommendations from previous studies, the current research focused on the detection and removal of H_2S from the landfill gas as the necessary first step for the future implementation of a fuel cell at Coffin Butte Landfill.

4. LANDFILL GAS CHARACTERIZATION

4.1 Background on Gas Chromatography

Chromatography is a method for separating components of a mixture and is carried out by an instrument called a chromatograph. The basic components of a chromatograph are a flowing mobile phase, a separation column containing the stationary phase, an injection port, and a detector. A simple diagram of a chromatograph can be seen in Figure 4.1.

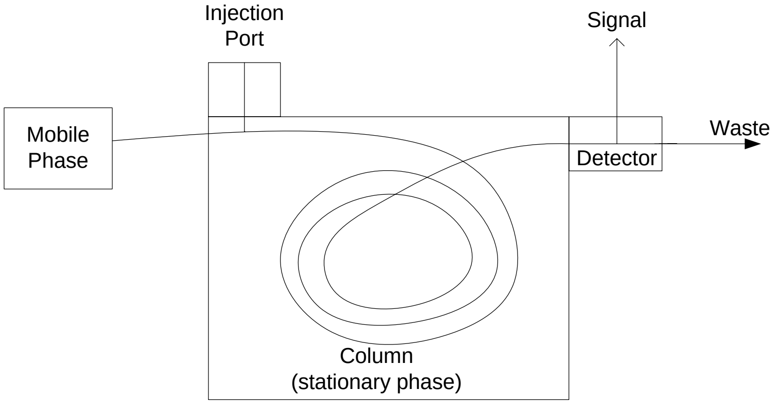


Figure 4.1: Basic Chromatograph

For this application gas chromatography (GC) was used. In gas chromatography, the mobile phase is usually helium gas. The mobile phase constantly moves through the column. When a sample is in injected into the column through the injection port it is carried through the column by the mobile phase.

There are two types of chromatographic columns: packed or capillary. Packed columns are typically a glass or stainless steel coil that is filled with the stationary phase or a packing coated with the stationary phase. Most packed columns are 1.5-10 m in length and have an internal diameter of 2-4 mm. Capillary columns are a thin fused-silica or metal capillary that has the stationary phase coated on the inner surface. Common capillary column dimensions are 10-100 m in length and an inner diameter of about 0.1-0.5 mm. For both column types (capillary and packed), the stationary phase is usually a cross-linked polymer such as polydimethyl siloxane (PDMS) or polydivinylbenzene (PDVB).

The different components in the sample partition between the mobile and stationary phases. Separation of the different components in the mixture is caused by the varied strength of forces between the different components and the stationary phase. The weaker the forces between a specific component and the stationary phase, the faster that specific component will elute from the column. The detector identifies the concentration of each component as it leaves the column. The detector signal versus time is recorded and displayed as a chromatogram. In the chromatogram, each component is represented by a peak. The area of each peak can be integrated and correlated to the amount of the substance that was present in the sample. A typical chromatogram can be seen in Figure 4.2. Each peak represents a different component of the sample. The size of the peak represents the amount of that component that was present in the sample (Hawkes).

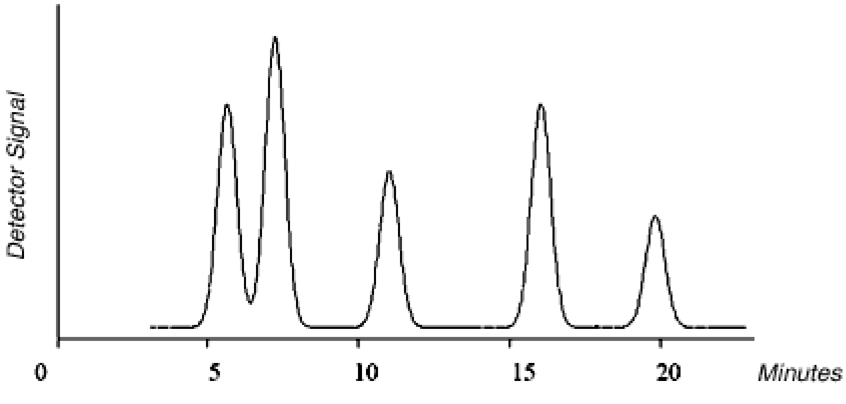


Figure 4.2: Typical Chromatogram (Ion Signature Technology, Inc.)

4.2 OSU ChE Department Gas Chromatographs

The OSU ChE Department has two SRI Gas Chromatographs (GC), an SRI Model 310 and an SRI Model 8610. Online manuals for the machines and detectors can be found at the SIR website (http://www.srigc.com/documents.htm). These GCs were used to determine the composition of the landfill gas. In the fall of 2004, work began to prepare the GCs to detect all possible components of the landfill gas. Both GCs were upgraded and then optimized to allow for the detection of H_2S, CH_4, CO_2, O_2, N_2, and H_2O.

4.2.1 SRI 310 GC with TCD

The SRI 310 GC was already equipped with a thermal conductivity detector and a 6 ft HayeSep®-D column. To allow for better separation, a longer, 10 ft HayeSep®-D column was installed. This packed column uses high purity polydivinylbenzene (PDVB) as the column packing (Valco Instruments Co., Inc.).

A thermal conductivity detector (TCD) measures the difference in thermal conductivity of the carrier gas and the sample. The TCD uses four general-purpose tungsten-rhenium filaments arranged in a Wheatstone bridge circuit. Two filaments are exposed only to the carrier gas, creating a baseline reference signal. The other two filaments are provided with the sample-laden carrier gas flow and create the actual chromatographic signal. When the effluent from the column flows over the two sample filaments, the bridge current is unbalanced with respect to the reference signal. This difference is translated into an analog signal and provides the quantitative amounts of each component in the sample (SRI).

The SRI 310 was used to determine the concentration of CH_4, CO_2, air (O_2 and N_2), and H_2O in the landfill gas. The species elute in the following order: air, CH_4, CO_2, and then H_2O. Operating parameters used for the SRI 310 are given in Table 4.1. Figure 4.3 is a chromatogram of a landfill gas sample taken in June 2006 and analyzed on the SRI 310 GC. Concentration data are given in Table 5.2.

Table 4.1: SRI 310 Operating Parameters

Parameter	Value
Detector Temperature	100°C
Oven Temperature	75°C
Carrier Gas	Helium
Carrier Gas Pressure	20 psi
TCD amplifier	Low-125 mA
Column Type	HayeSep®-D
Column Length	10 ft

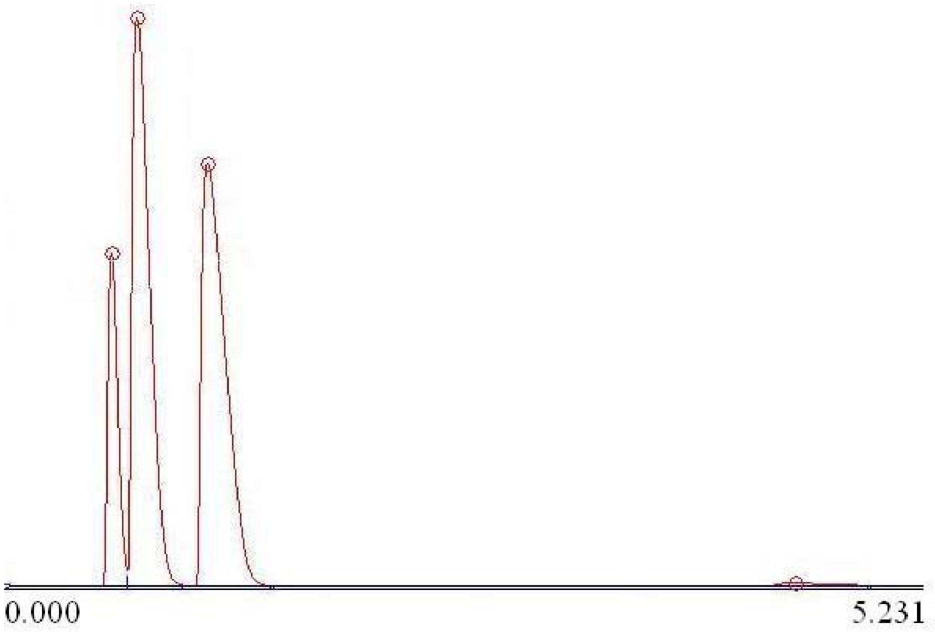


Figure 4.3: Chromatogram from the SRI 310 GC TCD, 1 mL injection of untreated landfill gas June 2006

In April 2005, the filaments in the TCD were believed to be burnt-out because the detector signal was significantly decreased. This was most likely caused by removing the septum cap while the GC was running. A procedure for testing for burnt out filaments can be found at http://www.srigc.com/TCDman2.pdf. When the septum is removed while the GC is running, the carrier gas exits the GC through the injector port without flowing over the filaments and this causes damage to the filaments. New filaments were ordered from SRI and installed. The GC was operated for about 10 hours and 120°C to "break-in" these new filaments. Throughout the 10 hours, the peak area for a 1 mL air injection increased from about 800 to 1500 mV. At that point, the peak area was back to the same size it was before the new filaments were installed and it stopped increasing.

4.2.2 SRI 8610 GC with FID and FPD

At the beginning of this project, the SRI 8610 was equipped with a flame ionization detector (FID) but had no column installed. In order to detect H_2S a flame photometric detector (FPD) was necessary. In the fall of 2004, the SRI 8610 was sent to SRI for an upgrade and an FPD was added. A 15 m MXT®-1 column with a 0.53 inner diameter and a 5.0 µm film thickness (df) was also installed. The inside of this capillary column is coated with Crossbond® 100% polydimethyl siloxane (PDMS).

An FID responds to any molecule with a carbon-hydrogen bond. The FID was used to corroborate results for CH_4 concentrations obtained with the SRI 310 TCD. In the FID, the effluent from the column is mixed with hydrogen and sent through a flame. This flame ionizes the sample molecules. Both positive and negative ions are produced as each component of the sample passes into the flame. A positive collector electrode attracts the negative ions to the electrometer amplifier, producing the analog signal that is converted into relative concentrations in the sample (SRI).

The FPD operation is similar to the FID. Instead of determining the concentration of a component by the amount of ions produced when the sample passes through a flame, it detects and measures the wavelength of the light that the component emits upon entering that same flame. A 394 nm band pass filter covers a photomultiplier tube (PMT) to selectively detect compounds containing sulfur. When these compounds are burned in the FPD flame, they emit photons of distinct wavelengths. The filter ensures that only those photons that are within the frequency range of the filter specifications can reach the PMT. The PMT converts the photon signal to an analog signal that provides the concentration of H_2S in the landfill gas (SRI).

A linear calibration curve was made for the FID to detect CH_4. The FPD has a non-linear response to H_2S causing the calibration to be a bit more complicated. Calibration curves for the FPD with the 15 m column can be seen in Figures 4.4, 4.5, and 4.6. Figure 4.4 shows the two non-linear calibration curves for the FPD at different concentration ranges with the 15 m column. The curve from 10-100 ppmv H_2S uses an injection size of 100 μL and the curve from 100-500 ppmv H_2S uses 10 μL. Figures 4.5 and 4.6 show the least-squares fit calibrations for the 10-100 ppmv H_2S and the 100-500 ppmv H_2S calibrations, respectively. Equations 4.1 and 4.2 give the H_2S concentration for the least-squares linear fit for the 10-100 ppmv H_2S and the 100-500 ppmv H_2S calibrations, respectively. Standard deviation and calibration data are given in Appendix A.

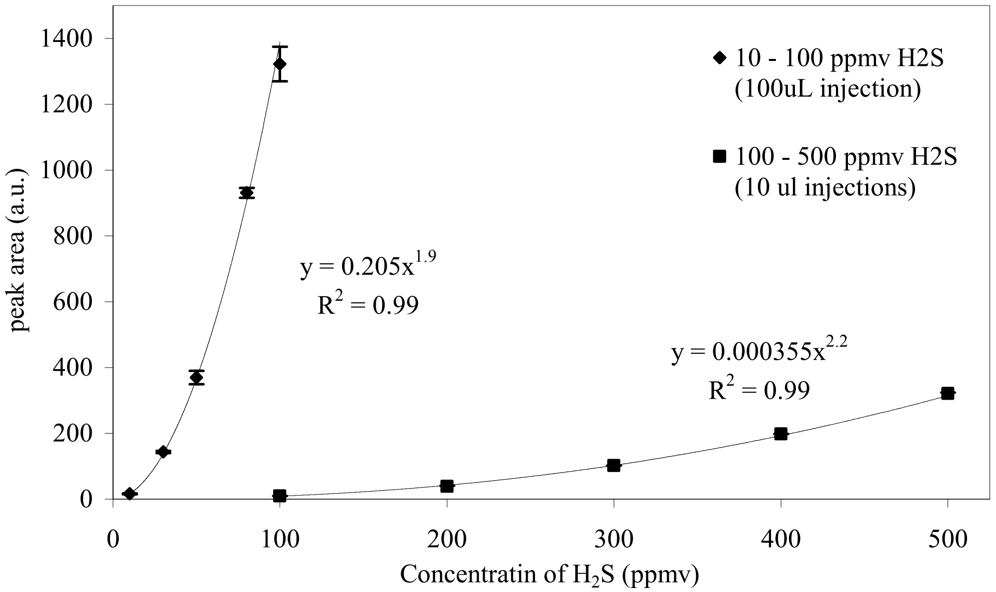


Figure 4.4: Non-linear FPD calibration, SRI 8610, 15 m column, two different injection sizes for different concentration ranges

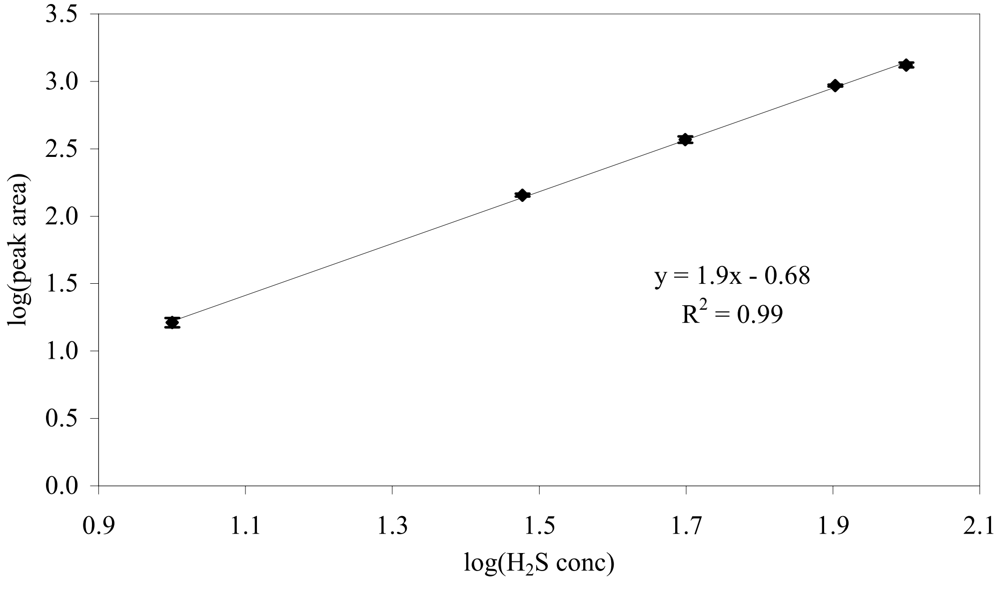


Figure 4.5: Least-Squares Linear Fit for FPD calibration, SRI 8610, 15 m column, 10-100 ppmv H_2S

H_2S Concentration (ppmv) = 2.28 (peak area)$^{0.526}$ *Eqn. 4.1*

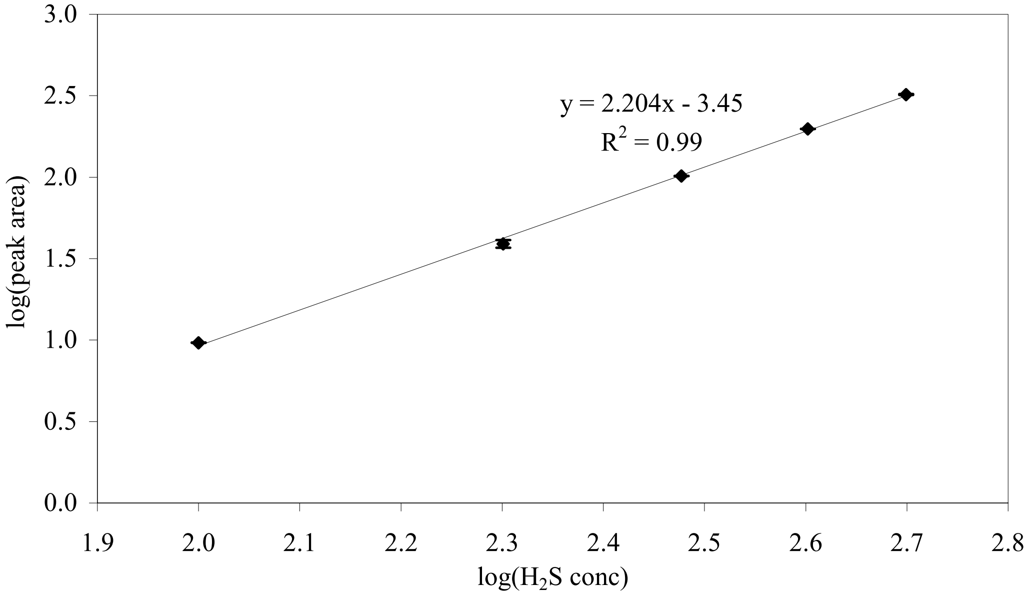


Figure 4.6: Least-Squares Linear Fit for FPD calibration,
SRI 8610, 15 m column, 100-500 ppmv H_2S

H_2S Concentration (ppmv) = 36.8 (peak area)$^{0.454}$ *Eqn. 4.2*

The FPD needed to be optimized to achieve the lowest possible detection of H_2S. This involves optimizing the air and H_2 flowrates, the volts supplied to the FPD PMT, and the temperature. Operating parameters for the SRI 8610 with a 15 m column are detailed in Table 4.2. This method was used to obtain all the data for the H_2S removal methods investigated in the project.

Table 4.2: SRI 8610 Operating Parameters for
15 m column (10 ppmv H_2S detection limit)

Parameter	Value
Carrier Gas	Helium @ 20 psi
Flame Gases	Air @ 6 psi H_2 @ 40 psi
Oven Temperature	40°C
Column Type	MXT®-1
Column Length	15 m
FPD PMT Volts	450 mV

4.2.3 GC Modifications to Improve H_2S Detection

SRI advertises a detection limit of 0.2 ppmv H_2S but the 15 m column only allowed a detection limit of 10 ppmv H_2S. Upon correspondence with SRI, it was determined that a longer column was necessary to separate the air and H_2S peaks. A 60 m MXT®-1 column with a 0.53 mm id and 5.0 µm film thickness (df) was ordered and installed. The SRI 8610 was re-optimized and re-calibrated with the 60 m column. The new H_2S detection limit was found to be 1 ppmv, higher than the SRI specification, but low enough for this application. The 60 m column SRI 8610 GC method can be seen in Table 4.3. In the process of calibrating the instrument, it was found that the amount of time the sample was allowed to flow into the syringe before being injected into the GC (sample up-take time) caused variance in peak areas. Longer sample up-take times resulted in larger peak areas. The peak areas continued to increase with increase sample up-take time until 30 seconds. Peak areas no longer increased at sample up-take times of more than 30 seconds. The reason for this is unknown, but it is important to keep this time constant for accurate results. Figure 4.7 shows the non-linear H_2S calibration with the 60 m column, which focuses on the low concentration range from 1 to 10 ppmv H_2S with a 1 mL injection. Figure 4.8 shows the least-squares linear fit for the 60 m column calibration. Equation 4.3 gives the H_2S concentration for the least-squares linear fit SRI 8610 FPD with 60 m column calibration. Standard deviation and calibration data are given in Appendix A.

Table 4.3: SRI 8610 Operating Parameters for 60 m column (1 ppmv H_2S detection limit)

Parameter	Value
Carrier Gas	Helium @ 24 psi
Flame Gases	Air @ 4 psi H_2 @ 42 psi
Oven Temperature	50°C
Detector Heat 2	50°C
Detector Heat 3	150°C
Column Type	MXT®-1
Column Length	60 m
FPD PMT Volts	500 mV
FPD Gain	High
FID Gain	High
Sample Up-take Time	30 sec

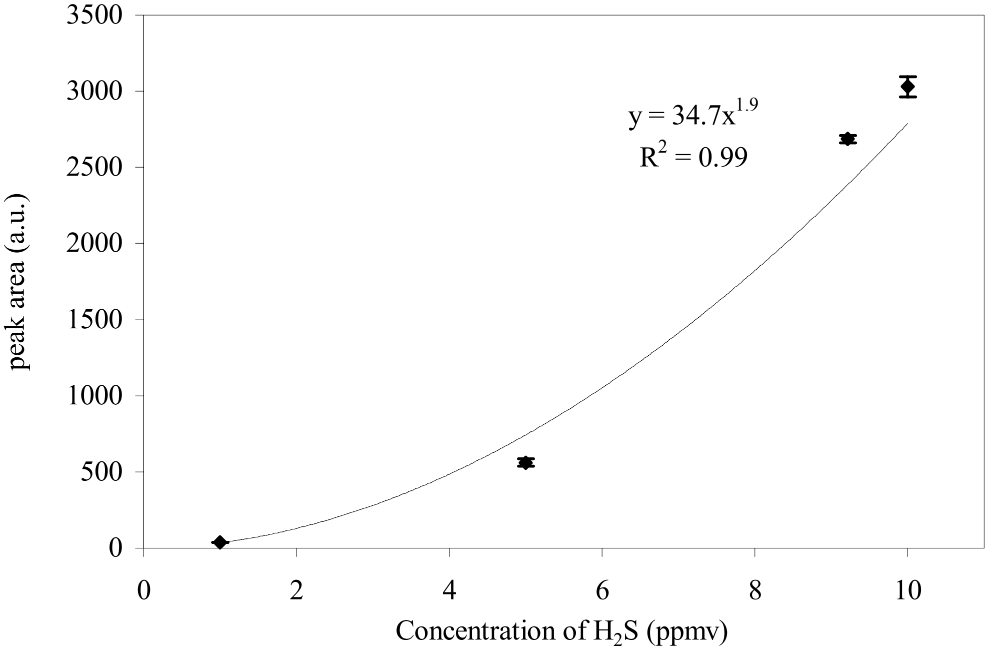


Figure 4.7: Non-linear FPD calibration, SRI 8610, 60 m column, 1-10 ppmv H_2S

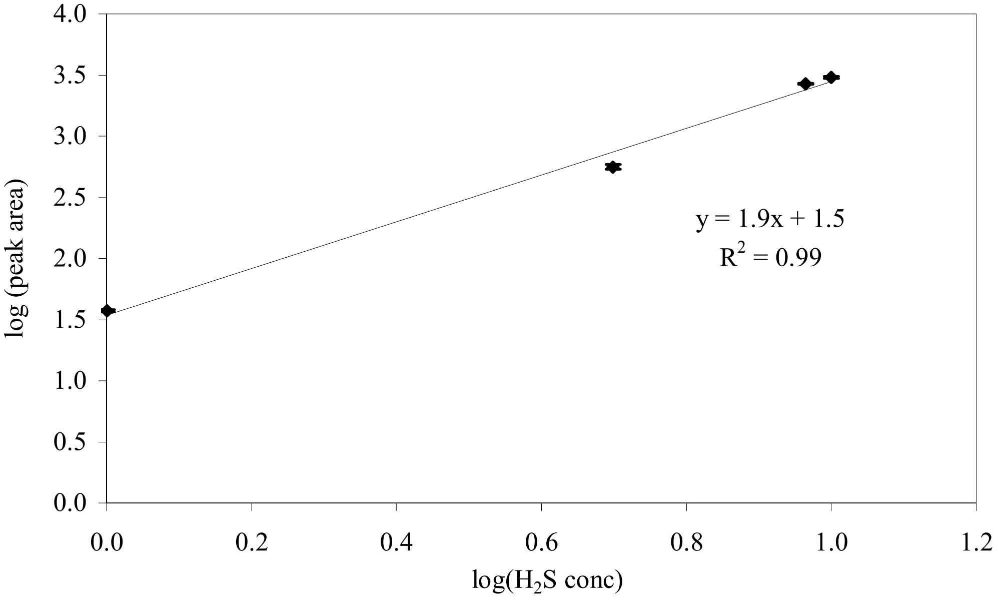


Figure 4.8: Least-Squares Linear Fit FPD calibration,
SRI 8610, 60 m column, 1-10 ppmv H_2S

$$H_2S \text{ Concentration (ppmv)} = 0.164 \text{ (peak area)}^{0.524} \qquad \textit{Eqn. 4.3}$$

Another advantage of a lower detection limit and a longer column is the ability to detect more species. Three other sulfur containing compound peaks were observed with the 60 m column. These larger compounds eluted after H_2S and are suspected to be light mercaptans. Figure 4.9 shows a chromatogram from a 1 mL injection of an untreated landfill gas sample taken in June 2006 (from Sample Port #2 in Figure 2.1) that was analyzed on the SRI 8610 with the FPD. The first peak is air and the second peak is H_2S. The H_2S concentration is high producing an off scale peak that cannot be integrated. The last three peaks are the other, non-H_2S sulfur compounds. Concentration data are given in Table 5.2.

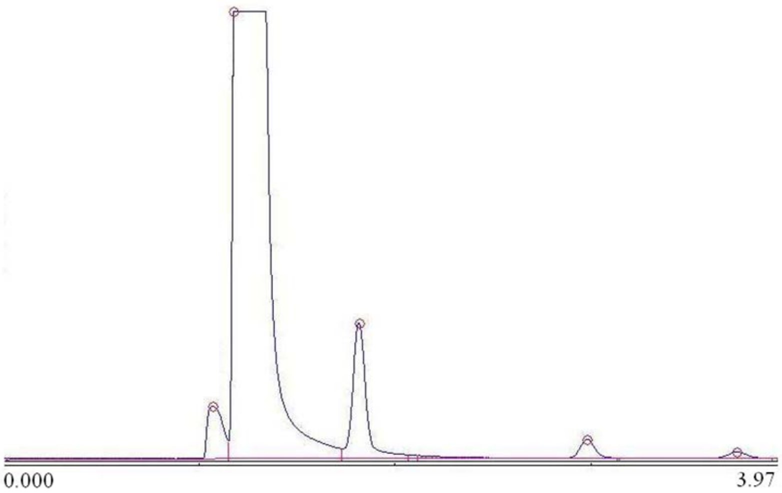


Figure 4.9: Chromatogram from the SRI 8610 GC FPD,
to determine non-H_2S sulfur compound concentration,
60 m column, 1 ppmv H_2S detection limit,
1 mL injection of untreated landfill gas June 2006

Figure 4.10 shows a chromatogram from a 1 mL injection of a 1:250 dilution in air of the untreated landfill gas sample taken in June 2006 (from Sample Port #2 in Figure 2.1) that was analyzed on the SRI 8610 with the FPD. The first peak is air and the second peak is H_2S. This dilution allows the H_2S peak to be integrated and the concentration to be determined. Concentration data are given in Table 5.2.

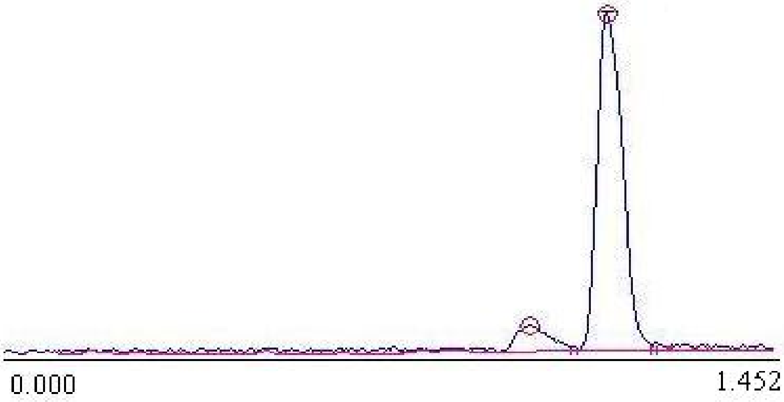


Figure 4.10: Chromatogram from the SRI 8610 GC FPD,
to determine H_2S concentration,
60 m column, 1 ppmv H_2S detection limit,
1 mL injection of diluted untreated landfill gas June 2006

4.3 RAE Systems Hand Pump

An additional method of analyzing the landfill gas is the RAE Systems Hand Pump and Colorimetric Gas Detection Tubes that CVHS purchased. The tubes can be purchased for different species and in different concentration ranges. This system draws 100 mL of gas through the colorimetric gas detection tube using a piston pump. The detection limit of the hand pump system is 0.2 ppmv H_2S which can be improved by increasing the sample size that is drawn through one tube. The sample size can be increased by drawing 100 mL of gas through the detection tube multiple times. Preliminary tests demonstrate agreement between the hand pump and the GC method.

Data sheets for the tubes can be found at the RAE website (http://www.raesystems.com/products/tubes). The data sheet includes accuracy and other important information, such as the conditions (humidity and temperature) in which each type of tube can be used (RAE Systems).

5. HYDROGEN SULFIDE REMOVAL

Silica gel and SulfaTreat® 410HP, two of the most promising hydrogen sulfide removal methods recommended by the previous group, were investigated.

5.1 Untreated Landfill Gas Composition

The composition of the untreated landfill gas was a necessary component to designing tests. Landfill gas samples were taken in April 2005 and analyzed with the SRI 310 and SRI 8610. The untreated landfill gas characterization from April 2005 can be seen below in Table 5.1. Another source of CH_4, CO_2, and O_2 concentrations was historical data from PNGC. This data agreed with the GC analysis and can be seen in Appendix B.

Table 5.1: Untreated Landfill Gas Composition, April 2005,
Taken from Sample Port #2 in Figure 2.1,
GC analysis with SRI 310 TCD and SRI 8610 FPD 15 m column

Component	Approximate Concentration
CH_4	55 vol %
CO_2	40 vol %
Air (O_2/N_2)	5 vol %
H_2S	400-500 ppmv
H_2O	<1 vol %

A sample of untreated landfill gas collected in June 2006 was analyzed on the SRI 8610 with the 60 m column. An increase in the H_2S concentration was observed as well as three other peaks for sulfur containing compounds larger than H_2S. Analysis of the landfill gas using the RAE hand pump also indicated the same increase in H_2S concentration (in June 2006). The methane, carbon dioxide, air, and water concentrations were the same as the sample taken in April 2005, Table 5.1. The gas composition as of June 2006 can be seen in Table 5.2

Table 5.2: Untreated Landfill Gas Composition, June 2006,
Taken from Sample Port #2 in Figure 2.1,
GC analysis with SRI 310 TCD and SRI 8610 FPD 60 m column

Component	Approximate Concentration
CH_4	55 vol %
CO_2	40 vol %
Air (O_2/N_2)	5 vol %
H_2O	<1 vol %
H_2S	1000 ppmv
Other sulfur	26 ppmv

Landfill gas and digester gas from wastewater treatment plants contain very similar sulfur compounds. In 2002, CH_2M Hill performed an analysis of the off-gas produced at the Corvallis Wastewater Reclamation Plant using a GC with an FPD. The results are listed in Table 5.3 (Hinton).

Table 5.3: CH_2M Hill Analytical Report of Sulfur Compounds in Corvallis
Wastewater Reclamation Plant Gas, 2002, GC with FPD (Hinton)

Sulfur Compound	Molecular Formula	Concentration (ppmv)
Hydrogen Sulfide	H_2S	272
Carbonyl Sulfide	COS	0.016
Methyl Mercaptan	CH_4S	0.049
Ethyl Mercaptan	C_2H_6S	0.057
Carbon Disulfide	CS_2	0.004
Isopropyl Mercaptan	C_3H_8S	0.074
tert-Butyl Mercaptan	$C_4H_{10}S$	0.039
n-Propyl Mercaptan	C_3H_8S	0.224
Thiophene	C_4H_4S	0.017
n-Butyl Mercaptan	$C_4H_{10}S$	0.004
3-Methylthiophene	C_5H_6S	0.003

These sulfur compounds are the most likely candidates for the three additional sulfur peaks detected in the June 2006 landfill gas sample (Figure 4.9). Every sulfur compound found in the digester gas has only one sulfur, excluding carbon disulfide.

Carbon disulfide is one of three lowest concentrations in the digester gas, and is therefore, not a likely possibility for any of the non-H_2S sulfur compounds found in the landfill gas in June 2006. Since the FPD responds to the total amount of sulfur in a sample, the calibration for H_2S on the SRI 8610 FPD (60 m column) was used to determine the approximate collective concentration of the other three sulfur peaks in the landfill gas. Using this method, the landfill gas sample taken in June 2006 had about 26 ppmv non-H_2S sulfur compounds (Table 5.2).

5.2 SILICA GEL FOR H_2S REMOVAL

5.2.1 Silica Gel Theory

Silica gel is traditionally used as a desiccant. It is a very porous material with a large amount of surface area. Water vapor is adsorbed onto the surface area and removed from the air. Silica gel can also be used to remove H_2S molecules from a gas stream due to the similar chemical structures of water and H_2S. The polarity of the H_2S molecule causes it to be attracted to polar hydroxyl groups on the surface of the silica gel matrix, as seen in Figure 5.1.

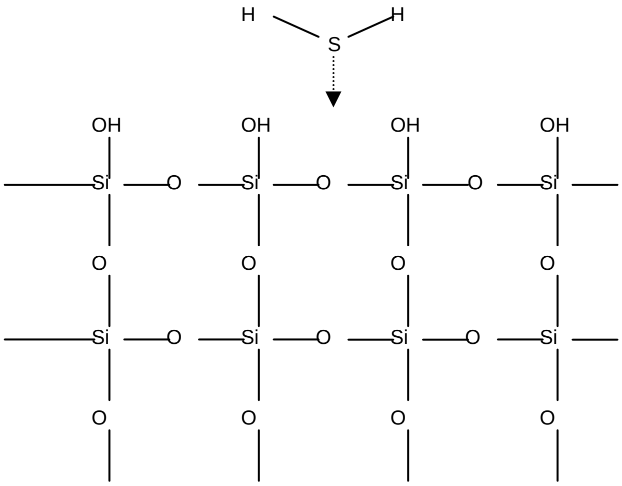


Figure 5.1: H_2S molecule adsorbed onto a silica gel bead

5.2.2 Silica Gel Testing Procedures

Testing of silica gel's effectiveness in removing H_2S from the landfill gas was performed at PNGC's landfill Gas Recovery Facility using packed-bed columns constructed of 3" schedule-40 PVC pipe and various fittings. Silica gel (6-12 mesh) was ordered from Eagle Chemical Co., Inc. (Mobile, AL).

A 4:1 ratio mixture of standard and indicating silica gel was used during testing. The indicating silica gel was added to provide a visual cue of silica gel saturation. The indicating silica gel uses cobalt chloride as an indicator. It begins as a cobalt blue color, turns black when saturated with H_2S, and pink when saturated with water. Because of the need to monitor this color change during testing, clear PVC pipe was chosen for the columns while standard white PVC fittings were used for the end caps because of their availability and relatively low cost. Three columns were constructed at the beginning of the project and subsequently pressure tested for leaks with compressed nitrogen. The columns were tested to 10 psig, approximately twice the pressure of the landfill gas stream, and any leaks were repaired using a polyurethane sealant.

A schematic of the testing system can be seen in Figure 5.2. Two different amounts of silica gel, 500 and 1000 grams, were tested at the landfill using a gas flowrate of 5 L/min. In order to ensure adsorption of H_2S, and not any water present in the landfill gas, the gas stream was dehumidified before entering the silica gel column (test column). This was accomplished by first passing the gas stream through an additional packed column (column 1) containing DrieRite® desiccant. DrieRite® is anhydrous calcium sulfate ($CaSO_4$) and does not react with H_2S.

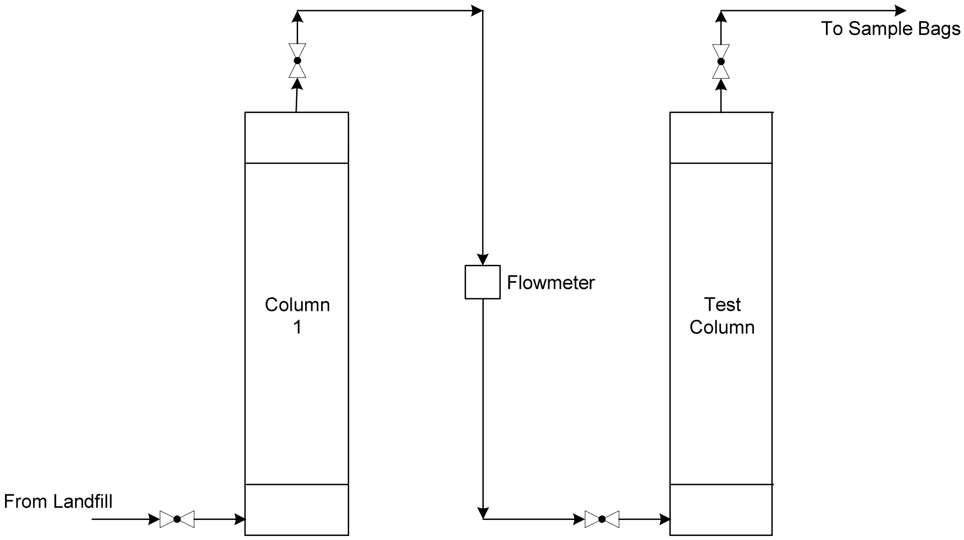


Figure 5.2: Silica gel and SulfaTreat® testing system

A sample of untreated gas was collected at the point before the gas stream entered the desiccant column and after the gas exited the desiccant column, to ensure no removal of H_2S and to make sure the gas was dry. Samples at the exit of the silica gel column were collected at 2 minutes, 10 minutes, and 10 minute intervals thereafter with the final sample being taken after all the indicating silica gel had turned black. The SRI 310 TCD (CH_4, CO_2, air, and H_2O) and the SRI 8610 FPD (15 m column with a 10 ppmv H_2S detection limit) were use to analyze the gas samples.

Gas samples were collected using 1 L Tedlar® gas sample bags, made from a polyvinyl fluoride film with a single polypropylene fitting that combines the hose/valve and the septum holder (SKC Inc.®). The sample bags were ordered from SKC Inc.®. The recommended holding time for gases containing H_2S and other sulfur compounds is 24 hours and for atmospheric gases is 72 hours. These gas sample bags were reused by thoroughly flushing the bags prior to reuse with purified air or nitrogen. A gas analysis of the final flush was performed to ensure that the background levels present in the bag were acceptable for its intended use. It is also recommended by SKC Inc.® to never fill a gas sample bag to more than 80% of its volume.

5.2.3 Silica Gel Results

Results for the new silica gel tests are presented in Figures 5.3 and 5.4. The outlet H_2S concentration remained below 10 ppmv H_2S (detection limit) for approximately 2 minutes in the 500 g test (Figure 5.3) and 20 minutes in the 1000 g test (Figure 5.4). This corresponds to an H_2S removal rate by the 1000 g sample of $6.9\text{x}10^{-5}$ grams of H_2S removed per gram of silica gel. After this point, the H_2S concentration level approached that of the untreated gas.

Another point of interest in regards to the silica gel was its ability to be reused in the H_2S removal process. To test this, the silica gel was regenerated in an oven at 150°C for 2.5 hours in order to remove the collected H_2S. The indicating silica gel returned to its bright blue color after being regenerated. Then, the same test described above was repeated at the landfill using the regenerated gel.

Results for the regenerated silica gel tests are presented in Figures 5.3 and 5.4. The regenerated gel showed a reduction in H_2S removal capability. The outlet H_2S concentration exceeded 10 ppmv at 2 minutes for the 500 g regenerated gel test (Figure 5.3) and 10 minutes for the 1000 g regenerated gel test (Figure 5.4). After exceeding 10 ppmv the outlet H_2S concentration in these regenerated gel tests approached that of the untreated gas faster than the new gel tests. An initial drop in removal capability after the first regeneration of the silica gel could be expected. Additional tests are needed to determine if subsequent regenerations cause further decreases in H_2S removal rates. Data for the silica gel tests are given in Table 5.4 and 5.5.

Table 5.4: Data for 500 g silica gel tests, outlet H_2S concentrations, SRI 8610 GC with FPD analysis, 10 ppmv H_2S detection limit

Time (min)	[H_2S] ppmv, New Silica Gel	[H_2S] ppmv, Regenerated Silica Gel
1	< 10	<10
10	21.6 ± 0.42	36.1 ± 1.14
20	144 ± 8.64	246 ± 0.40
30	235 ± 0.36	334 ± 0.79
40	254 ± 0.43	381 ± 1.06

Table 5.5: Data for 1000 g silica gel tests, outlet H_2S concentrations, SRI 8610 GC with FPD analysis, 10 ppmv H_2S detection limit

Time (min)	[H_2S] ppmv, New Silica Gel	[H_2S] ppmv, Regenerated Silica Gel
2	< 10	< 10
10	< 10	< 10
20	< 10	40.5 ± 1.14
30	39.4 ± 1.35	213 ± 0.29
40	85.3 ± 5.99	293 ± 0.59
50	216 ± 0.29	323 ± 0.74
60	249 ± 0.41	351 ± 0.89

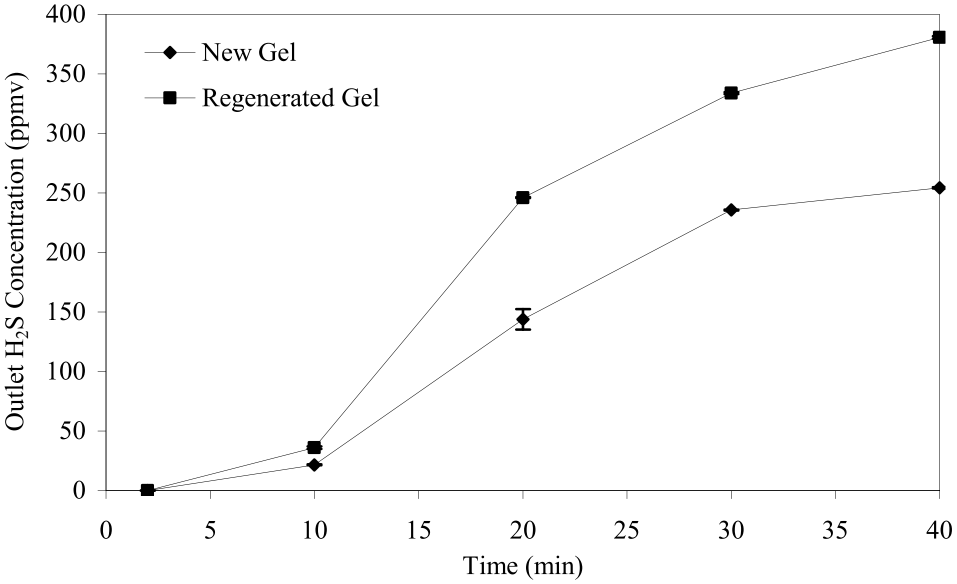


Figure 5.3: Outlet H_2S concentration over time from both new and regenerated 500 g silica gel tests, GC analysis with SRI 8610 FPD, 10 ppmv H_2S detection limit

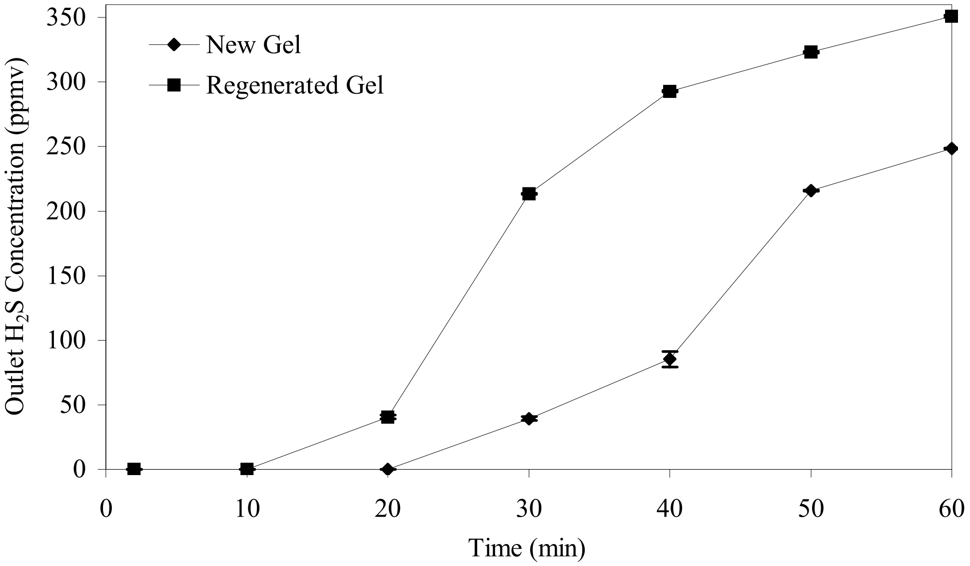


Figure 5.4: Outlet H_2S concentration over time from both new and regenerated 1000 g silica gel tests, GC analysis with SRI 8610, 10 ppmv H_2S detection limit

5.3 SulfaTreat® for H_2S Removal

5.3.1 SulfaTreat® Theory

SulfaTreat®, an H_2S scavenger, is a synthetic iron compound with an extremely porous, sponge-like surface. It removes H_2S from a gas through the reaction of iron oxide with hydrogen sulfide to form iron sulfide and water. SulfaTreat® is a single use product. Spent SulfaTreat® is non-hazardous and can be sent directly to the landfill. The SulfaTreat® Company (a business unit of M-I LLC based in Chesterfield, MO, contact Brian Kay at 636-532-2189) generously donated a 50 lb sack of their SulfaTreat 410HP product. They also provided some small-scale design specification for testing.

According to calculations provided by SulfaTreat, the 50 lb sack of product would treat a water saturated landfill gas stream of 5 L/min with an average H_2S concentration of 500 ppmv for 120 days with the maximum H_2S concentration at that time being less than 0.1 ppmv. They provided an expected removal rate of 1 lb H_2S per 25 lb (4.0×10^{-2} g H_2S per g SulfaTreat®) for the SulfaTreat® 410HP product. The vessel dimensions provided suggested a retention time of 1.5 minutes. The SulfaTreat® Company also suggests using a water saturated gas stream with the SulfaTreat® 410HP product for optimal performance.

5.3.2 SulfaTreat® Testing Procedures

The first test performed to investigate the capability of SulfaTreat® 410HP to remove H_2S was done using a small glass column. Eight grams of the product was tested at the landfill at a flowrate of 5 L/min and a retention time of 0.2 seconds. The outlet H_2S concentrations were measured with the RAE hand pump system. After 2 minutes, the outlet concentration of H_2S was 400 ppmv. The test was stopped due to the lack of H_2S reduction and considered to “blow-through” because of the small retention time.

To determine the minimum retention time required to allow SulfaTreat® 410HP to remove H_2S properly, a retention time study was performed with 6.75 lbs of SulfaTreat® 410HP in a set-up similar to that of the silica gel tests (Figure 5.2). To achieve optimal performance from the SulfaTreat® 410HP, column 1 in Figure 5.2 was filled with water, instead of desiccant, to saturate the gas stream. Flowrates from 1 L/min to 13 L/min, the maximum available flowrate from Sample Port #2, were tested. These flowrates correspond to retention times of 2.5 – 31 seconds. Outlet H_2S concentrations were tested with the RAE hand pump and no “blow-through” was observed.

A laboratory SulfaTreat® test was performed to test the H_2S removal rate of the SulfaTreat® 410HP product. An argon gas stream containing 1 vol% H_2S at a flowrate of 20 mL/min was bubbled through water and then a column containing 8.0 g of SulfaTreat® 410HP. This system had a retention time of 45 seconds. Samples were collected at the outlet every 15 mins and analyzed on the SRI 8610 GC with an H_2S detection limit of 10 ppmv.

SulfaTreat® was also tested at the landfill with the same specifications as the 1000 g silica gel test. A flowrate of 5 L/min of landfill gas (12 second retention time) was sent through column 1 filled with water to saturate the gas and then through 1000 g of SulfaTreat® 410HP. A sample of gas exiting the water column was first analyzed with the hand pump to insure that the H_2S concentration was that of untreated gas. Gas samples were then collected in gas sample bags at 2 minutes, 30 minutes, and at 30 minute intervals thereafter for 5.5 hours. Data were analyzed with the RAE hand pump using the multiple pull method. The RAE hand pump system was used (0.2-3 ppmv H_2S tubes) because this was the method with the lowest H_2S detection limit available at the time. The data sheet for these gas detection tubes (No. 10-103-04) is available at: http://www.raesystems.com/~raedocs/Data_Sheets/Tubes/HydrogenSulfide_103-04.pdf. A group from CVHS performed this same SulfaTreat® test with out a pre-water column at the landfill in May 2006. The procedure and results are given in Appendix C.

5.3.3 SulfaTreat® Results

The 1000 g SulfaTreat® test performed at the landfill had an average inlet H_2S concentration of 500 ppmv. RAE Systems states that the 0.2-3 ppmv H_2S tubes must be used at < 5% relative humidity (RH) and that the reading drops off sharply above 5% RH. The SRI 310 TCD results show that the method used in this test for saturating the gas stream was not effective. The concentration of water in the gas stream at the outlet of the water column was only about 10 ppmv H_2O. Since, 10 ppmv H_2O is 0.02% RH for the landfill gas stream, the 0.2-3 ppmv tubes could be used. The gas detection tube data sheet also states that the precision is ≤ ± 12% (when the RH is within specifications). The data are given in Table 5.6 and plotted in Figure 5.5. At no time during the 5.5 hours of testing did the outlet H_2S concentration exceed the required 1 ppmv H_2S. However, an unusual peak was observed in the data with the H_2S concentration reaching a maximum of 0.4 ppmv at 4 hours. The cause of this peak in concentration is unknown. Because the peak was still well below the 1 ppmv threshold for SOFC operation, it was not considered significant.

Table 5.6: Data for 1000 g SulfaTreat® test, 5 L/min 500 ppmv H_2S landfill gas, results obtained with hand pump, 0.2-3 ppmv H_2S tubes, error is ± 12%

Time (hr)	Sample Size (mL)	Outlet [H_2S] ppmv
0.03	100	0.00
1.5	500	0.00
2.0	100	0.00
2.5	500	0.04
3.0	400	0.10
3.5	200	0.35
4.0	300	0.40
4.5	200	0.10
5.0	200	0.08
5.5	500	0.04

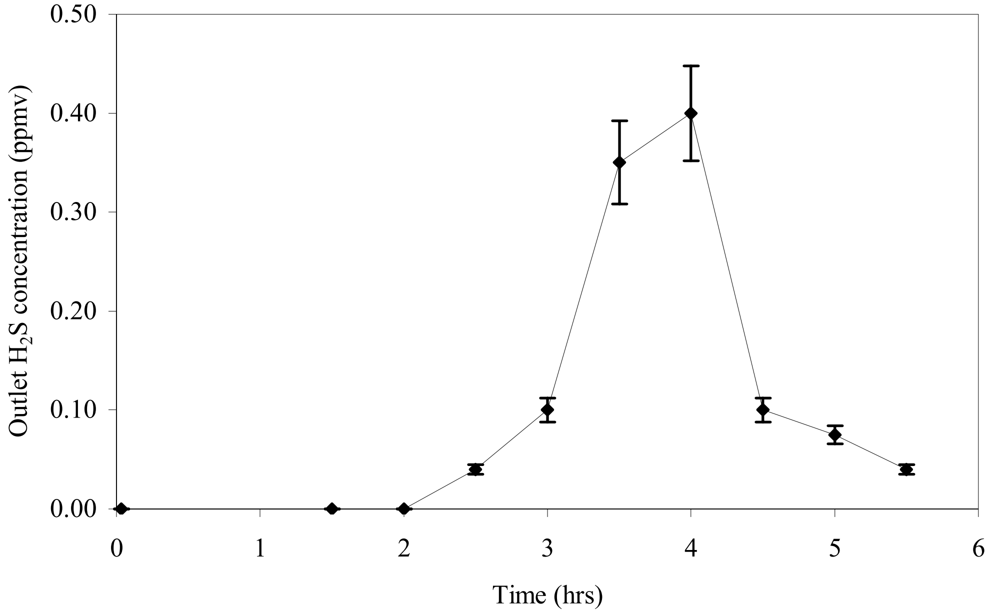


Figure 5.5: Outlet H_2S concentration, 5 L/min 500 ppmv H_2S landfill gas, 1000g of SulfaTreat®, results obtained with hand pump, 0.2-3 ppmv H_2S tubes,

The results from the controlled laboratory test with 1 vol% inlet H_2S and 8.0 g SulfaTreat® are presented in Table 5.7 and plotted in Figure 5.6. The results show that the outlet H_2S concentration stayed below 10 ppmv (the H_2S detection limit of the GC at the time of the test) for 4 hours before beginning to become saturated (Figure 5.6). Approximately $8.4x10^{-3}$ grams of H_2S were removed per gram of SulfaTreat® prior to this saturation point. At this removal rate, 1000 g of SulfaTreat® 410HP at 5 L/min of landfill gas would be able to bring the H_2S concentration from 500 ppmv to less than 1 ppmv for 1.2 days. This value should be compared to 20 minutes for the silica gel landfill test (Figure 5.2) and 120 days for the expected SulfaTreat® performance provided by the SulfaTreat® Company (4.0 x 10^{-2} g H_2S per g SulfaTreat®).

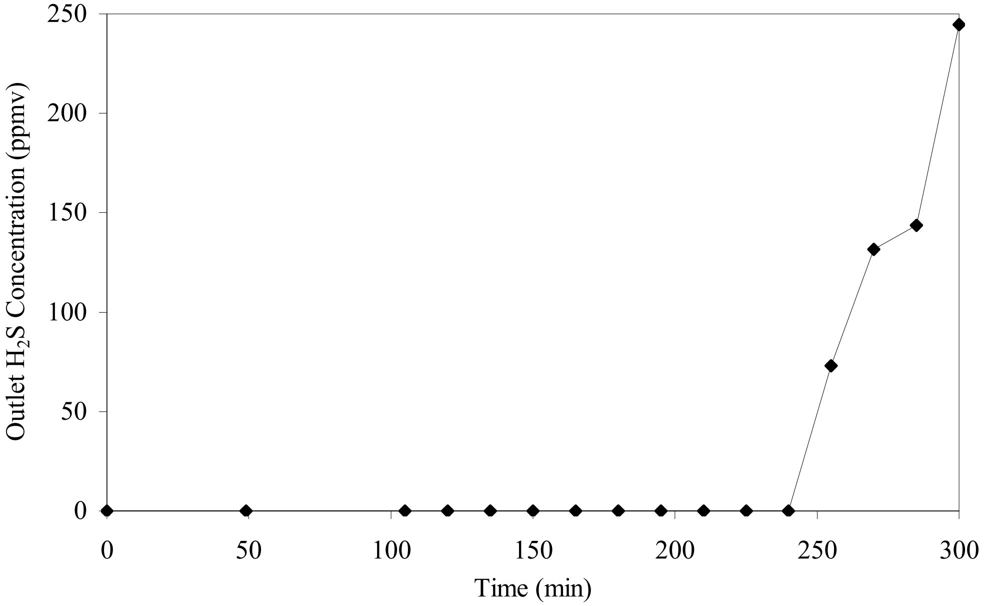


Figure 5.6: Outlet H_2S concentration, 8.0 g of SulfaTreat, 20 mL/min 1% H_2S in argon, controlled laboratory test, GC analysis with SRI 8610, 10 ppmv H_2S detection limit

Table 5.7: Data for laboratory SulfaTreat® test, 8.0 g of SulfaTreat®, 20 mL/min 1% H_2S in argon, SRI 8610 GC analysis with 10 ppmv H_2S detection limit

Time (min)	[H_2S] ppmv
0	< 10
49	< 10
105	< 10
120	< 10
135	< 10
150	< 10
165	< 10
180	< 10
195	< 10
210	< 10
225	< 10
240	< 10
255	72.9
270	131.6
285	143.5
300	244.5

6. CONCLUSIONS

It was determined that about 800 tons of silica gel per twelve hour period would be required to remove 1000 ppmv H_2S from the landfill gas stream (1700 SCFM) down to <1 ppmv H_2S. To utilize silica gel at the landfill, two sets of silica gel and two 250,000 gallon containers would be required. One set of silica gel would be on-line, removing sulfur while the other set would be regenerating, switching every twelve hours. If silica gel can be indefinitely regenerated to the original removal capability, at the 10,000 lb price of $0.82 per lb of silica gel, this is approximately $2.7 million (silica gel alone, no support equipment). If silica gel cannot be regenerated to the original removal capability, the cost would increase proportionately to the silica gel degradation. The amount of silica gel required, the accompanying equipment, and the projected cost make it an impractical method for sulfur removal from landfill gas at Coffin Butte Landfill.

Based on design specifications provided by the SulfaTreat® Company, Coffin Butte Landfill would need 1366 tons of SulfaTreat® 410HP per year. As the 2000-lb "super sack" price is $0.41 per lb, this equates to about $1.1 million per year. Using the removal rate calculated from the SulfaTreat® test performed in the laboratory, the necessary amount of SulfaTreat® is higher, at 6503 tons per year ($5.3 million per year). The lower H_2S removal rate obtained from the laboratory test results could be due to not using a fully saturated gas stream as recommended by the SulfaTreat® Company. SulfaTreat® 410HP is more feasible than silica gel for removing sulfur from the landfill gas at Coffin Butte Landfill.

For a landfill gas stream of 1700 SCFM with an average H_2S concentration of 1000 ppmv the removal capabilities, amounts required for one year, and raw material costs for one year are compared in Table 6.1.

Table 6.1: Comparison of H_2S Removal Methods for Processing 1700 SCFM Landfill Gas at 1000 ppmv H_2S for one year

H_2S Removal Method	Silica Gel Results*	SulfaTreat® Company	SulfaTreat® Lab Results
Grams H_2S removed per gram (before saturation of media)	9.1×10^{-5}	4.0×10^{-2}	8.4×10^{-3}
Amount required (tons)	1645	1366	6503
Raw material cost (Millions $)	$ 2.7	$1.1	$5.3

* Silica gel values are for a two 250,000 gallon container system (one on-line, removing sulfur and the other being regenerated, switching every 12 hours). Assuming silica gel can be regenerated to the original removal capacity for at least one year.

7. RECOMMENDATIONS FOR FUTURE WORK

1) To fully characterize the landfill gas, the additional sulfur compounds that were observed with the SRI 8610 GC (FPD and 60 m column) should be identified and the machine should be calibrated for these compounds.
2) Further investigation of SulfaTreat® is recommended.
    a) Additional long time tests should be performed at the landfill as well as further controlled laboratory tests to verify the sulfur removal rate. Work needs be done to develop a method for saturating the landfill gas for testing of SulfaTreat®.
    b) The SulfaTreat® Company should be contacted to obtain specifications for a system large enough to process all of the landfill gas produced at Coffin Butte. (Brian Kay at 636-532-2189)
3) If the RAE hand pump system is used for gas analysis, humidity specifications should be considered for every tube type, as erroneous results can be obtained for some tubes at high moisture content. Tubes with a pre-layer of desiccant are available for all H_2S concentration ranges and these should be used.
4) Other sulfur removing methods should also be explored. Gas Technology Products LLC markets several sulfur removal methods for landfill gas. Table 7.1 details the different technologies. Currently, about 300 lb of sulfur is produced per day at Coffin Butte Landfill. Sulfur-Rite® is a similar technology to SulfaTreat®. The LO-CAT® and the MINI-CAT® are iron redox technologies. Contact David Graubard from Gas Technology Products (1-847-285-3855, dgraubard@merichem.com, www.gtp-merichem.com).

Table 7.1: Sulfur Removing Technologies from Gas Technology Products LLC (Graubard)

Technology	When Normally Used	Capital Cost	Operating Cost per lb of sulfur
Liquid Scavenger: Eliminator®	< 50 lbs sulfur/day	Extremely Low	\$4.00 to \$10.00
Solid Media: Sulfur-Rite®	50-300 lbs sulfur/day	Low	\$3.00 to \$6.00
Iron Redox: LO-CAT or MINI-CAT	300 lbs to 15 tons/day	Medium to High	\$0.20 to \$0.40

5) Efforts should be made to contact landfills with operating fuel cells to inquire about economical sulfur removal methods.
6) After a reliable sulfur removal system is developed, the next step would be to install a pilot scale fuel cell at the landfill for testing. If successful, the fuel cell could be implemented to handle the excess landfill gas that is currently sent to a flare, as a means of doing long-term durability and stability testing.

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APPENDICES

APPENDIX A: SRI 8610, FPD Calibration Data

Table A.1: SRI 8610 FPD calibration data,
15 m column, 10 ppmv H_2S detection limit,
see Table 4.2 for operating parameters

Injection Size (µL)	[H_2S] (ppmv)	Peak Area	log (conc)	log (peak area)	Std Dev (peak area)	Std Dev (log(peak area))
100	10.0	17.55	1.00	1.244	1.25	0.0335
100	10.0	15.04	1.00	1.177	1.25	0.0335
100	30.0	139.52	1.48	2.145	3.42	0.0103
100	30.0	147.83	1.48	2.170	3.42	0.0103
100	30.0	142.81	1.48	2.155	3.42	0.0103
100	50.0	393.33	1.70	2.595	20.19	0.0239
100	50.0	372.45	1.70	2.571	20.19	0.0239
100	50.0	344.06	1.70	2.537	20.19	0.0239
100	80.0	910.54	1.90	2.959	15.07	0.0071
100	80.0	946.86	1.90	2.976	15.07	0.0071
100	80.0	934.39	1.90	2.971	15.07	0.0071
100	100	1341.64	2.00	3.128	52.54	0.0174
100	100	1250.99	2.00	3.097	52.54	0.0174
100	100	1375.43	2.00	3.138	52.54	0.0174
10	100	9.67	2.00	0.986	0.04	0.0017
10	100	9.60	2.00	0.982	0.04	0.0017
10	200	36.15	2.30	1.558	2.11	0.0238
10	200	39.91	2.30	1.601	2.11	0.0238
10	200	41.10	2.30	1.614	2.11	0.0238
10	300	101.71	2.48	2.007	0.10	0.0004
10	300	101.51	2.48	2.006	0.10	0.0004
10	400	197.49	2.60	2.296	0.20	0.0004
10	400	197.89	2.60	2.296	0.20	0.0004
10	500	317.80	2.70	2.502	2.69	0.0036
10	500	322.99	2.70	2.509	2.69	0.0036
10	500	323.89	2.70	2.510	2.69	0.0036

APPENDIX A: SRI 8610, FPD Calibration Data (Continued)

Table A.2: SRI 8610 FPD calibration data, 60 m column, 1 ppmv H_2S detection limit, see Table 4.3 for operating parameters

Injection Size (mL)	$[H_2S]$ ppm	Peak Area	log (conc)	log (peak area)	Std Dev (peak area)	Std Dev (log(peak area))
1	5.000	543.5	0.70	2.74	23.52	0.0179
1	5.000	546.0	0.70	2.74	23.52	0.0179
1	5.000	594.6	0.70	2.77	23.52	0.0179
1	1.001	36.25	0.00	1.56	0.71	0.0083
1	1.001	37.58	0.00	1.57	0.71	0.0083
1	1.001	38.19	0.00	1.58	0.71	0.0083
1	1.001	37.53	0.00	1.57	0.71	0.0083
1	10.00	3109	1.00	3.49	65.75	0.0094
1	10.00	2948	1.00	3.47	65.75	0.0094
1	10.00	3032	1.00	3.48	65.75	0.0094
1	9.216	2684	0.96	3.43	25.47	0.0041
1	9.216	2678	0.96	3.43	25.47	0.0041
1	9.216	2653	0.96	3.42	25.47	0.0041
1	9.216	2724	0.96	3.44	25.47	0.0041

APPENDIX B: Historical PNGC Landfill Gas Composition Data

Table B.1: Historical gas composition data from PNGC

	Concentration (vol%)		
Date	CH_4	CO_2	O_2
01/06/03	53.2	39.1	0.00
01/13/03	53.2	38.1	0.00
02/05/03	52.9	40.2	0.00
05/27/03	50.1	37.7	0.00
07/28/03	53.4	39.0	0.60
08/29/03	53.5	39.6	0.50
10/22/03	55.4	39.9	0.40
11/05/03	55.0	39.9	0.40
11/06/03	57.5	40.1	0.30
11/10/03	56.8	39.9	0.50
01/19/04	56.9	39.8	0.50
01/26/04	56.4	39.6	0.40
02/25/04	57.1	40.4	0.70
03/09/04	56.0	41.0	0.50
05/05/04	56.9	42.1	0.30
05/17/04	56.5	41.6	0.60
05/19/04	56.6	41.0	0.40
06/09/04	55.4	41.1	0.50
06/10/04	56.8	40.2	0.40
07/12/04	55.2	41.3	0.30
07/14/04	56.7	40.7	0.60
07/19/04	52.6	39.7	0.70
09/21/04	53.0	39.1	0.70
09/27/04	53.9	39.6	0.70
10/15/04	53.4	39.8	0.90
10/19/04	54.2	40.2	0.90
11/30/04	52.2	38.1	0.40
12/13/04	51.6	39.0	0.70
12/20/04	52.3	38.9	0.30
01/20/05	54.7	40.1	0.40
01/21/05	53.9	39.5	0.70
01/24/05	54.3	39.6	0.40
02/15/05	52.5	40.0	0.50
02/18/05	54.8	40.8	0.10
02/22/05	52.2	39.4	0.70

APPENDIX C: CVHS SulfaTreat® Tests with Dry Landfill Gas, Analyzed with the RAE Hand Pump System

A group from CVHS performed SulfaTreat® tests at the landfill with “dry” gas (no water column before the SulfaTreat® column). The test was performed twice using the same specifications. A 10 L/min landfill gas stream was sent through a single column filled with 1000 g of SulfaTreat 410HP. The average H_2S inlet concentration was 1000 ppmv. Data were analyzed with the RAE hand pump system. Data are considered accurate because the gas was less than 5% RH (SRI 310 TCD analysis resulted in 8.6 ppmv H_2O, 0.018% RH). Both tests resulted in break-through after about 110 minutes. This corresponds to an H_2S removal rate of 2.04×10^{-3} grams H_2S removed per gram of SulfaTreat®. Results are given in Figure C.1 and C.2. Data are available in Tables C.1 and C.2. Table C.3 compares this H_2S removal rate to the other results presented in Table 6.1

Table C.1: Data from CVHS Test #1, 1000 g SulfaTreat®,
10 L/min of 1000 ppmv H_2S dry landfill gas,
results obtained with hand pump, error is ≤ ± 12%

Time (min)	Outlet [H_2S] ppmv
1	0
10	0
20	0
30	0
40	0
50	0
60	0
72	0
81	0
121	7.2
207	56

APPENDIX C: CVHS SulfaTreat® Tests with Dry Landfill Gas, Analyzed with the RAE Hand Pump System (Continued)

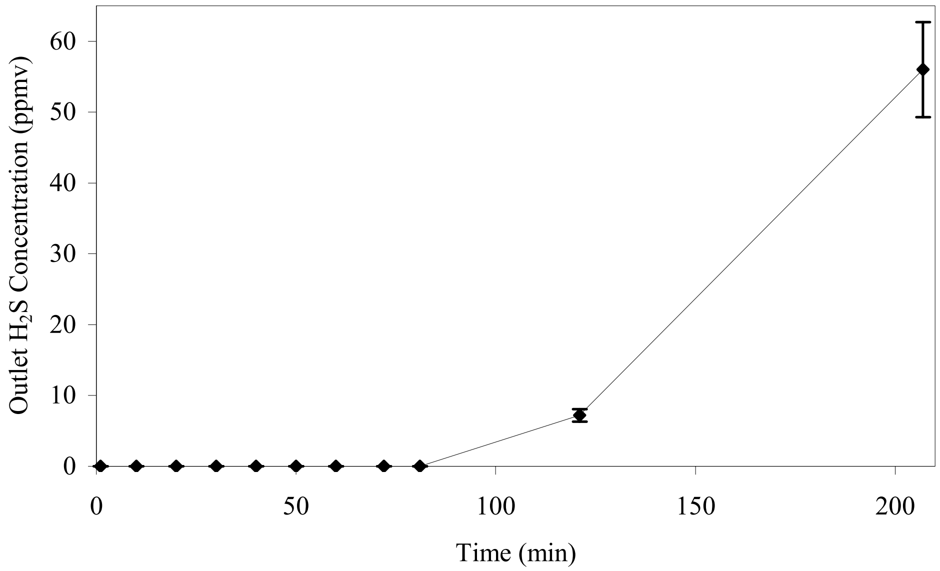

Figure C.1: CVHS Test #1, outlet H_2S concentration, 10 L/min 1000 ppmv H_2S dry landfill gas, 1000g of SulfaTreat®, results obtained with hand pump

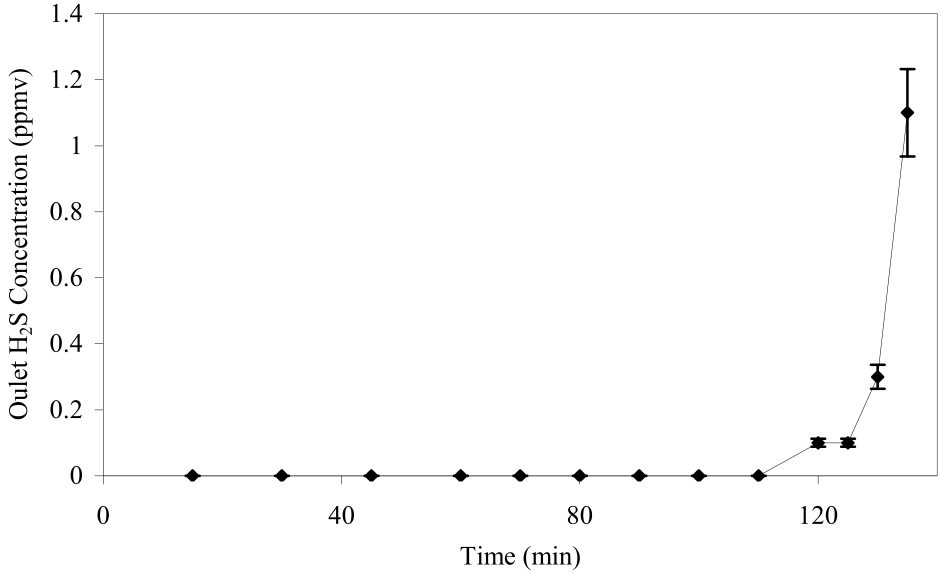

Figure C.2: CVHS Test #2, outlet H_2S concentration, 10 L/min 1000 ppmv H_2S dry landfill gas, 1000g of SulfaTreat®, results obtained with hand pump

APPENDIX C: CVHS SulfaTreat® Tests with Dry Landfill Gas, Analyzed with the RAE Hand Pump System (Continued)

Table C.2: Data from CVHS Test #2, 1000 g SulfaTreat®,
10 L/min of 1000 ppmv H_2S dry landfill gas,
results obtained with hand pump, error is ≤ ± 12%

Time (min)	Outlet [H_2S] ppmv
15	0
30	0
45	0
60	0
70	0
80	0
90	0
100	0
110	0
120	0.1
125	0.1
130	0.3
135	1.1

Table C.3: Comparison of H_2S Removal Methods
for Processing 1700 SCFM Landfill Gas at 1000 ppmv H_2S for 1 year

H_2S Removal Method	Silica Gel Landfill Results	SulfaTreat® Company	SulfaTreat® Lab Results	SulfaTreat® CVHS Results
Grams H_2S removed per gram before saturation of media	9.1×10^{-5}	4.0×10^{-2}	8.4×10^{-3}	2.04×10^{-3}
Amount required (tons)	1645	1366	6503	27,778
Raw material cost (Millions of $)	$ 2.7	$1.1	$5.3	$22