CALIFORNIA
ENERGY COMMISSION

Energy Research and Development Division

FINAL PROJECT REPORT

Advancing Novel Biogas Cleanup Systems for the Production of Renewable Natural Gas

Gavin Newsom, Governor
May 2020 | CEC-500-2020-032

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Contract Number: PIR-14-019

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DISCLAIMER

ACKNOWLEDGEMENTS

Gas Technology Institute acknowledges the California Energy Commission, Southern California Gas Company, the Orange County Waste and Recycling, and the Coyote Canyon Landfill personnel for the opportunity to evaluate and demonstrate this novel biogas cleanup technology. Gas Technology Institute also thanks its subcontractors: Nrgtek for the design, fabrication and operation of the LFG clean-up system in varying ambient conditions at the site; and SCS for site preparation to facilitate system deployment.

PREFACE

The California Energy Commission's Energy Research and Development Division manages the Natural Gas Research and Development Program, which supports energy-related research, development, and demonstration not adequately provided by competitive and regulated markets. These natural gas research investments spur innovation in energy efficiency, renewable energy and advanced clean generation, energy-related environmental protection, energy transmission and distribution and transportation.

The Energy Research and Development Division conducts this public interest natural gas-related energy research by partnering with RD&D entities, including individuals, businesses, utilities and public and private research institutions. This program promotes greater natural gas reliability, lower costs and increases safety for Californians and is focused in these areas:

- Buildings End-Use Energy Efficiency.
- Industrial, Agriculture and Water Efficiency
- Renewable Energy and Advanced Generation
- Natural Gas Infrastructure Safety and Integrity.
- Energy-Related Environmental Research
- Natural Gas-Related Transportation.

Advancing Novel Biogas Cleanup Systems for the Production of Renewable Natural Gas is the final report for the Advancing Novel Biogas Cleanup Systems for the Production of Renewable Natural Gas project (PIR-14-019) conducted by Gas Technology Institute. The information from this project contributes to the Energy Research and Development Division's Natural Gas Research and Development Program.

For more information about the Energy Research and Development Division, please visit the Energy Commission's website at www.energy.ca.gov/research/ or contact the Energy Commission at 916-327-1551.

ABSTRACT

The goal of this project is to design and build an innovative technology for cost-effective removal of contaminants from raw landfill gas. The developed cleanup process was demonstrated on a pilot-scale (100 standard cubic feet per minute of gas) and consisted of three subsystems for sequential removal of (1) hydrogen sulfide/siloxanes, (2) carbon dioxide, and (3) oxygen/nitrogen from raw landfill gas. The innovative technology uses absorbing materials that are more environmentally friendly compared with existing commercial solutions to produce renewable natural gas in compliance with natural gas pipeline injection standards.

Keywords: Landfill gas, renewable natural gas, physical adsorbents, Rule 30

Please use the following citation for this report:

Hill, Andy, Ken Kriha, Tony Lindsay, Chakravarthy Sishtla, and Subra Iyer. 2020. *Advancing Novel Biogas Cleanup Systems for the Production of Renewable Natural Gas*. California Energy Commission. Publication Number: CEC-500-2020-032.

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EXECUTIVE SUMMARY

Introduction

California leads the nation in efforts to reduce greenhouse gas emissions that cause climate change. The California Global Warming Solutions Act of 2006 (Assembly Bill 32, Nunez, Chapter 488, Statutes of 2006) established the state's commitment to reducing its carbon footprint, and the state has continued to promote progressively more ambitious policies to reduce emissions. In 2018, then-Governor Edmund G. Brown signed Executive Order B-55-18 calling for the state to achieve carbon neutrality by 2045 where all sectors of economy will remove as much carbon dioxide from the atmosphere as each put into it. The overall goal of carbon neutrality is to achieve a zero-carbon footprint.

Biogas, a type of biofuel naturally produced from the decomposition of organic waste, provides an opportunity to reduce the carbon footprint of energy generation compared to using fossil fuels and to support California's climate goals. To be interchangeable with traditional pipeline-quality natural gas, biogas must be upgraded to a quality similar to fossil natural gas and contain at least 90 percent or more of methane. However, production of renewable natural gas from biogas is currently a relatively costly, complex, and energy-intensive process. To expand the opportunities for renewable natural gas use in California—including injection into the natural gas pipeline, direct use for transportation, or more sophisticated electric power applications including turbines and fuel cells—the renewable natural gas production industry needs to lower the costs of biogas cleanup systems.

Project Purpose

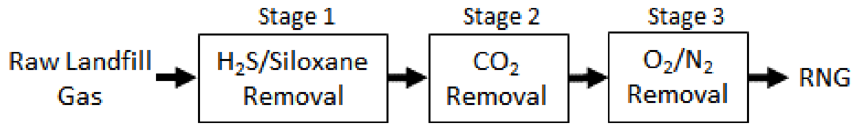
This project aimed to develop and demonstrate a novel cleanup technology to enable cost-effective upgrading of landfill gas to renewable natural gas. As a part of this project, the researchers tested and evaluated regenerative organic solvents to remove hydrogen sulfide (H_2S), siloxanes, carbon dioxide (CO_2), nitrogen (N_2), and oxygen (O_2) from biogas. Regenerative organic solvents, such as polyethylene glycol, can absorb impurities from biogas and desorb them using increased pressure or increased temperature, so that solvent can be re-used for many more cycles.

Project Approach

The research team designed a three-stage comprehensive landfill gas cleanup system for sequential removal of contaminants from raw landfill gas (Figure ES-1).

The researchers conducted laboratory scale experiments to select candidate solvents used in the cleanup system. The data from these experiments as well as prior experience with component removal at a different landfill was used to design the clean-up system. The equipment was assembled at the Nrgtek facility in Orange, California. The researchers chose the demonstration site based on the composition of the landfill gas, logistical criteria to ensure fast delivery and installation of the cleanup system, and testing conditions that were close to the average conditions found at landfill sites.

Figure ES-1: Original Plan for Landfill Gas Cleanup Demonstration System



Source: GTI

Project Results

The researchers carried out laboratory experiments that targeted each major contaminant in the landfill gas. The experiments evaluated a broad range of solvents and separation techniques to identify the most efficient and environmentally friendly operations. Results of experimental testing include:

- Oxygen – Removed O_2 in N_2 from landfill feed condition compositions to below Rule 30 RNG levels.
- Carbon dioxide – Identified physical solvents with high CO_2 absorption capacity and fast desorption times initiated solely by agitation.
- Hydrogen sulfide – 92 percent removal efficiency to within 4 parts per million of Rule 30 RNG level in landfill gas sample at target landfill gas flow rate.
- Siloxanes – Positive visual precipitation tests and solvents regeneration with the addition of air into the solvent.
- Nitrogen – Identification of a solvent that showed a 3:1 selectivity of methane to nitrogen.

These tests mimicked the contaminant level of the landfill gas feed compositions, but the complexity of the interactions between multiple components was not fully reproduced in the lab experiments. The researchers designed and built the demonstration equipment with a range of flexibility to allow for adjustments in the field as necessary.

Field tests showed lower than expected performance of the novel solvents used in the project during the first stage of contaminant removal despite the successful testing in the laboratory environment. The amount of impurities removed at the first stage of cleanup was insufficient for moving on to the next stage of the removal process. Thus, the researchers were unable to demonstrate all three stages of landfill gas cleanup and produce high quality renewable natural gas.

Technology/Knowledge Transfer

The technology developed under this project sparked the interest of several municipalities and private companies because if successful, it would allow to reduce costs of renewable natural gas and make it competitive with natural gas from fossil sources. For example, RealEnergy LLC in Napa, California expressed interest in hosting cleanup equipment at a different landfill site in California to allow continued operation to validate the quality of the produced renewable natural gas. Additional data on solvent performance will improve the draw conclusions about the ability of the system to remove all landfill gas contaminants. The research team transferred ownership of the cleanup system to RealEnergy, who in turn agreed to make future test results available to the California Energy Commission.

Benefits to California

While the project had some success in the laboratory and in assembling and deploying the gas cleanup technology at a landfill site, delays caused by the need to change the demonstration site and other critical issues severely limited the time to collect data and address the problems encountered during system commissioning and testing. Furthermore, the project obtained unsatisfying results for the CO_2 removal at the stage 1 of the cleanup system. Lower than expected removal rate of CO_2 from landfill gas restricted the testing for the stages 2 and 3 of the cleanup system. Therefore, there was insufficient data to draw conclusions about the technology and to use as a basis for projecting the benefits to California. However, the transfer of the technology to the RealEnergy, which will continue testing and improving of the designed cleanup system, laid the groundwork for continued pursuit of this technology in California.

CHAPTER 1:
Project Purpose

Biogas use in California offers an opportunity for lower-cost renewable energy production that has a dramatically reduced carbon footprint when compared to fossil fuels. Currently, cleaning and upgrading biogas to high quality renewable natural gas (RNG) can be costly, complex, energy intensive, and consume raw materials that cannot be easily or cost-effectively regenerated. Sites with sources of biogas have predominately chosen to produce electricity using reciprocating engines. These engines can be very forgiving regarding the constituents and varying energy content of the gas used to power them. To expand the opportunities for RNG use in California including injection into the natural gas pipeline, direct use for transportation, or more sophisticated electric power applications including turbines and fuel cells, RNG will need to more closely resemble pipeline quality natural gas.

State-of-the art methods for removing these contaminants include:

- Use of solid adsorbents (hydrogen sulfide [H_2S]/siloxanes).
- Pressure swing adsorption (carbon dioxide [CO_2]/dinitrogen [N_2]/oxygen [O_2]).
- Cryogenic (CO_2/N_2).
- Membranes (CO_2/N_2).
- Catalytic oxidation (O_2).

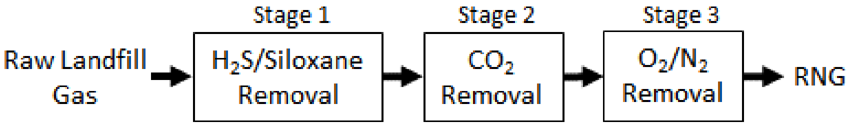
These processes have been successful in removing the targeted contaminants, but each process has characteristics that add to deployment costs.

The goal of this project was to design and demonstrate the operation of a novel biogas cleanup system. The system would ultimately produce high quality RNG suitable for pipeline injection or transportation fuel. The process would use off-the-shelf, benign solvents that could be regenerated during the process, operate at moderate pressure (80-100 pounds per square inch gauge [psig]), and result in no additional hazardous waste production.

CHAPTER 2: Project Approach

This project combined the experience of two teams, Gas Technology Institute (GTI) and Nrgtek, to design, construct, and demonstrate a pilot-scale landfill gas cleanup process. The approach leveraged Nrgtek's experience and patented technologies to develop and demonstrate a three-stage comprehensive landfill gas (LFG) cleanup system. The three-stage gas-liquid contactors would sequentially remove CO_2, O_2/ H_2S/siloxanes, and O_2/N_2 from raw LFG as shown in Figure 1.

Figure 1: Original Plan for Landfill Gas Cleanup Demonstration System



Source: GTI

Site Selection

Otay Landfill

Otay Landfill in Chula Vista, California was initially selected as the site for the LFG-to-RNG demonstration. The landfill was equipped to supply LFG to accommodate the slipstream of 100 standard cubic foot per minute (SCFM) flow and 80-100 psig pressure needed for operation of the GTI LFG cleanup system. The Otay Landfill made available a graded area for deployment of the GTI equipment and a convenient electrical power takeoff location to reduce deployment costs. GTI began site-specific design drawings and also obtained an exemption from the local jurisdictional permitting agencies[1] to operate the cleanup system for research purposes.

GTI and Nrgtek made several trips to the Otay landfill site to meet with personnel and discuss the details of the equipment installation and operation. During one of these visits, researchers took a sample of the raw LFG and performed a comprehensive gas analysis on the sample. The cleanup equipment design was initiated based on the results of the analysis.

In February 2016, the Otay Landfill decided not to participate in the demonstration due to issues related to gas production and maintenance problems. The research team then surveyed possible new demonstration sites (Table 1).

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1 County of San Diego Department of Environmental Health Solid Waste Local Enforcement Agency and San Diego County Air Pollution Control District.

Table 1: Gas Composition at Alternate Landfill Sites Considered

	CH4 (vol%)	CO2 (vol%)	O2 (vol%)	N2 (vol%)	Sulfur* (ppm)	Total (vol%)	Pressure (psig)
Coyote Canyon (OCWR)	45.3	33.3	3.4	17.7	**	99.7	5
Puente Hills ICE (LACSD)	39.7	32.1	4.0	22.6	145	98.4	57
Puente Hills PERG (LACSD)	34.9	27.4	6.4	28.8	125	97.5	3
Puente Hills Spadra (LACSD)	26.1	21.9	8.1	41.5	29	97.6	3
Calabasas (LACSD)	29.0	25.8	6.6	36.8	91	98.2	90 or 490
Bowermann (OCWR)	52.0	40.0	1.0	6.5	**	99.5	33
Scholl Canyon (LACSD)	32.0	28.0	6.0	34.0	**	100	50

* **Total reduced sulfur compounds**

**** Not available**

Source: Gas Technology Institute

Coyote Canyon Landfill

The Coyote Canyon Landfill, operated by Orange County Waste and Recycling (OCWR) in Newport Beach, California, was chosen as an alternative demonstration site. Of the six potential sites evaluated, Coyote Canyon exhibited the highest CH_4 and lowest N_2 contents which are the preferred characteristics for cleanup and RNG production. Formal contract negotiations for usage of the site began with OCWR as well as a comprehensive evaluation of the specifics of the Coyote Canyon LFG feed gas.

The LFG at the Coyote Canyon site was only available at ~3 pounds per square inch gauge (psig). The cleanup process equipment requires a feed pressure of 80-100psig. To achieve the desired operating pressure, a LFG booster compressor was procured. This equipment was not needed at the original Otay site. The additional compression equipment also required chilling and water removal system and doubled the overall footprint of the proposed demonstration system.

In addition, as the site is under the jurisdiction of the South Coast Air Quality Management District, a permit to operate the cleanup system was required to be obtained.

Bid documents were sent to vendors for the required civil, mechanical and electrical construction work. The two bids received were much higher than the allocated budget in the contract primarily due to more extensive modifications to the site being required and the added installation expense associated with the biogas booster compressor that was not originally required. To mitigate the budget shortfall, an alternative approach of setting the equipment on two trailers to make it mobile (instead of on a concrete containment pad) was pursued. This approach eliminated the civil costs and the concrete removal costs. A portion of the mechanical costs were also reduced by setting the equipment on the trailers which allowed Nrgtek to complete the majority of the interconnections between the cleanup system skids at their shop in California. Despite these measures, and with in-kind cash contributions from GTI and Nrgtek, there was still a budget shortfall of approximately $100,000.

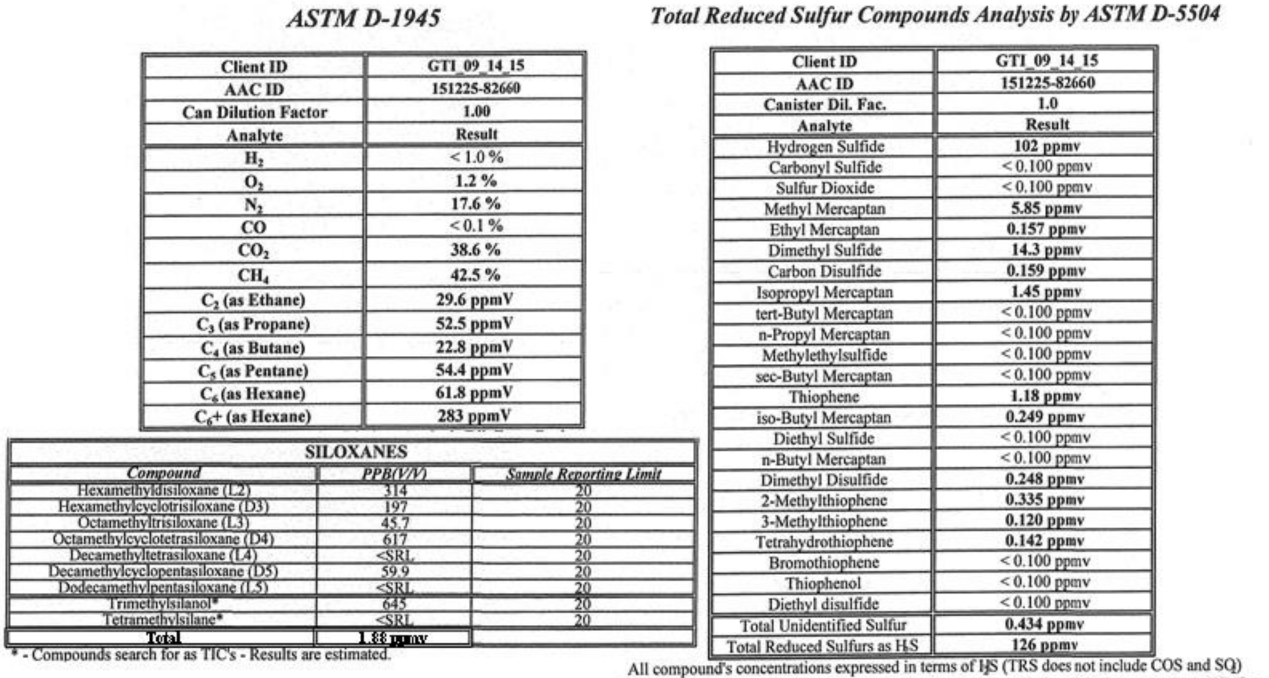
GTI's cost share partner, Southern California Gas (SoCalGas), agreed to increase its contribution in order to allow for the trailers, permits, and added site construction contractor costs. Unfortunately, the additional cost share funds were not available to GTI until August 2018. Additional delays getting the site contractor pushed the equipment installation at the Coyote Canyon site to December 2018.

Laboratory Testing

Oxygen, Hydrogen Sulfide, and Siloxane Removal

The design of the O_2/H_2S/siloxane removal subsystem was based on the LFG composition of the Otay Landfill (Chula Vista, CA), where the demonstration of RNG generation was first planned to be conducted. The composition of the Otay LFG (sampled July 30, 2015) is shown in Figure 2 and indicates that concentrations of O2 (1.2 vol percent), H2S (102 ppmv), total reduced sulfurs as H2S (126 ppmv) and siloxanes (1.9 ppmv), are comparable to typical LFG.

Figure 2: Otay Landfill Landfill Gas Composition



ASTM D-1945

Client ID	GTI_09_14_15
AAC ID	151225-82660
Can Dilution Factor	1.00
Analyte	Result
H_2	< 1.0 %
O_2	1.2 %
N_2	17.6 %
CO	< 0.1 %
CO_2	38.6 %
CH_4	42.5 %
C_2 (as Ethane)	29.6 ppmV
C_3 (as Propane)	52.5 ppmV
C_4 (as Butane)	22.8 ppmV
C_5 (as Pentane)	54.4 ppmV
C_6 (as Hexane)	61.8 ppmV
C_6+ (as Hexane)	283 ppmV

SILOXANES		
Compound	*PPB(V/V)*	*Sample Reporting Limit*
Hexamethyldisiloxane (L2)	314	20
Hexamethylcyclotrisiloxane (D3)	197	20
Octamethyltrisiloxane (L3)	45.7	20
Octamethylcyclotetrasiloxane (D4)	617	20
Decamethyltetrasiloxane (L4)	<SRL	20
Decamethylcyclopentasiloxane (D5)	59.9	20
Dodecamethylpentasiloxane (L5)	<SRL	20
Trimethylsilanol*	645	20
Tetramethylsilane*	<SRL	20
Total	**1.88 ppmv**	

* - Compounds search for as TIC's - Results are estimated.

Total Reduced Sulfur Compounds Analysis by ASTM D-5504

Client ID	GTI_09_14_15
AAC ID	151225-82660
Canister Dil. Fac.	1.0
Analyte	Result
Hydrogen Sulfide	**102 ppmv**
Carbonyl Sulfide	< 0.100 ppmv
Sulfur Dioxide	< 0.100 ppmv
Methyl Mercaptan	**5.85 ppmv**
Ethyl Mercaptan	**0.157 ppmv**
Dimethyl Sulfide	**14.3 ppmv**
Carbon Disulfide	**0.159 ppmv**
Isopropyl Mercaptan	**1.45 ppmv**
tert-Butyl Mercaptan	< 0.100 ppmv
n-Propyl Mercaptan	< 0.100 ppmv
Methylethylsulfide	< 0.100 ppmv
sec-Butyl Mercaptan	< 0.100 ppmv
Thiophene	**1.18 ppmv**
iso-Butyl Mercaptan	**0.249 ppmv**
Diethyl Sulfide	< 0.100 ppmv
n-Butyl Mercaptan	< 0.100 ppmv
Dimethyl Disulfide	**0.248 ppmv**
2-Methylthiophene	**0.335 ppmv**
3-Methylthiophene	**0.120 ppmv**
Tetrahydrothiophene	**0.142 ppmv**
Bromothiophene	< 0.100 ppmv
Thiophenol	< 0.100 ppmv
Diethyl disulfide	< 0.100 ppmv
Total Unidentified Sulfur	**0.434 ppmv**
Total Reduced Sulfurs as H_2S	**126 ppmv**

All compound's concentrations expressed in terms of H_2S (TRS does not include COS and SO_2)
Sample Reporting Limit (SRL) is equal to Reporting Limit x Canister Dil. Fac. x Analysis Dil. Fac.

Source: Nrgtek

Continued on-line analyses of the LFG conducted by the landfill operator throughout the remainder of 2015, however, indicated a significantly higher O2 content in the range of 2.7-3.7 vol percent (average 3.3 vol percent) as compared to the above analysis. The LFG N2 content was found to be 17.6 vol percent, which is substantially higher than typical LFG (which can vary in the range of 1-11 vol percent N2) thereby reducing the CH4 content to 42.5 vol percent and the CO2 content to 38.6 percent. The design window was based on this LFG composition and a flow rate of 100 SCFM entering stage 1 at pressures from 80-100 psig for meeting RNG specifications.

To accomplish the removal of the H_2S/siloxane contaminants in the LFG in stage 1, various organic solvent mixtures were initially proposed and evaluated using the Nrgtek-fabricated 100-SCFM test rig set up at the Toland Road Landfill site in Ventura County, CA, shown in Figure 3. As shown in the PFD, the unit essentially consists of an ejector-venturi scrubber, electro-catalytic converter (for electrochemically converting dissolved sulfides into solid sulfur), ductwork and blower system, spent scrubbing liquid separator and an exhaust stack. In the scrubber, the contaminant-laden gas stream contacts the scrubbing solvent in a highly turbulent, high velocity venturi throat and flows into the diverging discharge section where further liquid-gas contact enhancement occurs. The clean gas with entrained contaminant is discharged from the scrubber to a gas-liquid separator.

A 10- to 100-SCFM slipstream from the 2000-SCFM main landfill gas stream containing 100-ppmv of H_2S and 30-ppmv of siloxanes was used for this testing. Two tests were conducted. The first test used three different solvent mixtures conventionally employed for H_2S and CO_2 scrubbing: aqueous (50 percent) monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA) solutions, each mixed with 25-vol percent tetraethylene glycol methyl ether (tetraglyme), to remove organic sulfides. H_2S is presumed to react almost instantaneously with the amines by proton transfer as in reaction (1). CO_2 is believed to react with primary and secondary amines to form a carbamate via reactions (2) and (3). Since MDEA is a tertiary amine and does not have a hydrogen attached to the nitrogen, the CO_2 reaction can only occur after the CO_2 dissolves in the water to form a bicarbonate ion as in reactions (4)-(7).

$$H_2S + \text{Amine} \rightarrow [\text{Amine}]H^+ + HS^- \quad (1)$$

$$CO_2 + H_2O + \text{Amine} \leftrightarrow [\text{Amine}]COOH^- + OH^- \quad (2)$$

$$CO_2 + H_2O + R_2NCH_3 \leftrightarrow R_2NCH_4^+ + HCO_3^- \quad (3)$$

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+ \quad (4)$$

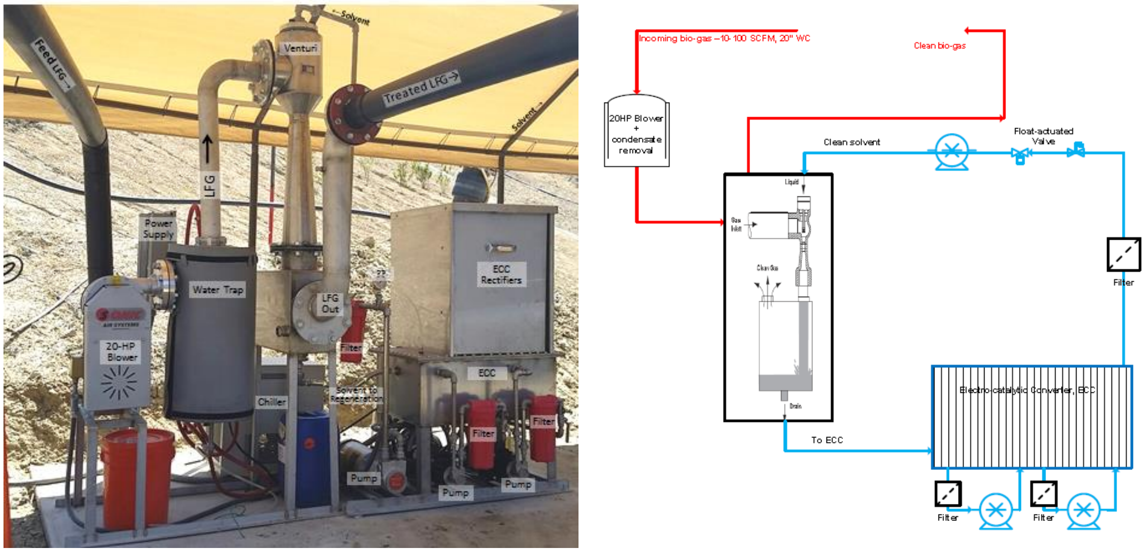
$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \quad (5)$$

$$H_2O \leftrightarrow OH^- + H^+ \quad (6)$$

$$RR'R'NH^+ \leftrightarrow RR'R'N + H^+ \quad (7)$$

Where R corresponds to a methyl group and R' to an ethanol group.

Figure 3: Pilot Unit Installed by Nrgtek at Toland Road Landfill Site (left) and PFD (right)

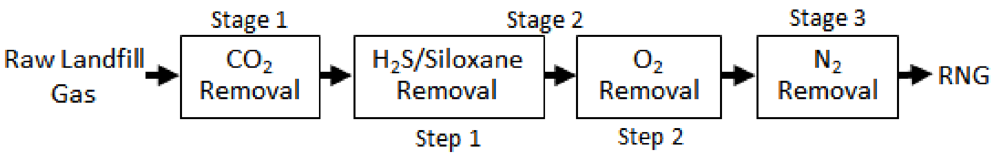


Source: Nrgtek

The results of the first test were not positive for H_2S scrubbing (i.e., did not reach 4-ppmv H_2S in the product gas as required for RNG as measured by Draeger colorimetric indicator tubes) in the presence of the substantial quantities of CO_2 (up to 45 percent) in the landfill gas. In the second test, the same three solvent mixtures were used but without any added water as H_2S is soluble in the neat amine solutions per reaction (1), and CO_2 is not as described. The results showed that the neat amine solutions alone were still not able to reduce H_2S to below the 4-ppmv target.

Because the proposed scheme (Figure 1) did not yield the desired results in stage 1 as originally expected, the sequence of the contaminant removal steps was modified to the scheme shown in Figure 4. In this scheme, the 100 SCFM of raw LFG entering stage 1 gets reduced to 62 SCFM after removal of CO_2, followed by removal of H_2S/siloxanes and O_2 in stage 2, and lastly N_2 removal in stage 3. Additionally, a liquid redox scheme reported in the literature[1-7] was used by Nrgtek for reducing H_2S to the low levels required for RNG, which also has the added benefits of simultaneous reduction in the level of O_2 and siloxanes and not being affected by CO_2 presence in the LFG. The liquid redox scheme is described in detail.

Figure 4. Revised Scheme for the LFG Demonstration System



Source: Gas Technology Institute

The H_2S/siloxane/O_2 removal process uses a two-stage liquid redox scheme via the oxidation-reduction of ferric and ferrous sulfate in aqueous solvent. In the first stage, a 20-wt percent water solvent of ferric sulfate, $Fe_2(SO_4)_3$ (at a pH of 3.5-4.5 to keep the iron solubilized), is used to oxidize H_2S and other water-soluble sulfides in the LFG to solid elemental sulfur (S), which precipitates out of the solvent and is removed and recovered by filtration for safe disposal. During this oxidation step, the ferric sulfate is chemically reduced to ferrous sulfate ($FeSO_4$) by the presence of the sulfur species via the overall reaction (8):

$$Fe_2(SO_4)_3 + H_2S \rightarrow 2FeSO_4 + S\downarrow + H_2SO_4 \quad \Delta G^o = -13.74 \text{ kcal/mole} \qquad (8)$$

Simultaneously, siloxanes are also oxidized to silica (SiO_2), due to the sufficient oxidizing power of the ferric sulfate solvent. The acidic nature of the ferrous sulfate (pH 2.5-3.5) is expected to be sufficient to also cleave the siloxane bonds, thereby enabling the siloxanes to be oxidized to silica.

In the process reported in the literature, the acidified ferrous sulfate solvent formed in reaction (8) is normally regenerated to ferric sulfate (for continued reaction with H_2S) with O_2 in air via reaction (9).

$$2FeSO_4 + H_2SO_4 + \tfrac{1}{2}O_2 \rightarrow Fe_2(SO_4)_3 + H_2O \quad \Delta G^o = -34.8 \text{ kcal/mole} \qquad (9)$$

Alternatively, in the proposed liquid redox scheme, the O_2 present in the LFG could be used to regenerate the ferric sulfate back to the ferrous sulfate formed in reaction (8) thereby simultaneously removing O_2 via reaction (9). But because there is less H_2S present than O_2 in the Otay LFG, there is insufficient H_2S to react with the ferric sulfate formed by reaction (9) to regenerate the required amount of ferrous sulfate needed for reacting with the O_2. Therefore, in place of using O_2 in LFG for regeneration, the ferric sulfate solvent will be electrochemically regenerated using Nrgtek’s proprietary electrocatalytic converter or ECC (Figure 5). In electrochemical terms, the regeneration reaction is as follows:

$$2Fe^{2+} + 2H^+ \rightarrow 2Fe^{3+} + H_2 \qquad (10)$$

As a result, O_2 in the product gas from the H_2S scrubber will be directed to a second vessel containing ferrous sulfate solvent and removed per the scheme shown in Figure 6. The ferric sulfate produced in reaction (9) can be regenerated to ferrous sulfate for recycle to continued O_2 absorption by two pathways: a) electrochemically, using an ECC, shown in electrochemical terms as reaction (11), or b) chemically, using consumable materials like iron sponge, steel wool or iron scrap as in reaction (12):

$$2Fe^{+3} + H_2O \rightarrow 2Fe^{+2} + 2H^+ + \tfrac{1}{2}O_2 \qquad (11)$$

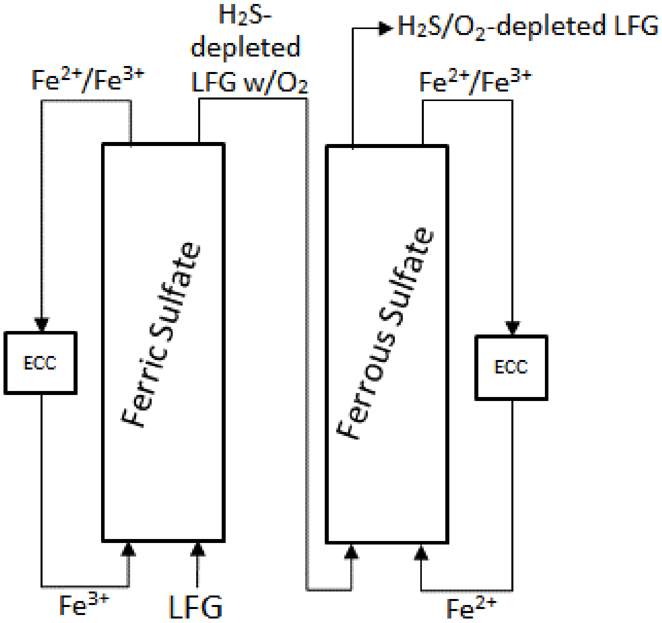
$$Fe_2(SO_4)_3 + Fe \rightarrow 3FeSO_4 \quad \Delta G^o = -52.9 \text{ kcal/mole} \qquad (12)$$

Pathway (11) is the preferred route as only electrical power is consumed and no iron-containing waste is produced requiring handling and disposal. Since the O_2 level in the LFG is relatively low at 1.2-3.7 vol percent, power needs are expected to be minimal.

Figure 5: Electro-Catalytic Converter

Source: Nrgtek

Figure 6: Liquid Redox Scheme for O_2/H_2S/Siloxane



Source: Gas Technology Institute

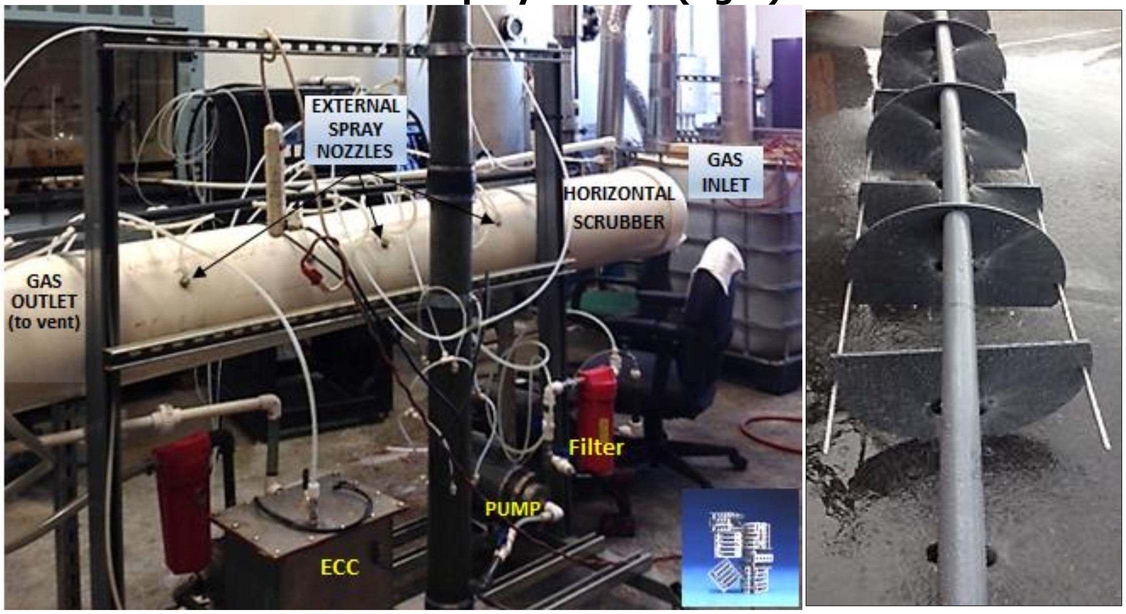
Also, because there is much more O_2 than H_2S in the Otay LFG, it was decided to reverse the sequence of the H_2S/siloxane and the O_2 removal sections wherein O_2 is removed first followed by H_2S/siloxane removal. This allows any ferrous sulfate that is oxidized by O_2 to ferric sulfate to reduce the H_2S to elemental sulfur and form ferrous sulfate. The downstream H_2S removal section, containing ferric sulfate, would therefore serve to do a final polishing of any remaining H_2S and allow for attainment of the 4-ppmv target H_2S level in the LFG.

The redox scheme operates at ambient temperature and requires no heating or cooling of the solvents. Both the ferric and ferrous solvents used are highly water soluble and cheaply available chemicals, and are extensively used in agriculture for soil remediation and acidification. The scheme produces no additional hazardous waste byproducts.

Verification of the Liquid Redox Scheme

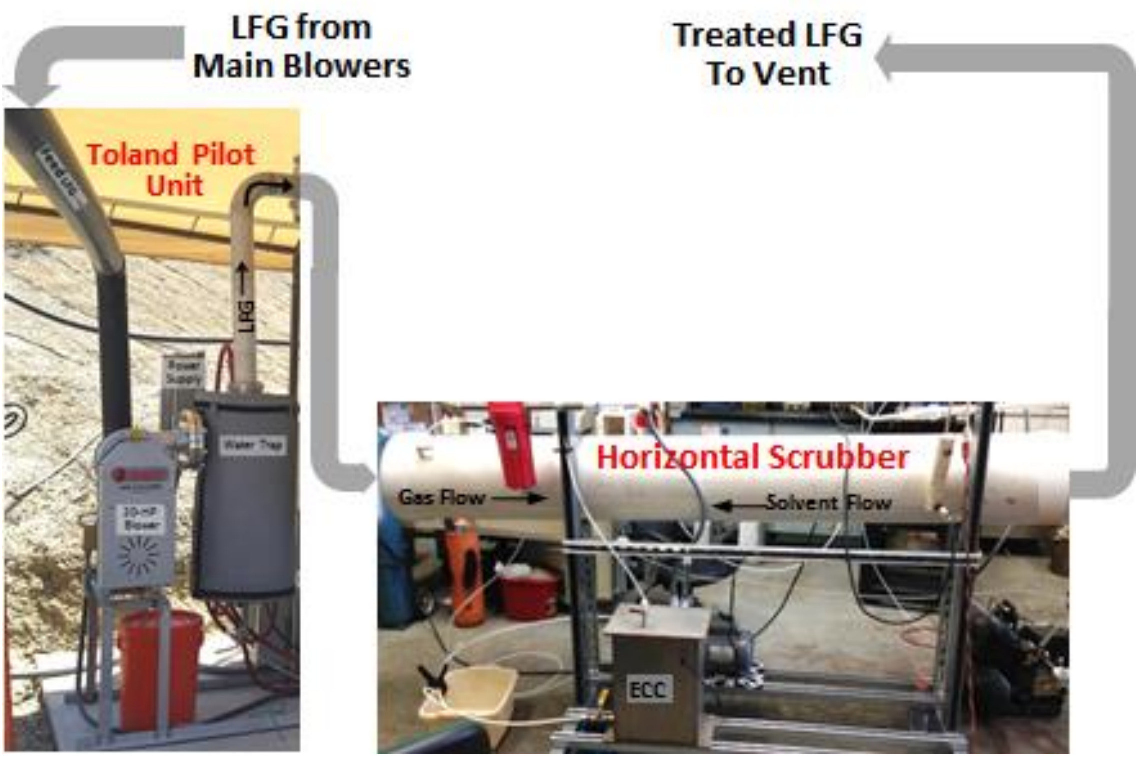
Testing of the liquid redox scheme for the O_2/H_2S/siloxane removal process was conducted both in Nrgtek's laboratory and in the field at the Toland Road Landfill site mentioned above. Fifteen tests were conducted at various conditions (solvent and gas flow rates, gas compositions, column diameters and bed heights) using the test setups shown in Figures 7-10 and used for the design window. It should be noted that Nrgtek, being a small business has limited in-house testing capabilities and to keep project costs in check no extra equipment was purchased for this testing. Therefore, detailed parametric testing was not performed at this time and will be reserved for the one-year demonstration.

Figure 7: Horizontal Scrubber Lab Unit and Lantec Stainless Steel Packing (left) and Scrubber Internal Baffles and Spray Nozzles (right)



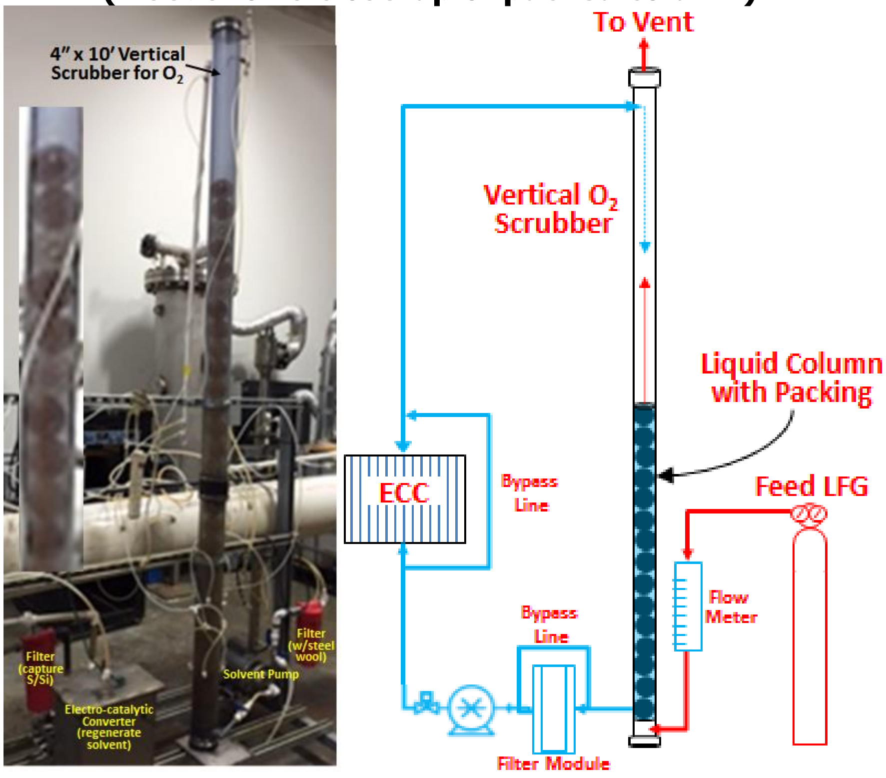
Source: Nrgtek

Figure 8: H_2S Removal Test Setup Installed at Toland Road Landfill Site



Source: Nrgtek

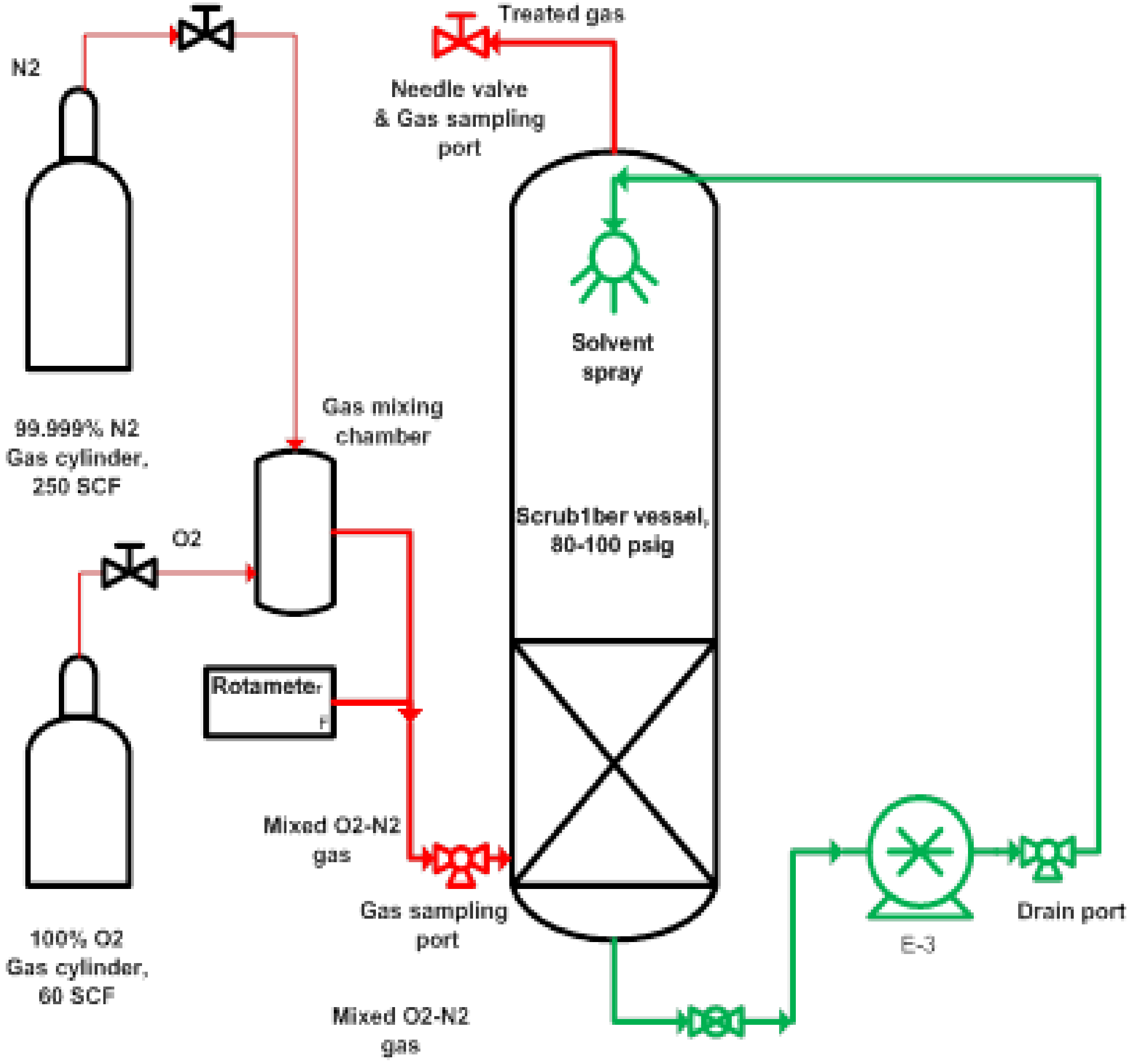
Figure 9: Photograph and Diagram of Lab-Scale O_2 Removal Test System (inset shows close-up of packed column)



Source: Nrgtek

To demonstrate the redox scheme, two scouting tests were initially conducted using H_2S followed by a representative siloxane, hexamethyldisiloxane (designated as L2). In the first test, a metered flow of 200-ppmv H_2S in air was bubbled into a saturated solvent of 20-wt percent ferric sulfate at ambient temperature and precipitation of elemental sulfur was immediately observed. In addition, the solvent turned green (an indication of the formation of ferrous sulfate). No H_2S was detected in the outlet gas using Draeger indicator tubes (measurement range of 0-30 ppm H_2S) indicating complete removal of H_2S.

Figure 10: Pressurized O_2 Removal Test System



Source: Nrgtek

Based on the above positive results, proof-of-concept testing was conducted to assess H_2S/siloxane and O_2 and removal. Tests 1-6 were conducted in the laboratory for H_2S removal at ambient pressure in the horizontally-configured packed-bed scrubber system shown in Figure 7 that was designed to provide a convoluted gas flow pathway for increasing gas residence times to allow for sufficient dissolution of the H_2S into solvent at atmospheric pressure. It was fabricated from a 12-in diameter by 10 foot (ft) long PVC pipe containing eight scrubbing zones filled with random metal packing (Figure 7) to enhance gas-liquid contact, along with an array of twelve spray nozzles deployed along the length of the scrubber and internal baffle spray assembly. The ECC electrochemically regenerated the ferric sulfate from the ferrous sulfate formed by reaction with H_2S as evidenced by a color change of the respective solvents observed during testing.

Tests 7-10 were conducted in the field at the Toland Landfill site using a slipstream from the main LFG stream both with and without the same horizontal packed-bed scrubber. The setup for test 7 was as configured in Figure 3 (without the horizontal scrubber) and modified for tests 8-10 to accommodate the horizontal scrubber as shown in Figure 8. These tests were performed similarly to the pilot-unit test described above, except that a ferric sulfate solvent was used in place of the amine solutions. An ECC was included as shown for regenerating the ferric sulfate.

Testing of O_2 removal under ambient conditions via reaction (9) was conducted in laboratory Tests 11-13 in the setup and flow scheme shown in Figure 9. The setup included a vertical column comprised of a 4-in diameter by 10-ft tall translucent PVC pipe assembly containing 4-in plastic spheres (to simulate the packed-bed in the demonstration scrubber), feed gas supply and gas metering system (high pressure gas cylinder and rotameter), liquid recirculation pump, filter module (filled with carbon-steel wool), and an ECC. The ECC and filter module were configured with bypass lines. For this testing a 4-ft-high liquid column of a 20 percent solvent by weight of ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) in water (maximum solubility of ~21 percent) was used for oxygen removal, which also provided required acidity for preventing undesirable iron hydroxide formation. Both ferrous sulfate regeneration schemes, specifically reactions (11) via the ECC and (12) via Fe (carbon steel wool) reduction, were evaluated. Steel wool was added to evaluate its reduction capabilities so that during testing both regeneration methods could be brought into play to assess functionality.

Tests 14 and 15 were conducted in the 6-in diameter by 4-ft tall scrubber vessel at pressure as shown in Figure 10 using gas flows of 1 and 5 SCFM, respectively. The 6.1-vol percent O_2/N_2 gas mixture was bubbled into the vessel via two 1/8-in tubes while the ferrous sulfate solvent was recirculated at 2 gallons per minute (GPM) using a positive displacement pump to maintain a 2-ft liquid level for visibility through a sight glass on the side of the vessel. The inlet gases were allowed to contact the liquid column at a back pressure of 85 psig maintained in the system with a needle valve. For this short duration test no ECC was included to assess O_2 removal without any regeneration of the solvent.

Table 2 summarizes test results conducted under the following operational conditions:

- Ambient temperature
- Column diameters of 4-12 inches
- Liquid bed heights of 2-10 ft
- Gas flow rates from of 0.01-100 SCFM
- Solvent recirculation rates of 2-12.4 GPM
- Pressures of ambient and 85 psig

Table 2: Laboratory and Field Tests Conducted with Packed-bed Columns using Liquid Redox Scheme

Test	Feed Composition, vol%	Gas Rate, SCFM	Solution Circulation Rate, GPM	P, psig	Column Diam., in.	Liquid Bed Height, ft.	L/G[g]	Duration, min	Residual Concen.	Gas Residence Time, min	Comment
1	150-ppmv H_2S/bal N_2	0.011	2	0	12	10	24303	180	<0.5 ppmv	714	Lab[c]
2	LFG w/90-ppmv H_2S	0.033	2	0	12	10	8101	60	3 ppmv	238	Lab[c]
3	LFG w/90-ppmv H_2S	0.033	2	0	12	10	8101	120	3 ppmv	238	Lab[c]
4	LFG w/90-ppmv H_2S	0.033	2	0	12	10	8101	90	3 ppmv	238	Lab[c]
5	LFG w/90-ppmv H_2S	0.067	2	0	12	10	3990	180	4 ppmv	117	Lab[c]
6	LFG w/90-ppmv H_2S	0.067	2	0	12	10	3990	90	4 ppmv	117	Lab[c]
7	LFG w/120-ppmv H_2S	18	12.4	0	2-6[f]	4	92	180	2 ppmv	0.02	Field[b]
8	LFG w/95-ppmv H_2S	60	5	0	12	10	11	60	6 ppmv	0.13	Field[c]
9	LFG w/95-ppmv H_2S	80	5	0	12	10	8.4	120	8 ppmv	0.10	Field[c]
10	LFG w/105-ppmv H_2S	100	5	0	12	10	6.7	60	8.5 ppmv	0.08	Field[c]
11	4.5% O_2/ bal N_2	0.5	5	0	4	4	1337	60	<0.2 vol%[a]	0.70	Lab
12	4.5% O_2/ bal N_2	0.5	5	0	4	4	1337	120	<0.2 vol%[a]	0.70	Lab
13	4.5% O_2/ bal N_2	0.5	5	0	4	4	1337	150	<0.2 vol%[a]	0.70	Lab

Test	**Feed Composition, vol%**	**Gas Rate, SCFM**	**Solution Circulation Rate, GPM**	**P, psig**	**Column Diam., in.**	**Liquid Bed Height, ft.**	**L/G[g]**	**Duration, min**	**Residual Concen.**	**Gas Residence Time, min**	**Comment**
14	6.1% O_2/ bal N_2	1	2	85	6	2	267	30	<0.3 vol%[a]	2.6	Lab[d]
15	5.4% O_2/ bal N_2	5	2	85	6	2	53	10	<0.02 vol%[a]	0.52	Lab[d]

a: O_2 meter inaccurate at these low levels.

b: Ejector-venturi gas scrubber.

c: Horizontal scrubber unit.

d: Without packing.

e: Higher accuracy O_2 meter used in this test.

f: Diverging section of the venturi gas scrubber.

g: Liquid (solvent)-to-gas ratio in L/Nm^3

Source: Nrgtek

H_2S/Siloxane Removal Testing Results

Test 1 employed a bottled gas mixture containing 150-ppm H_2S and balance N_2 to simulate H_2S levels in LFG. The test results indicated a consistent reduction of the H_2S to below the Draeger tube detection limit of 0.5 ppmv (complete removal) over a three-hour test duration. In tests 2-6, actual LFG (obtained from the Toland Road Landfill site and stored in a pressurized tank) containing 90-ppmv H_2S (as measured by Draeger indicator tubes) was used as feed. The test results indicated a reduction in H_2S to 3-4 ppmv in the outlet gas (a reduction of 96-97 percent) over a two-hour test period as monitored by Draeger indicator tubes in the measuring range of 0.75-300 ppmv H_2S.

Based on the positive proof of concept results obtained in tests 1-6, H_2S/siloxane removal was field tested. While performing field testing it was noticed that the H_2S levels in the Toland Road LFG varied with time in the range of 90-120 ppmv. Test 7 was conducted at ambient pressure with an LFG flow rate of 18 SCFM containing 120-ppmv H_2S and 30-ppmv total siloxanes (based on a previous LFG analysis provided by landfill staff) and a ferric sulfate solvent flow rate of 12.4 GPM for a duration of three hours. Analysis of the treated LFG demonstrated a removal of H_2S down to 2 ppmv (below California's RNG specification of 4-ppmv H_2S), a reduction of 98 percent, at the outlet as monitored by Draeger indicator tubes (measuring range of 0.5-40 ppmv H_2S). Although no analysis was done for siloxanes, based on the Nrgtek earlier scouting tests with the hexamethyldisiloxane, it can be assumed that the siloxanes were also removed and converted to silica. This will be confirmed during shakedown testing of the subsystem at the Otay landfill site before commencing the one-year demonstration for meeting RNG specifications.

Tests 8-10 were performed in the horizontal scrubber (Figure 7) to determine the effects of higher gas flow rates expected in the demonstration at the Otay landfill. In the proposed scheme of the Otay LFG cleanup demonstration unit, 100 SCFM of LFG are fed to the CO_2 removal subsystem wherein ~38 SCFM of CO_2 are removed (in stage 1 of Figure 4) resulting in a feed of ~62 SCFM to the O_2/H_2S/siloxane removal in stage 2. These three tests were therefore conducted at 60, 80 and 100 SCFM of LFG and a constant 5-GPM liquid flow rate to determine the effect of LFG flow rate on H_2S removal. The results indicated that the H_2S concentration in LFG was reduced from 95 ppmv to 6 ppmv in the outlet gas at a flow rate of 60 SCFM and decreased from 95 and 105 ppmv to 8 and 8.5 ppmv, at 80 and 100 SCFM, respectively. The H_2S removal efficiency was about 94 percent at 60 SCFM, and 92 percent at the higher flow rates compared to the target 96 percent at 4-ppmv H_2S.

Oxygen Removal Testing Results

Tests 11-13 were conducted with a feed gas containing 4.5 percent O_2 + balance N_2 (to simulate O_2 levels in LFG at Otay) injected at the bottom of the packed PVC column and controlled at 30 SCFH flowing counter-flow to the solvent at a recirculation rate of 5 GPM. In test 11, the feed gas was injected into the recirculating ferrous sulfate solvent for one hour with both the ECC and filter module (containing the steel wool) bypassed. The test results indicated a reduction in the feed O_2 concentration from 4.5 vol percent to <0.2 vol percent as continuously monitored by an O_2 monitor (Apogee Oxygen Meter, MO-200 Series). In test 12, the ferrous sulfate was regenerated back to the ferrous form as confirmed by the solvent color change with the ECC brought on line (while bypassing the filter module) before recycling the ferrous sulfate to the column for O_2 absorption. In test 13, the ECC was bypassed and the filter module containing the steel wool was placed in line to assess regeneration of the ferrous sulfate solvent. Tests 12 and 13 were operated for a total of 4.5 hours, and no change in oxygen removal levels (0.2 vol percent) was observed in either test.

Tests 14 and 15 were conducted with a feed gas containing 6.1 percent O_2 + balance N_2 at a pressure of ~85 psig (Otay demonstration conditions) to determine the extent of O_2 removal without any packing and confirm observed removal levels obtained in tests 12 and 13 at ambient conditions. The O_2 concentration in the treated gas came down to 0.3 vol percent in test 14 and 0.02 vol percent (indicated by a Watchdog Trace Oxygen Analyzer accurate to 0.01 vol percent) in test 15 and remained constant during the 10-min test period.

Design of Oxygen/Hydrogen Sulfide/Siloxane Removal Subsystem

As mentioned above, because limited measurement equipment resources were available at Nrgtek, only a few parametric variations were employed in the above testing to provide design data. None of the subsystem design was performed according to the traditional packed-bed tower design criteria (using e.g., mass-transfer coefficients, flooding velocities, NTUs, etc.), but instead was based on the laboratory and field-testing results as limited design data, and insufficient rigorous equilibrium or packing data were available and as this scheme is not widely used in industry as for example, amines.

From the above data, tests 6-9 and 14 were the relevant tests on which the subsystem design was based. In tests 6-9, conducted at LFG flow rates of 60-100 SCFM, the RNG specifications for H_2S were not met as the tests were conducted at ambient pressure. It is well known, however, that higher partial pressure for gas absorption in liquids per Henry's law of partial pressures is expected to promote effective gas/liquid mass transfer for achieving the target H_2S level (4 ppmv) in the cleaned gas at the higher Otay demonstration unit pressure of 80-100 psig. O_2 removal tests 10-14 were conducted at gas flowrates from 0.5 to 5 SCFM. In test 14, at 5 SCFM gas flow rate and 85 psig, the RNG target for O_2 was reached only due to the large excess of ferrous sulfate solvent to O_2 in the feed gas as compared to that processed in the Otay demonstration unit. The remaining tests were performed for trending purposes. Although the test conditions used in the O_2 removal tests are not directly correspond to the Otay demonstration conditions, qualitatively the results provide a basis for the design of the O_2/H_2S/siloxane removal unit.

Various bases are reported in the literature and used industrially for the liquid-to-gas (L/G) ratios[8-12] such as L/Nm^3, GPM/1000 ACFM, and mol/mol and range from 2-35 mol/mol, 2-350 GPM/1000 ACFM and 0.1-105 L/m^3 depending on the contact device used. In tests 6-9 and 14 (Table 1), L/G ratios are seen to range from 7-57 L/m^3, which are in line with literature values. The reason for the higher L/G ratios in the other tests in Table 1 is that Nrgtek could not accommodate the higher gas flow rates at their facility needed to reach the lower ratios. The use of higher ratios, however, may be warranted as very high levels of cleanup are needed to meet pipeline purity goals.

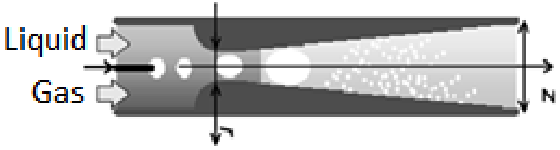
Therefore, to attain RNG specifications for O_2 and H_2S at the Otay site and based on these lab and field test data, 8-in diameter vessels with 4-ft liquid bed heights at a solvent circulation flow rate of ~12 GPM (L/G ratio of 27 L/Nm^3) were selected to process the 62 SCFM of LFG in the O_2 and H_2S removal subsystem. Despite the much lower concentration of H_2S compared to the O_2 in the Otay LFG, the H_2S scrubber vessel was kept at the same dimensions as the O_2

vessel to accommodate for any increases in H_2S, other sulfides and siloxanes levels in the LFG with time.

Since the whole subsystem design is based on gas-liquid contact (packed-bed counter-current), an alternative approach to accomplish this was also investigated via the use of a revolutionary micro-bubbler (MB) generator concept incorporated into the current design for RNG generation. Nrgtek became aware of microbubble generation and it was felt that this might be an effective way to accomplish the gas-liquid contact. Microbubbles, because of their size, offer much more surface area for gas-liquid contact and longer residence time in the bed.

In a venturi-type micro-bubbler shown in Figure 11, by combining high pressure solvent (produced by a high-pressure pump) and LFG (at a lower pressure) microbubbles are generated in the throat and diverging sections of the nozzle by cavitation and fluid shear mechanisms due to the highly turbulent liquid flow. Nrgtek carried out a trial test injecting water and air into an improvised MB venturi bubble generator (similar to the one in Figure 11), with the outlet mixture sent to a vessel containing water. The emerging jet (as viewed in the vessel sight port) appeared to be similar to typical microbubble generation, an example of which is shown in Figure 12.

Figure 11: Example Venturi MB Generator (Mazei, Japan)



Source: Nrgtek

Figure 12: Example of MB Sparging Air into Water

Source: Nrgtek

The MB technology is new and Nrgtek does not have field experience with these devices. The MB was installed into the 8-in vessels in a manner which allows for easy replacement if issues were identified during LFG testing.

Design Window of Oxygen/Hydrogen Sulfide/Siloxane Removal Subsystem

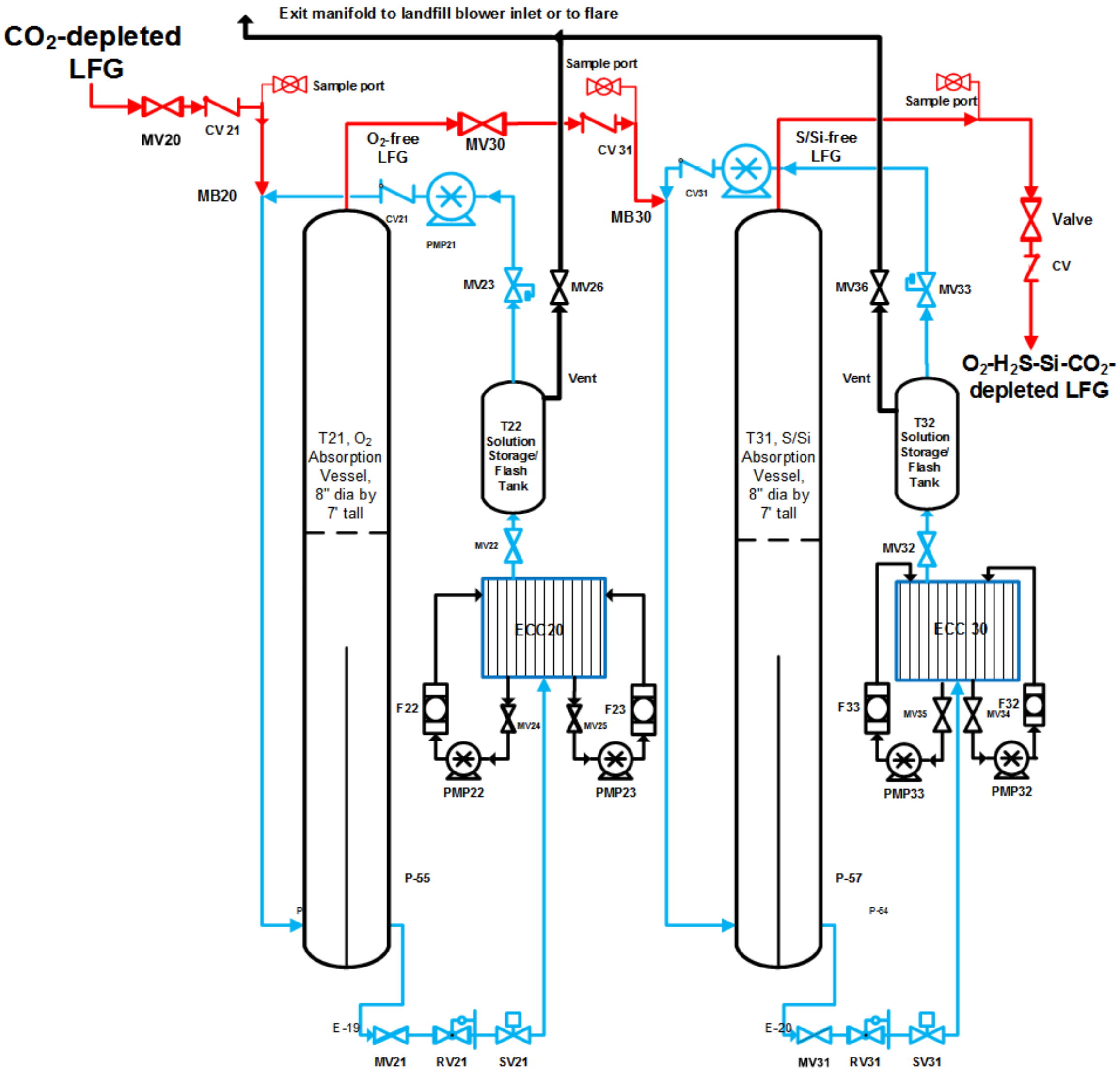
Equipment and material selection for the system was based on the following parameters:

- System pressure: 80-120 psig
- LFG flow rate: 20-100 SCFM (turndown of 5 to 1)
- Solvent flow rate: 10-15 GPM
- LFG H2S concentration: 100-200 ppmv
- LFG O2 concentration: 0-6.5 vol percent

Process Flow Diagram and Pipine and Instrumentation Diagram for Oxygen/Hydrogen Sulfide /Siloxane Removal Subsystem

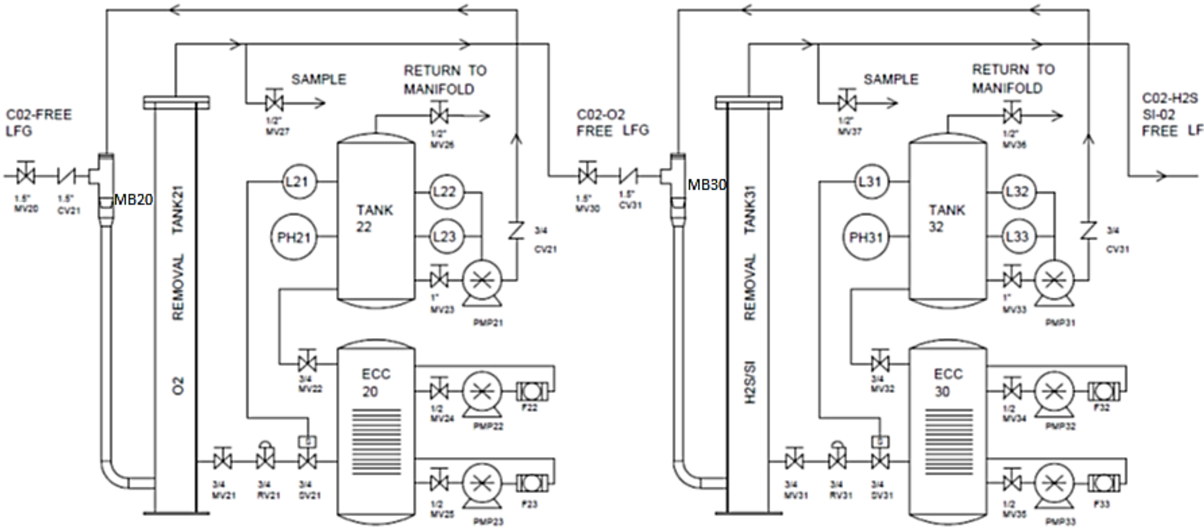
To aid in construction a process flow diagram (PFD) and piping and instrumentation diagram (P&ID) for the O_2/H_2S/Siloxane removal subsystem were created as shown in Figures 13 and 14, respectively. As shown in the PFD, each scrubber vessel is fitted with a MB and 3-ft tall vertical partition separating the inlet and outlet solvent flows to prevent liquid with occluded gas from short circuiting directly into the downstream ECCs and recirculating pumps and avoid any decrease in electrochemical efficiency and cavitation, respectively. Both scrubber vessels are also equipped with demister pads placed at the gas outlets to prevent any liquid droplet carryover from the beds.

Figure 13: Oxygen/Hydrogen Sulfide /Siloxane Removal Subsystem Process Flow Diagram



Source: Nrgtek

Figure 14: Piping and Instrumentation Diagram for Oxygen/Hydrogen Sulfide/Siloxane Removal Subsystem

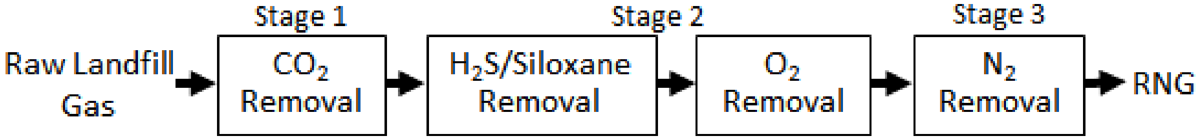


Source: Nrgtek

Carbon Dioxide Removal

The original proposed scheme in which the CO_2 removal occur in the Stage 2 did not yield the desired results in stage 1 due to the presence of CO_2, so the sequence of the contaminant removal steps was modified to the scheme shown in Figure 15 (this is same as Figure 4 and presented for clarity). In this scheme, the 100 SCFM of raw LFG entering stage 1 is reduced to ~62 SCFM after removal of CO_2 using an organic solvent for CO_2 removal, followed by removal of O_2 and H_2S/siloxanes in stage 2, and lastly N_2 removal in stage 3, also using an organic solvent.

Figure 15: Revised Scheme for the Landfill Gas Demonstration System



Source: Nrgtek

The approach used for CO_2 removal in stage 1 was to test various solvents that have demonstrated an affinity for the absorption of CO_2. Some literature results[2] for the solubility of CO_2 in various solvents at ambient pressure and 25°C measured using a thermogravimetric technique are presented in Table 3. Data for the common solvents methanol and water are included in Table 3 for reference. Literature also indicates that polyethylene glycols have appreciable solubility for CO_2 under pressure, so the desorption of CO_2 from PEG solvents can easily be accomplished by pressure reduction techniques.

In previous testing by Nrgtek, polyglycol organic solvents were seen to exhibit CO_2 absorption with a solubility reversal, or cloud point, in the range of 35-85°C, depending on the composition of the organic solvent. A cloud point solute such as CO_2 is soluble in this type of

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[2] Aschenbrennera, O., and P. Styring, Comparative Study of Solvent Properties for Carbon Dioxide Absorption, Energy Environ. Sci., 2010, 3, 1106-1113.

solvent at lower temperatures but "clouds out" of the solvent as a cloudy precipitate at higher temperatures. The photographs in Figure 16 illustrate the described phenomena. In addition, it was also shown that CO_2 solubility increases with pressure and that absorbed CO_2 readily desorbs by simple release of pressure.

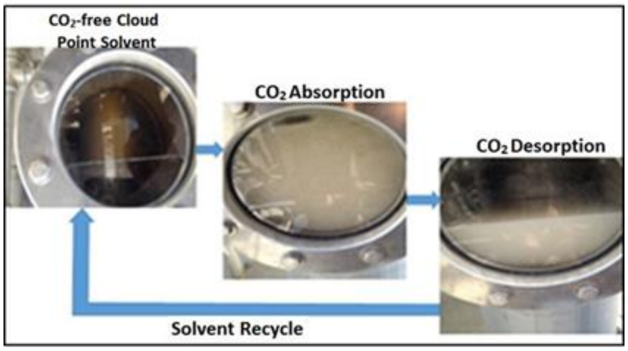
The first solvent tested for CO_2 absorption was a copolymer of PEG-PPG, with a molecular weight of 2500, as obtained from BASF Corporation. This solvent was selected because it has a known cloud point in water at 35°C at a 50 percent concentration in water. Literature searches indicate that the higher the proportion of PEG in the polymer, the greater the amount of CO_2 physically absorbed.

Table 3: Solubility of Carbon Dioxide at 25°C and Ambient Pressure

Substance	Solvent density in g l	Solubility in mg g	Solubility in g l
Glycerol	1250	13.8	17.2
Glycerol carbonate	1400	7.9	11.0
Tetraglyme	1011	4.8	4.9
PEGDME 150	1089	6.4	6.6
PEG 200	1124	13.4	15.1
PEG 300	1124	13.5	15.1
PEG 600	1124	7.7	8.7
Poly(ethylenimine)	1030	>3.0	>3.1
Methanol	788	7.7	6.1
Water	997	1.5	1.5

Source: Yang, Z-Z., Song, Q-W. and He, L-N., Capture and Utilization of Carbon Dioxide with Polyethylene Glycol, SpringerBriefs in Green Chemistry for Sustainability, DOI: 10.1007/978-3-642-31268-7.

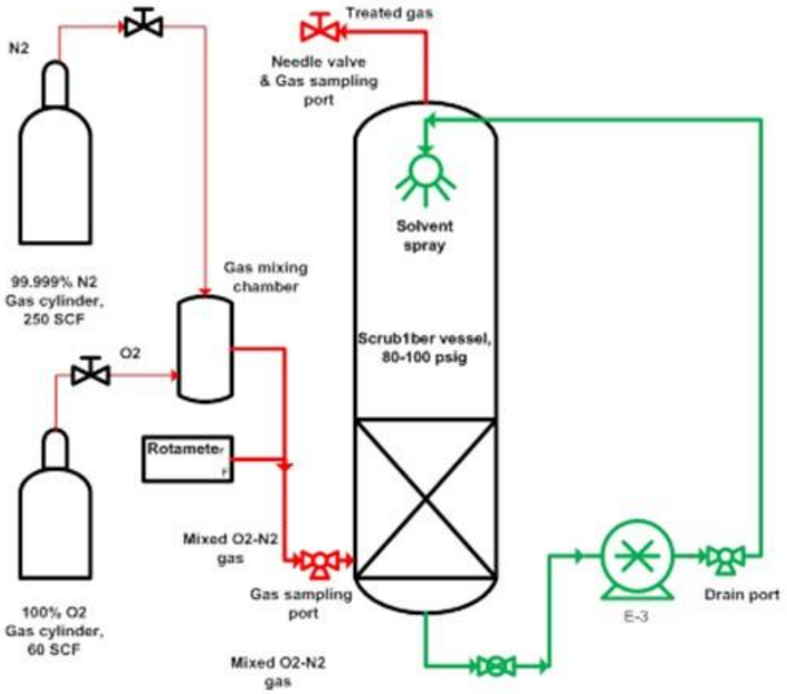
Figure 16: Cloud Point Phenomena with Carbon Dioxide



Source: Nrgtek

Testing was conducted in the setup shown in Figure 17 and Figure 18, which was used for the O_2 removal testing, except that the O_2 cylinder was exchanged for a CO_2 cylinder. The 100-vol percent CO_2 was fed into the pressurized vessel at 1 SCFM and the solvent was recirculated in the 6-inch diameter by 4-foot tall pressure vessel at 2-GPM using a positive displacement pump. The liquid level was maintained at 2 feet for visibility through a sight glass on the side of the vessel. The inlet gas was allowed to contact the liquid column at a back pressure of 30 psig maintained in the system with a needle valve for a 30-minute test period. The copolymer was not diluted with water in this test to avoid possible interference from any hydroxyl radicals formed with CO_2 absorption and solubility. No cloud point formation was observed, however.

Figure 17: Diagram of Pressurized Carbon Dioxide Removal Test System



Source: Gas Technology Institute

Figure 18: Carbon Dioxide Removal Test Setup

Source: Nrgtek

No clouding behavior was observed during testing with the PEG-PPG solvent and testing continued with other pure PEGs for CO_2 absorption tendencies. It has been postulated in literature that for physical solvents, the ethylene oxide (EO) monomers of polyethylene glycol

(PEG) have and affinity to CO_2 (and other acid gases), due to the acid-base reactions of the acidic carbon dioxide to the electron-rich ether oxygen in the PEG molecules.

Thus, the four EO monomers in tetraethylene glycol dimethyl ether (the active component in Selexol and Genosorb) enable the physical absorption of acid gases, in spite of having methyl end-caps. Some reports have also shown the influence of polymer chain length on CO_2 absorption[3]. However, polymer chain lengths cannot be continuously increased, due to the adverse effects of viscosity on gas-liquid mixing. In addition, larger chain lengths also increase the melting point of the polymer. Both of these parameters have an adverse effect on gas-liquid mixing as well as higher pumping energy needs. Thus, PEG200 (EO=4), PEG300 (EO=6) and PEG400 (EO=8) have lower viscosity and are liquids at room temperatures, as compared to PEG 600 (EO=10), which is a waxy solid at room temperature. It is possible that the higher viscosity associated with higher ethylene oxide (EO) groups (higher alkyl chain length) in PEG 600 may have decreased gas absorption shown in Table 3. Thus, just increasing polymer chain length is not sufficient to optimize acid gas absorption. In addition, higher viscosity also has adverse effects on gas desorption, and thus, higher polymer chain lengths may need high temperature desorption (due to the lower viscosity at higher temperatures). It has also been suspected that the terminal -OH groups of these PEG molecules may also have an affinity for acid gases like CO_2.

Based on these literature findings, in addition to testing PEG200 and 300 for CO_2 absorption, PEG400 was tested as an optimized polymer with sufficient EO monomers, an OH end group, as well as liquid at room temperature and with manageable viscosity. Nrgtek also investigated a new class of solvents (Nrgtek A, B, C and D), with the importance of lowered viscosity, room-temperature liquidity, low vapor pressure and high gas absorption as the main parameters of interest.

As previous experimental CO_2 solubility data in the literature for some of these solvents were obtained with very different experimental methods, a systematic study was needed in order to evaluate all the selected solvents for CO_2 removal. An experimental procedure was therefore devised to screen the solvents for CO_2 absorption capacity and the most suitable solvent for CO_2 removal was selected for the demonstration unit. A test apparatus was fabricated that consisted of a CO_2 supply (gas cylinder 99.5 percent purity CO_2), rotameter, clear PVC bubbler and tubing with a porous-metal gas diffuser assembly and magnetic stirrer, as shown in Figure 19. The experimental procedure consisted of the following steps. Initially, the test solvent (50-ml) was heated up to 100°C in a separate glass flask to remove any absorbed moisture or gases (e.g., air). The solvent was then placed in a dehumidification chamber. Once at room temperature, the solvent was poured into the gas bubbler and weights were taken of the bubbler using a Mettler Toledo PG503-S weigh station (accuracy = 1 mg), before and after filling with the test solvent. CO_2 was then bubbled from the gas cylinder into the solvent and the sample was weighed after each 30-minute interval up to three hours at a flow rate of 5.66 SLPH, until a constant weight was obtained indicating attainment of maximum solubility in the solvent.

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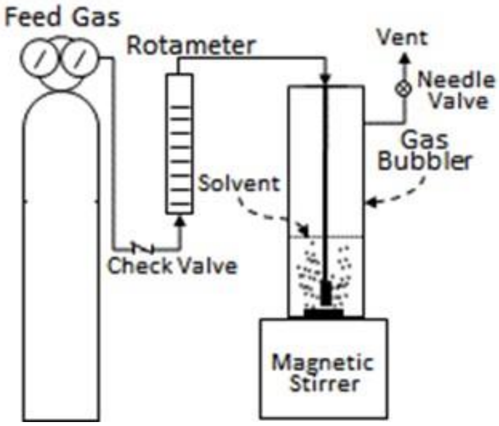
[3] Pedrosa, N., et al., Phase Equilibria of Ethylene Glycol Oligomers and Their Mixtures, Ind. Eng. Chem. Res. 2005, 44, 7027-2037.

Figure 19: Carbon Dioxide Absorption Test Apparatus



Source: Gas Technology Institute

In most of the tests, it was observed that the maximum CO_2 uptake was attained in the first 30 minutes, after which no appreciable weight gains were obtained. The only exception was PEG-PPG2500, where the maximum weight was recorded after two hours, however, to maintain consistency all tests were continued for the full three hours. In addition to CO_2 absorption testing, CO_2 desorption was also tested. The procedure consisted of stirring the CO_2-solvent mixture with a magnetic stirrer for increments of five minutes to expel desorbed CO_2 and re-weighing the solvent each time. Desorption times ranged from about 5 to 20 minutes for all the solvents tested (as observed by cessation of bubbling from the solvent). It is important to know desorption time for the design of the CO_2 desorption system.

Carbon Dioxide Absorption/Desorption Test Results

The CO_2 absorption and desorption tests were performed five times for each solvent (for repeatability), and the average values are reported in Table 4.

Table 4: Test Results of CO_2 Absorption/Desorption

Solvent #	Solvent	Solvent Density, g/ml	Solvent Viscosity, cS	mg CO_2/g solvent	mg CO_2/ml solvent	Desorption Time
1	Butyl Diglyme (Genosorb 1843) Diethylene glycol dibutyl ether	0.874	3.36 @ RT	4.90	4.29	10 min
2	Tetraglyme (Genosorb 1753) Tetraethylene glycol dimethyl ether	1.03	3.69 @ RT	7.32	7.54	10 min
3	Nrgtek A	1.14	ND	12.8	14.6	<5 min
4	Nrgtek B	1.10	ND	13.1	14.5	<5 min
5	PEG 200 (EO=4)	1.13	4.3 @ 100˚C	11.6	13.0	10 min
6	PEG-PPG 2500 (Clout point polymer) equimolar EO-PO	1.30	8.2 @ 100˚C	8.28	10.8	10 min
7	PEG 300 (EO=6)	1.13	5.8 @ 100˚C	13.4	15.0	10 min
8	PEG 400 (EO=8)	1.25	7.3 @ 100˚C	11.5	14.4	20 min
9	Nrgtek C	1.20	ND	1.77	2.12	10 min
10	Nrgtek D	1.20	ND	7.09	8.51	5 min

PEG=polyethylene glycol; EO=ethylene oxide; PPG=polypropylene glycol; PO=polypropylene oxide.

Source: Nrgtek

The test results indicate that two of the solvents, Nrgtek A and B, show higher CO_2 absorptions as compared to tetraglyme (Selexol or Genosorb 1753). Also, the experimental CO_2 absorption values for PEG 200 of 11.6 mg/g and 13.4 mg/g for PEG 300 compare favorably with the literature values of 13.4 and 13.5 mg/g, respectively, for these two solvents. The CO_2 desorption in the solvents Nrgtek A and B was observed to be relatively fast (<5 minutes) in comparison to others tested. Based on these results, Nrgtek A and B were selected for further evaluation in the cleanup system during an initial three-month shakedown period at the landfill site (under actual flow conditions) and the best solvent will be used for the demonstration testing phase.

Carbon Dioxide Removal Subsystem Design

The CO_2 subsystem designs in this task was not performed according to the traditional packed-bed tower design criteria (using e.g., mass-transfer coefficients, flooding velocities, number of transfer units (NTUs), etc.), but instead were based on the laboratory data as limited design data, and insufficient equilibrium data were available and because the selected solvents (other than Genosorb) are not used in industry for gas treating.

A detailed P&ID for the CO_2 removal subsystem is shown in Figure 20. The raw LFG feed is treated in three steps: (1) water/moisture removal (using a glycol mixture in a separate column), (2) CO_2 absorption (in a packed-bed contactor), and (3) desorption using a nanofiltration (NF) membrane and a venturi. The CO_2 absorption solvents to be used in the second stage of the subsystem are very miscible with water, and hence it is preferred that no moisture enters the CO_2 scrubber system via the LFG. Accordingly, a commercially available cloud-point co-polymer glycol, Pluronic 10R5, from BASF, was investigated for use in the water absorption stage, upstream of the CO_2 removal system. Due to its high intrinsic osmotic pressure of 187 atm, 10R5 attracts and absorbs water to a high degree. The hydrophobic end (commonly fatty acids, fatty alcohols, polypropylene glycols or polybutylene glycols) of this cloud-point glycol causes a solubility inversion, and thus, the combined polymer exhibits water solubility at lower temperatures, but water immiscibility at higher temperatures. The transition temperature is usually called the "cloud point". Above the transition temperature, the glycol co-polymer phase separates into water-rich and glycol-rich layers due to density differentials, and therefore the two layers can be easily separated by decantation techniques. State-of-the-art water recovery from glycols consists of heating to 100°C (to boil off the water) in a separate loop for repeated use. The energy requirements for such a system are quite high, due to the high heat of vaporization of water.

The results of the cloud-point testing of the 10R5 glycol are shown in Table 5. As can be seen, a 25 percent mixture of 10R5 in water phase separates completely into water and polymer layers, in the same proportion, at 67°C. Fresh 10R5 when injected into the wet LFG in the demonstration system, will absorb up to three times its volume of water, at which point the water-glycol mixture can be removed, phase separated by thermal means using the cloud-point phenomena, and the glycol-rich solvent re-introduced into the water removal system.

Table 5: Cloud Pont Phenomena of Pluronic 10R5 Mixtures

Test #	10R5 in H_20,vol %	Onset of Cloud Point, ˚C	Cloud Point Complete, ˚C	10R5/H_2O Phase Separation
1	90	80	>80	None
2	75	80	>80	None
3	50	64	73	80/20
4	25	59	67	25/75*
5	10	57	61	8/92

***Optimum solvent/water separation.**

Source: Nrgtek

The absorber design was completed for a design window of raw LFG flow rate of 100 SCFM, CO_2 concentration of 38 vol percent and a pressure of 100 psig. The CO_2 scrubber vessel dimensions were determined to be 2-ft in diameter and a 7-ft height. This design was based on Genosorb 1753 (Selexol), a solvent used industrially and for which properties and CO_2

absorption data (5.6 mg/g·bar at 25°C) are readily available in the literature[4]. The design will be evaluated at the site to see if any adjustments should be made based on its performance. This design is adequate based on the solubility data of the potential candidates, Nrgtek A and B of 12.8 and 13.1 mg/g expected to remove CO_2 to desired levels because the solubilities are six times higher under actual (100 psig) conditions than Genosorb. Based on the above sizing, the fabricated skid-mounted CO_2 removal subsystem is shown in Figure 21. The pressure vessels were welded and pressure tested per ASME code and revealed no loss of pressure at 150 psig for 1½ hours.

The CO_2 subsystem design is dependent on gas-liquid contact, an alternative approach to accomplish this was investigated via the use of a novel micro-bubbler generator concept incorporated into the current design for RNG Testing of the MB could not be done at Nrgtek's facility due to the large quantity and pressure of LFG required. Therefore, the MBs were installed into the scrubber vessel and planned for testing during the initial three-month shakedown period at the landfill site prior to demonstration of RNG production. The scrubber vessel was also fitted with a 3-ft tall vertical partition separating the inlet and outlet solvent flows to prevent liquid with occluded gas from short circuiting directly into the downstream recirculating pumps and thereby avoiding possible cavitation effects. The scrubber vessel is also equipped with demister pads to prevent any liquid droplet carryover from the beds. If results indicate insufficient removal of CO_2 to meet RNG specifications, the design of the subsystems are flexible enough to revert back to the original packed-bed configuration for gas/liquid contact.

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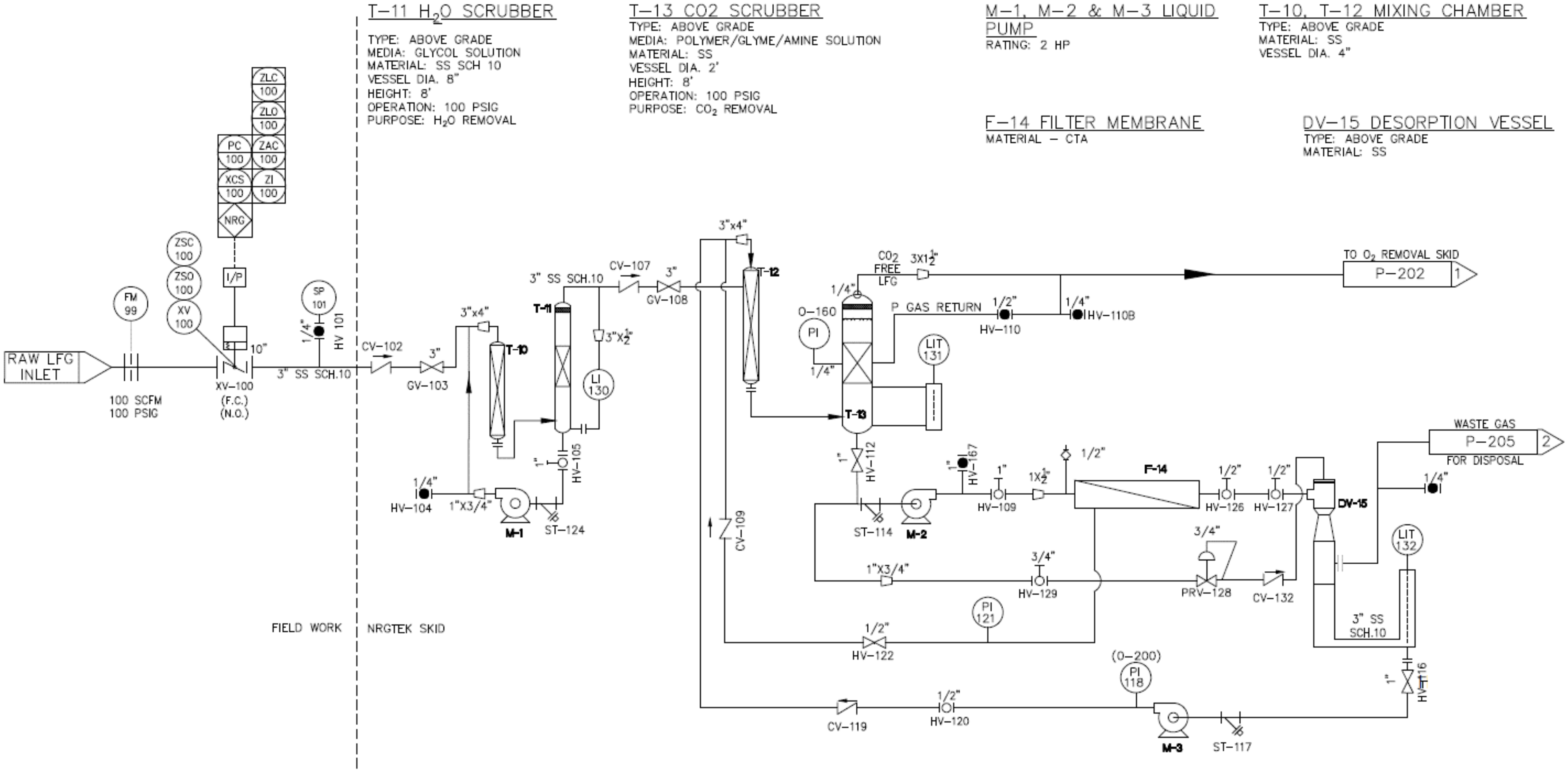
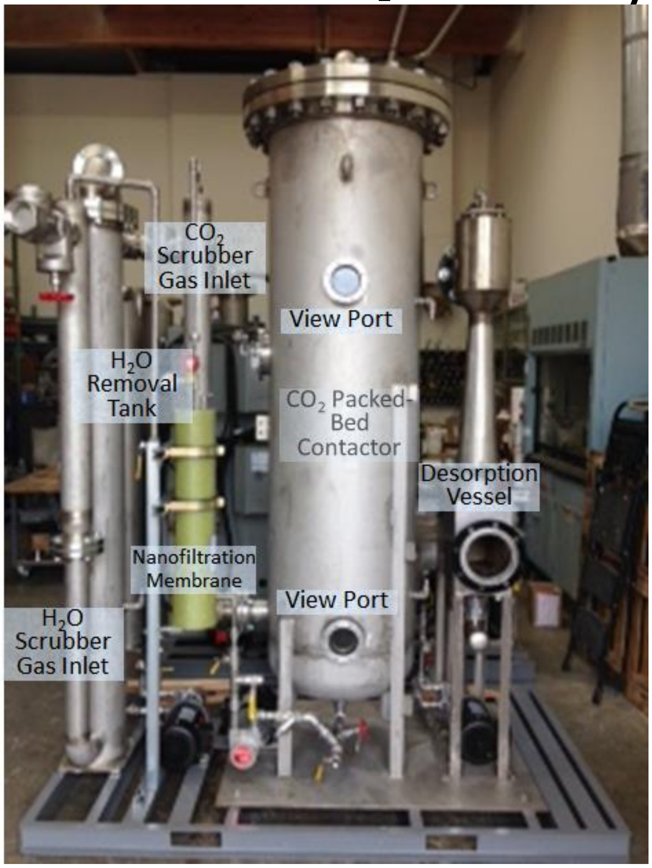
[4] Scrubbing Waste Air and Waste Gas Streams, Clariant. http://2002_AbsorptionFluidsForGasTreatment_Newsroom_Brochures_Genosorb_d.pdf.

Figure 20: P&ID of the CO_2 Removal Skid



Source: Gas Technology Institute

Figure 21: Skid-Mounted CO_2 Removal Subsystem



Source: Nrgtek

N_2 Removal Technology

As shown in Figure 1, it was originally proposed to remove both O_2 and N_2 from the LFG by absorption in a solvent and recover CH_4 in the last stage of the three-stage-cleanup process. Since O_2 removal is now included in the second stage along with H_2S and siloxanes, N_2 and CH_4 remaining in the LFG after CO_2 and O_2/H_2S/siloxane removal will be separated using a solvent that has a high selectivity of CH_4 absorption over N_2, followed by desorption and recovery of the CH_4 as RNG and rejection of N_2 in a separate stream.

N_2/CH_4 Absorption/Desorption Testing

The approach used for N_2 removal in stage 3 was to test various solvents that have demonstrated an affinity for the absorption of CH_4 over N_2. As an example, the solubility of different gases in various perfluorocarbons[5] is shown in Table 6 (perfluorodecalin is designated as PP6).

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[5] http://www.f2chemicals.com/pdf/technical/Gas%20solubility.pdf.

Table 6: Solubility of Different Gases in Various Perfluorocarbons

	PP1	PP2	PP3	PP6	PP9
Helium	6.6	5.5	4.6	3.9	3.4
Hydrogen	10.7	9.0	7.4	6.3	5.6
Nitrogen	26.3	22.0	18.3	15.6	13.8
Carbon Monoxide	26.3	24.2	20.0	17.1	15
Argon	39.8	33.5	27.7	23.7	20
Oxygen	41.0	34.6	28.6	24.4	22
Carbon Dioxide	156	132	109	93	82
Sulfur Hexafluoride	167	140	116	99	87
Ethane	263	221	183	156	138
Propane	5.90				
Chlorine	781	657	542	463	408
Fluorine	44				
Ozone	7.8	7.4		6.3	6.3

(ml gas per 100 g of liquid at 25°C and 1 atm)

Source: GTI

Alternative solvents include mineral oil, silicone oils, and polydimethyl silicone (PDMS), as listed in Table 7.

Table 7: Comparative Solubility of Different Gases in Various Oils

Gas Name	Gas Symbol	Mineral Oil	Synthetic Ester	Natural Ester
Nitrogen	N_2	0.091	0.091	0.074
Oxygen	O_2	0.172	0.152	0.134
Hydrogen	H_2	0.0504	0.0479	0.0471
Methane	CH_4	0.423	0.378	0.341
Ethane	C_2H_6	2.88	2.20	2.14
Ethylene	C_2H_4	1.81	1.85	1.67
Acetylene	C_2H_2	1.25	4.26	2.58
Carbon Monoxide	CO	0.125	0.130	0.108
Carbon Dioxide	CO_2	1.10	2.08	1.54

Source: GTI

Table 8 shows the diffusivity and permeability in PDMS membranes, the selectivity for CH_4 over N_2 is only around four, but since several versions of PDMS are available as liquids, this chemical was also investigated in this task.

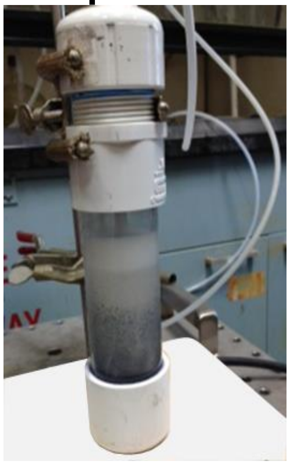
Table 8: Gaseous Permeability of Dimethylsilicone Rubber

Gas	Permeability * 10^9 $cm^3*cm/(s*cm^2*cmHg)$	Diffusivity * 10^6 cm^2/s	Solubility $cm^3/(STP)/cm^3*atm$
H_2	65	43	0.12
He	35	60	0.045
CO_2	323	11	2.2
N_2	28	15	0.15
O_2	62	16	0.31
CH_4	95	13	0.57

Source: GTI

Gravimetric absorption experiments to measure N_2 and CH_4 capacities in fluorodecalin and four other selected solvents were performed with pure N_2 and pure CH_4 as shown in Table 9. The same test apparatus (Figure 19) and procedure previously employed for CO_2 absorption testing was also used for this testing. Initial results with CH_4 indicated a consistent loss (rather than a gain) in weight for all the solvents tested, which was attributed to insufficient degassing of the solvent. Continued testing was therefore conducted after modifying the experimental procedure as follows. After first dewatering the solvent by heating it to 100°C and allowing it to cool to ambient temperature in a sealed dehumidification chamber and, as it was suspected that the solvents were not adequately degassed by this method, a vacuum pump was then used to evacuate the gas bubbler for 30 minutes and after any apparent residual gas bubbling ceased, the solvent weight was recorded. As was done in the CO_2 absorption testing, the gas was then allowed to flow into the solvent at near ambient pressure for three hours at a rate of 5.7 standard liters per hour (SLPH) and its weight recorded to determine the amount of gas absorbed. The test was performed three times for each solvent tested.

Figure 22: CH_4 Desorption with Magnetic Stirring



Source: Nrgtek

Using the revised procedure, the results for the absorption capacities of CH_4 and N_2 are shown in Table 9. Polypropylene glycol and the two propoxylates (a form of propylene glycol with lower viscosity, faster desorbing solvents) indicate the lowest absorption capacities for N_2 over CH_4 and are unacceptable for use in the final stage of the LFG cleanup system for RNG production. The results further indicate higher absorption capacities for both gases in perfluorodecalin than in silicone oil and a higher CH_4:N_2 selectivity ratio of ~3.3 for perfluorodecalin as compared to ~2.3 for silicone oil. A photo of CH_4 readily degassing from the silicone oil (similarly for the perfluorodecalin) after the absorption test is shown in Figure 22. It is important to note, however, that the selectivity ratio increases with total pressure of the system, which is 100 psig at the site, as solubility is proportional to the partial pressure of each gas in the mixture per Henry's law.

Table 9: CH_4/N_2 Relative Absorption Capacities at Ambient Conditions

Solvent	CH_4 Absorption ml/g	N_2 Absorption ml/g	$CH_4:N_2$ Selectivity
Silicone oil, 200cS	2.08	0.92	2.26
Perfluorodecalin	10.2	3.06	3.33
Glycerol Propoxylate MW 266	1.53	1.23	1.24
Pentaerythryitol Propoxylate MW 486	1.57	1.27	1.24
Proplyene Glycol MW 400	1.42	1.17	1.25

Source: GTI

As perfluorodecalin has shown the highest absorption capacity for CH_4 in comparison to N_2 it was chosen to be used for the demonstration system at the site. The data will need to be verified at pressure with actual LFG in the presence of all the other gases during shakedown testing at the site.

N_2 Removal Subsystem Design

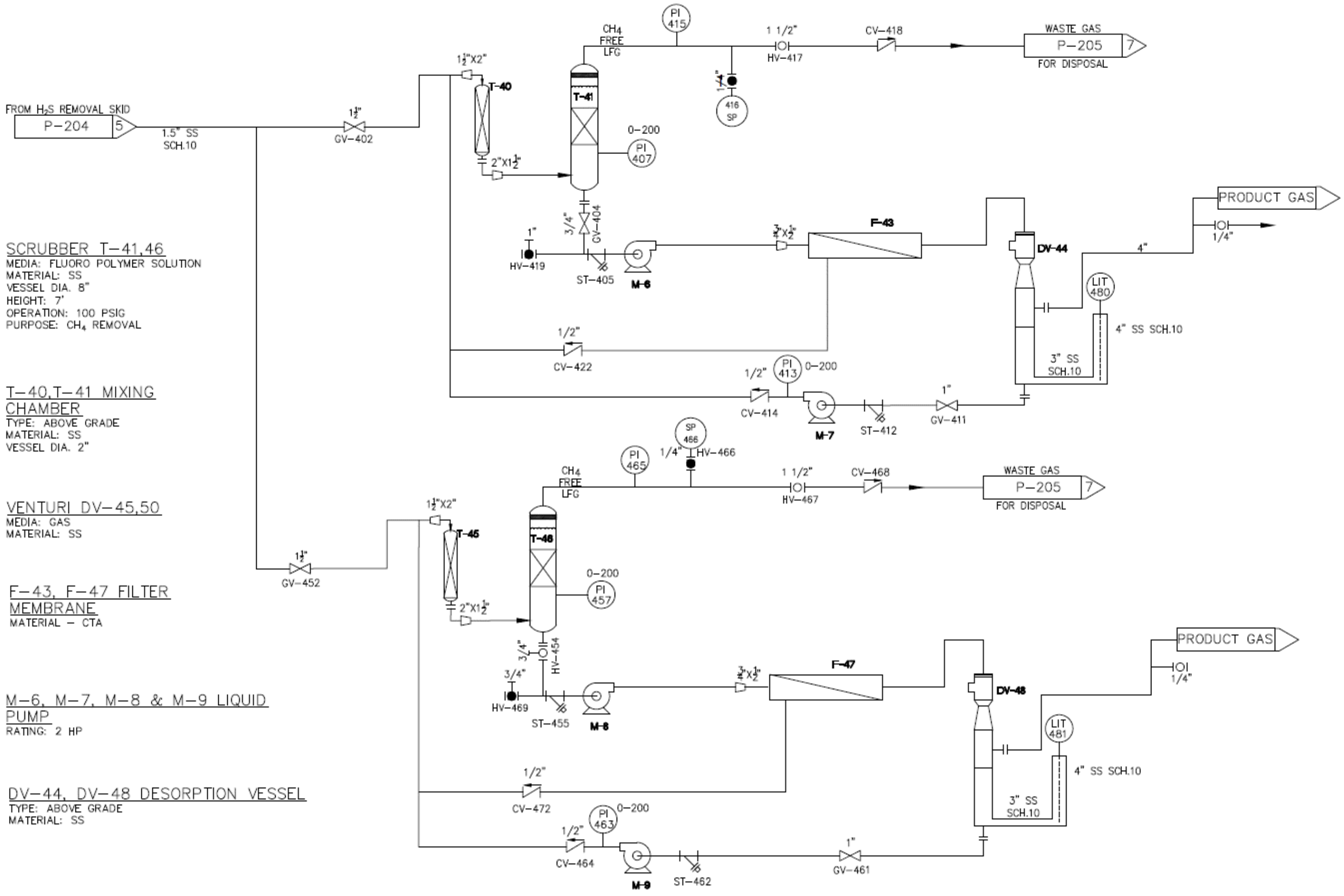
The N_2 subsystem designs in this task was not performed according to the traditional packed-bed tower design criteria (using e.g., mass-transfer coefficients, flooding velocities, NTUs, etc.), but instead were based on the laboratory data as limited design data, and insufficient equilibrium data were available and because the selected solvents (other than Genosorb) are not used in industry for gas treating.

Detailed P&IDs for the N_2 removal subsystem in parallel mode of operation is shown in Figure 23. The absorber designs were completed for a design window of LFG flow rate of ~62 SCFM, N_2 and CH_4 concentrations of 29 and 72 vol percent, respectively, a solvent flow rate of 10-15 GPM, and a pressure of ~100 psig. The N_2 removal subsystem was built with two 8-in diameter by 7-ft tall scrubber vessels, each capable of preferential removal of CH_4 over N_2. The subsystem incorporates a 50 percent overdesign for allowing longer gas-liquid contact time to accommodate the high N_2 in the LFG and meet required RNG production levels as no mass transfer data are available for these solvent systems. Each of the main vessels was fabricated by ASME Code from stainless steel 304/316, and rated for 100 psig operation. It should be noted that all lab tests for N_2/CH_4 separation were performed at atmospheric pressure, while testing at the demonstration site will be conducted at 80-100 psig, leading to higher absorption capacities per Henry's law of partial pressures. This design will be evaluated extensively during the three-month shakedown period at the site and any required changes will be made prior to the demonstration of the system for RNG production. The completed subsystem is shown in Figure 24.

The N_2 subsystem design is dependent on gas-liquid contact, therefore, the micro-bubbler (MB) technology used in the CO_2 separation process was also tapped for use in the N_2 separation. Once again, the MBs were installed in a flexible manner so they could be removed if issues were discovered during initial trials of the system at the landfill site and it becomes necessary to revert back to the original packed-bed configuration for gas/liquid contact.

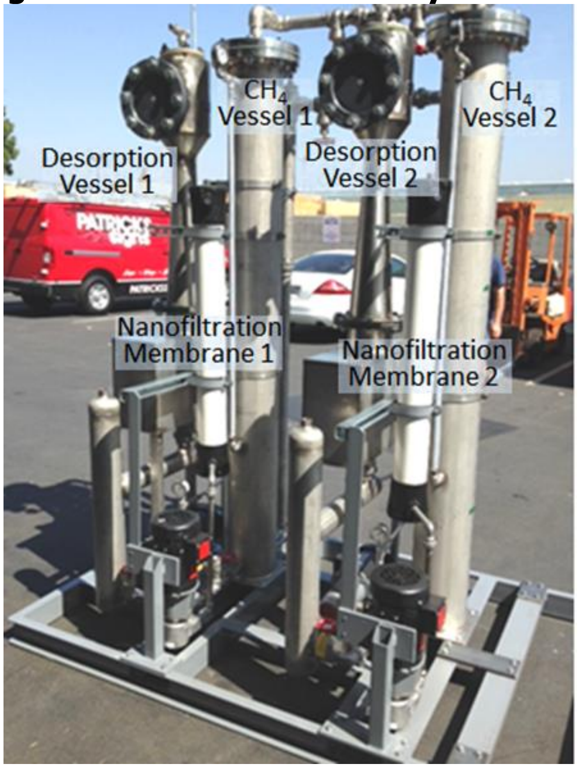
The N_2 scrubber vessel was also fitted with a 3-ft tall vertical partition separating the inlet and outlet solvent flows to prevent liquid with occluded gas from short circuiting directly into the downstream recirculating pumps and thereby avoiding possible cavitation effects. The scrubber vessel is also equipped with demister pads to prevent any liquid droplet carryover from the beds.

Figure 23: P&ID of the N_2 Removal Skid in Parallel Mode of Operation



Source: Gas Technology Institute

Figure 24: N_2 Removal Subsystem Skid

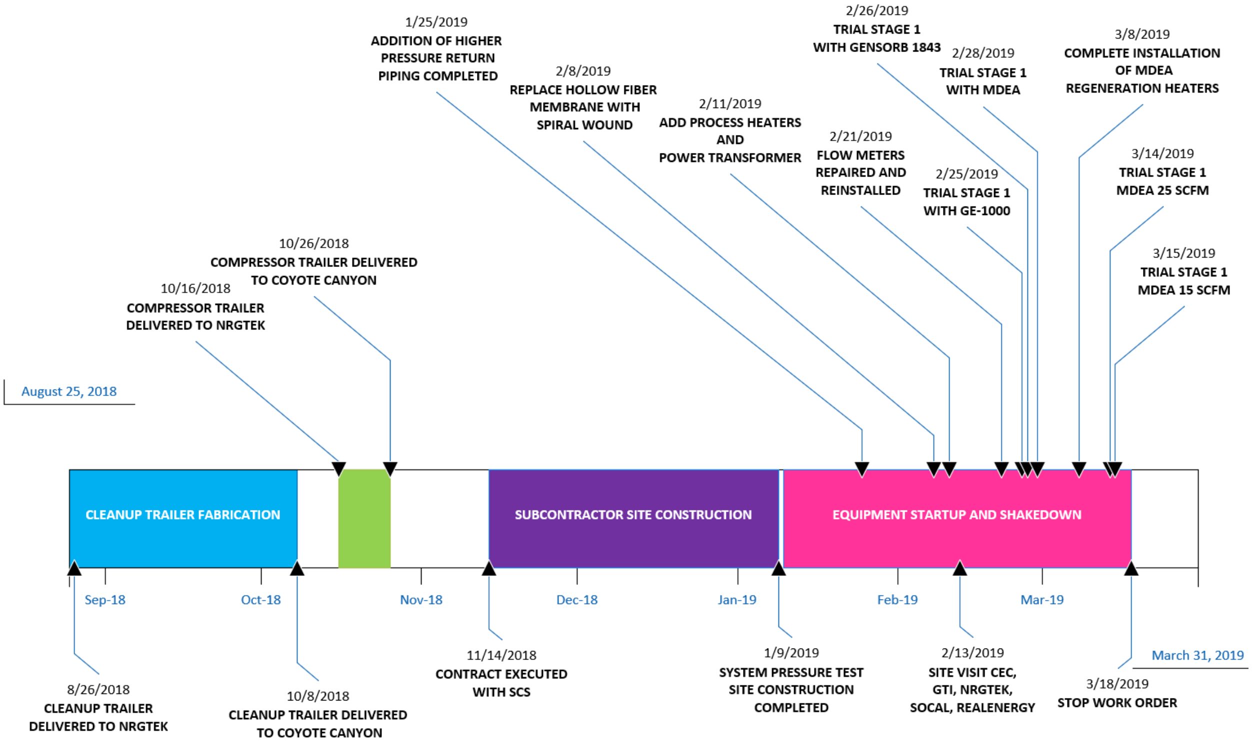


Source: Nrgtek

CHAPTER 3:
Project Results

As discussed previously in this report, a change in demonstration site location and subsequent delays in acquiring additional cost-share funding and contracts resulted in the equipment not being deployed at the Coyote Canyon site until January 2019. The project end date of March 2019 left only three months to start up and operate the equipment. Best efforts were made to overcome start up issues as quickly as possible, however, several issues encountered during system shakedown limited the amount of data that could be collected leading to minimal project results to report. A timeline of the equipment deployment and operation activities is shown in and described in greater detail in the following sections.

Figure 25: Timeline for Deployment and Startup Activities for LFG Cleanup Equipment at Coyote Canyon



Source: Gas Technology Institute

Equipment Deployment

In order to minimize site construction costs and delays, two flatbed trailers were purchased. These trailers were sequentially delivered to Nrgtek. Nrgtek first installed the three stage clean up system on a 16-foot-long trailer including all inter-stage connections, PLC control system, and spill collection drip pans. This trailer shown in Figure 26.

Figure 26: Three Stage Cleanup System Installed on 16’ Trailer

Source: Nrgtek

The booster compressor equipment was then sent from GTI to Ngtek. The equipment was installed on an 18-foot-long trailer. The compressor trailer is shown at the Coyote Canyon site in Figure 27.

Figure 27: Booster Compressor Trailer at Coyote Canyon Landfill

Source: Nrgtek

SCS Engineers was selected to perform the installation of the equipment at the landfill. The scope of this installation involved:

1. Mechanical Piping
    a. Connecting the raw LFG feed line to the inlet of the compressor trailer
    b. Assembling and connecting a manifold to collect process exhaust streams
    c. Connecting the exhaust manifold from the cleanup trailer to the suction piping of the landfill gas blower
2. Electrical
    a. Identified and connected the required 480V 100A circuit to the test equipment

    b. Install a lock out mechanism as required by OCWR to shut down power to cleanup equipment upon loss of plant power
3. Civil
    a. Level and secure trailers at designated location on site
    b. Provide crash protection for trailers

SCS Engineers and GTI agreed to terms and conditions of the work scope in late November 2018 and work was completed in January of 2019. Evidence of this work is shown in Figure 28. SCS Engineers was called back several times to the site to facilitate the operation of this equipment. One of these visits included the installation of an additional return pipe back to the blower suction to accommodate a higher-pressure exhaust stream from the system.

Figure 28: Integration of Cleanup System Equipment at Coyote Canyon Landfill

Lock-out Circuit Breaker

Cleanup Exhaust Return to Blower

Blower Discharge Connection

Feed to Compressor Trailer

Source: Nrgtek

The following tasks were completed in January, 2019:

1. Installation of equipment ESD (emergency shut down) circuit
2. Construction of a work platform and weather protection above operator interface monitor
3. Installation of process flow meters
4. Interconnection of piping between the compressor and cleanup trailers
5. Verify input and output signals between PLC and instruments
6. Complete and verify PLC code including tuning of control loops and safety shut down sequence

System Start-Up

The booster compressor was activated to increase the pressure of the system in order to check for leaks. This pressure check revealed several issues. The gas connections from the water removal system to the CO_2 removal system (stage 1) and the outlet line to the oxygen removal system (stage 2) were found to have minor leaks. On closer inspection, it was noticed that the SS 304 unions were galled at their mating/sealing surfaces. Chips and cracking were also observed on sight glasses installed on the cleanup system. These issues were resolved by replacing the damaged parts and the system eventually passed the pressure integrity testing.

Flow testing was then performed on each stage. The common manifold for the clean-up skid exhaust lines was installed to accept both lower pressure exhaust streams and a higher pressure concentrated product methane stream. During shakedown testing it was discovered that the 2-inch manifold line did not have enough volume to keep the pressure in the exhaust manifold from building. As a result, the back pressure in the exhaust manifold was preventing the low-pressure exhaust streams from flowing out of their respective stages and in some cases misdirected back flow was occurring. The issue was resolved by identifying another port in the landfill blower suction line to tap into for the higher-pressure methane discharge stream. SCS Engineers were brought back to the site to install a new line, about 15 feet long, from the clean-up trailer to this new port.

Flow testing continued after the installation of the new exhaust line and exposed an issue with the process flow meters. It was discovered that the digital flow meters installed on the cleanup trailer were not functioning properly. Not only was the display showing erroneous values, but the flow meter was not transmitting pulses to the clean-up system's PLC. Multiple calls to the supplier, Measurement and Control Systems, were made in an effort to diagnose and solve the problem over the phone. As these calls could not resolve the problem and the meters were removed from the test skid and delivered to the supplier. A defective pressure sensor within the transmitter was identified as the source of the problem. Two meters needed to be removed from the process and sent to the vendor for repair.

Nrgtek prepared Stage 1 of the process for operation by pumping the pre-selected solvents into their process reservoirs. The water removal stage uses Pluronic 10R5 polymer. This polymer was found to be too viscous to be circulated with the existing liquid pump due to the cold weather experienced at the site in February 2019. A filament resistance heating system was installed at the base of the H_2O removal system. In order to power this system, a 480V to 110 VAC transformer needed to be added to the skid.

GE-1000 (referred to ad Nrgtek A previously in this report), the first polymer solvent selected for CO_2 removal, was even more viscous than Pluronic 10R5. The high viscosity of the polymer in the low-temperature conditions (50-55^{o}F) contributed to the failure of system pumps. Additional filament wound heating elements were installed to warm the GE-1000 and two pumps were replaced.

Also, the Toyobo CTA hollow-fiber high-surface membrane element, installed for CO_2 desorption under pervaporation conditions (high pressure on the feed side and vacuum on the permeate side) was also found to be contributing to a very high pressure for solvent flow. Therefore, it was replaced with a spiral-wound CTA membrane element and exhibited a much lower pressure drop.

System Operation

During the last week in February 2019, stage 1 (CO_2 removal), was trialed for the first time. The physical absorption solvent GE-1000 was pumped into the stage 1 reservoirs. Once steady state flow and pressure conditions were established, samples were taken from the inlet and outlet of the CO_2 removal stage and processed through the portable gas analyzer per a gas sampling plan (see Appendix A) devised to assess effectiveness of the cleanup system. The results shown in Table 10 indicated a slight removal of CO_2, but at 20 percent of the design LFG feed flow rate of 100 SCFM. This poor result and project time constraints drove Nrgtek to begin trials with the next selected solvent, Butyl Diglyme. The test results with this solvent are shown in Table 11. Once again, minimal CO_2 removal was observed with this solvent.

Table 10: CO_2 Removal Stage Results with GE-1000

Result	Inlet	Outlet
Pressure (psig)	95	
Flow Rate (SCFM)	20	
% Methane	37.9	40.4
% Carbon dioxide	34.3	31.7
% Oxygen	4.3	2.7
Hydrogen sulfide (ppm)	39	18
% Balance (N_2)	23.5	25.2

2/25/2019 Gas Analysis with GE-1000, Glycerol Ethoxylate

Source: GTI

Table 11: CO_2 Removal Stage Results with Butyl Diglyme, Gensorb 1843

Result	Inlet	Outlet
Pressure (psig)	95	
Flow Rate (SCFM)	20	
% Methane	40	39.3
% Carbon dioxide	34	33.4
% Oxygen	3.1	3.3
Hydrogen sulfide (ppm)	42	18
% Balance (N_2)	22.9	24

2/26/2019 Gas Analysis with Butyl Diglyme, Gensorb 1843

Source: GTI

Knowing that the excess CO_2 inhibited the removal of H_2S, a decision was made to attempt the CO_2 removal using a chemical absorption known to be successful in industry. Methyl diethanol amine (MDEA) is a tertiary amine, commonly used for absorption of acid gases like carbon dioxide, hydrogen sulfide or sulfur dioxide. This approach required the installation of immersion heaters to the stage 1 equipment in order to boil the captured CO_2 out of the MDEA solvent. In order to operate the immersion heaters, additions and modification that had to be made to the PLC code.

A 50 percent mixture of MDEA and water was pumped into stage 1 and run through the heaters in order to remove the residual CO_2. The system was then operated at a flow rate of 25 SCFM and the results are shown in Table 12.

Table 12: CO_2 Removal Stage Results with MDEA, 25 SCFM

Result	11:10AM Inlet	11:10AM Outlet	12:00PM Inlet	12:00PM Outlet
Pressure (psig)	95		95	
Flow Rate (SCFM)	25		25	
% Methane	38.2	40.4	39.4	39.7
% Carbon dioxide	33.9	28.8	34	31.1
% Oxygen	2.8	2.7	2.8	2.9
Hydrogen sulfide (ppm)	41	1	41	1
% Balance (N_2)	26.1	28.2	23.9	26.3

3/14/2019 Gas Analysis with MDEA, 50% v/v H_2O

Source: GTI

With the minimal CO_2 removal observed at a flow rate of 25 SCFM, the MDEA solution was regenerated and the system was run again at a reduced flow rate of 15 SCFM. The testing results of the lower flow rate test are shown in Table 13. The results show a significant decrease in the CO_2 composition from the inlet to the outlet of stage 1 of the cleanup system. Also, as expected, the MDEA was able to capture the H_2S in the LFG.

Table 13: CO_2 Removal Stage Results with MDEA, 15 SCFM

Result	10AM Inlet	10AM Outlet	11AM Inlet	11AM Outlet	12PM Inlet	12PM Outlet
Pressure (psig)	82		82		82	
Flow Rate (SCFM)	15		15		15	
% Methane	40	52.5	38.7	51.2	37.2	51.7
% Carbon dioxide	34	**6.2**	33.5	**3.4**	31.9	**2.9**
% Oxygen	2	1	2.5	3.7	3.4	3.8
Hydrogen sulfide (ppm)	23	3	23	0	22	0
% Balance (N_2)	24.1	38.5	25.2	41.6	27.5	41.7

Source: GTI

Encouraged by positive results finally observed in stage 1 of the system and warmer weather conditions at the landfill site, Nrgtek decided to trial the innovative physical solvent GE-100 again. The MDEA solution was removed from the stage 1 reservoirs and replaced it with GE-1000. Initially, the system pumps were able to circulate the fluid, but the solution became very frothy and the process pumps began to cavitate. The operation of the system with GE-1000 was stopped because the pumps were unable to circulate the fluid through the CO_2 removal equipment.

In preparation for Stage 2 operation, a comprehensive analysis of the raw LFG feed gas was sampled and performed by AccuLabs Inc. located in Arcadia, CA. This analysis is presented in Appendix B and includes siloxane analysis which was to be used as a starting point for the ability of Stage 2 to remove siloxanes.

GTI received a stop work order from CEC on March 18, 2019 and subsequently issued the same to Nrgtek. This caused the operation to cease at the Coyote Canyon Landfill.

Decommissioning of Equipment

To decommission the equipment at the Coyote Canyon landfill, Nrgtek, pumped all the solvents from the vessels on the cleanup trailer into drums. The work platform and weather protection equipment were removed from the trailer as well as miscellaneous equipment being stored at the site to facilitate the operation of the equipment.

SCS Engineering was brought back to the site to restore it to its original condition. This work included the removal of the inlet piping to the compressor trailer and both of the exhaust lines connected to the site's blower suction piping. The electrical circuit to the cleanup system was also removed. The concrete equipment protection barriers were picked-up and hauled off-site.

On April 24, 2019, SCS Engineering met with personnel from OCWR to walk through the site to assure that the decommissioning was satisfactorily performed. Figure 29 shows photos of decommissioning activities performed at Coyote Canyon.

Figure 29: Completion of Decommissioning at Coyote Canyon Landfill

Feed piping to compressor trailer removed

Feed to compressor trailer capped off

Work platform and concrete barriers removed

Exhaust return piping to landfill removed

Source: Nrgtek

CHAPTER 4: Technology/Knowledge/Market Transfer Activities

During this project, SCAQMD, EPA-LMOP, SoCal Gas, and Cambrian Energy expressed interest in this technology and participated in technical action meetings to help shape the direction of the project. In addition, a privately-owned company, RealEnergy LLC, expressed willingness in hosting the equipment at a different site to allow for additional validation testing for RNG production beyond the project's end term.

The data collected during this project was insufficient to draw conclusions about the effectiveness of the process to remove contaminants from LFG for RNG production. GTI will not proceed with any technology transfer of market adoption plans at this time, but GTI did transfer ownership of the equipment to RealEnergy, LCC. RealEnergy agreed to share operational data with CEC as they proceed to verify the operation of the equipment.

CHAPTER 5:
Conclusions and Recommendations

Based on the short duration operation of the LFG clean-up system for RNG production, the following conclusions and recommendation can be drawn.

- Due to the unforeseen delays caused by the search for a new demonstration site, various repairs at the new Coyote Canyon Landfill site, and OCWR's sanctioning a final location to deploy the cleanup system, the project demonstration time was reduced from twelve to three months. During these three months, only the CO_2 removal skid (Stage 1) was trialed. The testing using the novel physical absorption solvents showed poor results (12-17 percent CO_2 removal). Ultimately, the lack of demonstration time resulted in obtaining less data and insufficient validation of technology performance and consequently the project goals and objectives could not be met.
- The frothing of the solvent mixture generated when operating the micro-bubbler at pressures other than a discharge to atmospheric pressure (as was done in the lab) was not anticipated at the site. The frothing resulted in pump cavitation issues which prevented achieving targeted partial pressures for optimal absorption of CO_2 from the LFG.
- The micro-bubbler was tested in the lab showed reduce in frothing, when used at atmospheric pressure. However, in the skids, the discharge pressure at both the water removal stage and the CO_2 outlet stage, was above the atmospheric pressure and bubble dissipation wasn't successful. Therefore, the developed micro-bubbler didn't prevent solvents from frothing at a larger scale, such as during the field testing.
- The varying ambient conditions at site required the stage 1 solvent fluid streams to be heated up to 220F in order to maintain a viscosity suitable for the pumps to feed the reactor vessels and this increased temperature resulted in a reduced effectiveness of the solvent to absorb CO_2

Recommendations

This project identified that at the current technology readiness level of the Nrgtek equipment, more time under real world operating conditions is needed to evaluate the potential of the cleanup system. Nrgtek has worked under tight timeline trying to achieve the full demonstration of the system. Equipment modifications, unforeseen repairs, and parts replacement occurred during a brief operational period. Thus, only stage one of the biogas upgrading has been tested and demonstrated under real life conditions.

Therefore, collected data are insufficient to draw conclusions about the performance of built equipment with actual LFG.

The installation of the equipment on trailers makes this system easily deployable. It is recommended that the system be re-deployed to complete the sequential shake down of each stage of the system. Further recommendation is limiting the scope of the testing to one stage at a time with a limited number of solvents. This would include increasing the level of instrumentation and data collection of each stage.

Landfill Gas Flow Meters

The performance of the meters selected for this project originally was not satisfactory and no useful readings could be achieved for the CO_2 exhaust stream. This was due to the stream being connected to the suction side of the landfill blower and assumingly the high flow of that line produced erroneous meter readings.

Temperature of Solvents

The brief operation of stage 1 of the cleanup system did expose the system design had an issue operating at temperatures below 55F. The target design of the system was to account for operating temperatures between 40-120F, the ambient operating temperature range for California landfills. However, temperatures below 55F at the site made solvents in the system too viscous to pump and heaters needed to be installed to warm the solvents. Warming the solvents to allow for circulation exposed the upper temperature limitation of the solvent. The performance of solvents to physically absorb contaminants is inversely proportional to the solvent temperature. Therefore, it is possible that the need to warm the solvent to reduce viscosity lead to the reduction in the solvents ability to absorb CO_2 in the GE-1000 and the butyl diglyme trials.

Partial Pressures

Another possibility for the vastly reduced CO_2 absorption observed during stage 1 testing of GE-1000 and butyl diglyme could be due to the lower partial CO_2 pressure in the inlet LFG flow (≈24-25 psig) compared to the partial CO2 pressure in the gas used for testing in the laboratory. Physical gas absorption is based on partial pressures governed by Henry's law. Laboratory tests had indicated a high amount of absorption at 50 psig partial pressures in static test apparatus system. The performance did not translate to lower partial pressures and dynamic conditions at the landfill site.

To prove the commercial viability of a cost-effective system and to keep construction costs reasonable for the separation pressure vessels, booster compressor, and piping in the system, Nrgtek capped the operating pressure of the system at 120 psig. The limited number of tests performed were conducted at about 95 psig. Additional testing adjusting the feed pressure incrementally closer to the 120 psig maximum operating pressure may have shown if increasing the partial pressure of CO_2 in the feed LFG would lead to increased physical absorption in the dynamic landfill conditions. Unfortunately, time was not available to conduct this type of testing.

Microbubbler

It is not clear that the use of micro-bubblers to increase gas-liquid contact and allow for the reduction of vessel size was a success. High levels of frothing observed suggests that insufficient time was available for the gases and liquids to separate after the microbubbles were formed. The frothy gas-liquid mixture caused pump cavitation and ultimately loss of solvent circulation.

Time did not allow for adjustments to be made to the micro-bubbler system. Testing allowing variable flows through the bubbler or additional volume for gas liquid separation may have alleviated the cavitation issue. The system was designed to be able to revert all the way back to a conventional packed bed. Additional investigations with the micro-bubbler are needed before it is known whether it is beneficial for LFG cleanup systems.

LIST OF ACRONYMS AND ABBREVIATIONS

Term	Definition
ACFM	Actual cubic feet per minute
°C	Degrees Celsius
CO_2	Carbon Dioxide
ECC	Electro-catalytic converter
EO	Ethylene Oxide
°F	Degrees Fahrenheit
ft	Foot
ft^3	Cubic foot
GPM	Gallons per minute
H_2S	Hydrogen Sulfide
Hr	Hour
In	Inch
L	Liter
L/G	Liquid-to-gas ratio, L/Nm^3
LFG	Landfill gas
LPM	Liters per minute
MB	Micro-bubbler
MDEA	Methyl di-ethanol amine
mg	Milligram
min	Minute
ml	Milliliter
N_2	Nitrogen
Nm^3	Normal (standard) cubic meter
NTU	Number of transfer units
O_2	Oxygen
OCWR	Orange County Waste and Recycling
PDMS	Polydimethyl silicone
PFD	Process flow diagram
PEG	Polyethylene glycol

Term	Definition
P&ID	Piping and instrumentation diagram
ppmv	Parts per million by volume
psig	Pounds per square inch gauge
RNG	Renewable natural gas
SCFH	Standard cubic foot per hour
SCFM	Standard cubic foot per minute
SLPH	Standard liters per hour
SoCalGas	Southern California Gas
vol%	Percent by volume

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APPENDICES

Appendix A: Gas Sampling Plan and Appendix B: Comprehensive Raw Landfill Gas Analysis (Publication Number CEC-500-2020-032-APA-B) are available upon request by contacting Katharina Gerber at Katharina.Gerber@energy.ca.gov.