

REMOVAL OF SILOXANES FROM  
LANDFILL GAS BY SAG™  
POLYMORPHOUS POROUS GRAPHITE  
TREATMENT SYSTEMS

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## **Abstract**

Widespread commercialization of the conversion of landfill gas to electricity has been hampered by the costly removal of siloxanes required to protect power generation equipment from damage. Controlling the costs for converting landfill gas into energy is vital if this resource is to be used to make electricity or pipeline purity gas.

An effective and low cost measurement and removal method for siloxanes in landfill gas has been developed by Applied Filter Technology. The SAG™ Process has been tested on a number of sites over the past seven years and it is now operating at landfills throughout the country.

The company has perfected both a low cost method for analyzing the siloxanes at the landfill with the SIL 1 Field Test Kit and a low cost method for removing siloxanes with SAG™ Polymorphous Porous Graphite Filters. These specialized porous graphites have been designed to selectively remove the siloxanes in the presence of other contaminants in the gas stream. The company combines its guaranteed SAG™ technology with compression and chilling when needed, to provide a complete integrated package for landfill gas treatment.

## **Summary**

For some time it has been known that the low, medium and high molecular weight contaminants in methane-rich biogas produced primarily by landfills and anaerobic digesters need to be removed. Once removed, the biogas can be upgraded for injection into natural gas pipelines or used for other purposes, such as firing boilers or generation of electricity. New uses for landfill gas are appearing on the horizon. One of these is the production of LNG for use as a commercial truck fuel. AFT has been involved for more than seven years in projects where it is desired to convert biogas to electricity by means of internal combustion engines that drive generators. The SAG™ Technology was the first to allow the successful use of an SCR catalyst in power generation.

Early on (dating back to the 1970s and perhaps even before then) it was discovered that landfill gas was contaminated with literally dozens of aromatic and aliphatic organics. Some of these organics contained chlorine, such as chlorinated solvents. The chlorinated species posed a problem for manufacturers of gas-separation membranes because they could cause the membrane matrix to fail and reduce the gas yield. Removal of these organics proved to be necessary, but also too expensive to allow for broad commercialization of membranes for biogas upgrade.

The market response to effective utilization of biogas was to use generator engines that can burn the contaminated low BTU biogas. But once again, biogas contaminants have become an issue. One group of contaminants in biogas has proved to be problematic for internal combustion engines—the siloxanes. Siloxanes, or silicones, as they are sometimes called, are either linear or cyclical organic compounds comprised of silicon, carbon, hydrogen and oxygen. Use of siloxanes is prevalent in personal care products such as cosmetics, shampoos, deodorants, detergents and hairsprays. They are also used in pharmaceuticals, inks, adhesives, lubricants and heat transfer

fluids. Through the discard of used containers and other items from personal care products, consumer and industrial additives, the siloxanes find their way to municipal landfills. Due to their volatility, they become a contaminant in the methane gas produced. Municipal wastewater also contains siloxanes from home laundry products and clothing as well as from industrial sources. These siloxanes are released in the landfill and become entrained in biogas by anaerobic digesters. The use of landfill or digester biogas containing siloxanes in power generation engines has resulted in operation and maintenance problems. AFT has worked to find and implement an economical solution to the problem of siloxane contamination. This paper will discuss the experiences gained in treating biogas, the analytical considerations and the cost to remove siloxanes.

## **Landfill Gas Collection**

AFT has provided sampling and site reviews on over 400 locations. From this effort and monitoring of existing SAG™ Systems for siloxane reduction, we have found some common similarities between sites. These geographic, and demographic characteristics provide valuable information which can be used in the design and operation of a SAG™ System for effective reduction of siloxanes.

- Northern vs. Southern Landfills can have different levels of key organic groups based on geography. These include Freon used in air conditioning along with other regionally specific organics and solvents.
- Urban vs. Suburban Industrial and metropolitan landfills show higher levels of chlorinated organics and siloxanes used in such products as adhesives and caulks, than regional landfills in bedroom community locations.
- Dry vs. Wet Climate Dry landfills in the Southwest are typically lower in volatilization of siloxanes as well as organic solvents than their wetter more Northern counterparts.
- Rainfall Landfills that receive 20 inches or more of rainfall per year show higher levels of siloxane volatilization than dryer sites. Siloxane concentrations in landfill biogas also appears to be in direct proportion to moisture levels.
- Siloxane Evolution Period Landfills in moist areas typically have a longer period of siloxane evolution than those in dryer areas.
- Age Landfills closed more than 10 years ago appear to show lower biogas concentrations of siloxanes than more recently closed sites. This is believed to be a direct result of the use and increasing popularity of siloxanes in a wide variety of consumer and industrial products. (An industry estimate indicates a 3% to 5% annual increase in the volume of siloxanes sold over the next 20 years).
- Atmospheric Pressure Barometric pressure changes appear to have a larger impact on evolution of siloxanes in dryer landfills. This seems to result in bigger swings in gas volume and commensurate siloxane concentrations in the dryer landfills of the Southwest than in other wetter areas.
- Contaminants in the Biogas The presence of moisture, organic and inorganic species (as well as other factors) in the biogas impacts the solubility and volatilization of the siloxanes. For example 1,1,3,3 Tetramethyldisiloxane appears to degrade quickly in the presence of some chlorinated solvents. There is evidence that It can combine with other siloxanes to form higher molecular

weight species. Because of phenomena such as this, it is important to sample the influent gas periodically to determine any changes in contaminant levels that would require an adjustment in the SAG™ removal process.

- Sulfur Species High levels of hydrogen sulfide and other organic sulfur species can impact the removal of siloxanes and create corrosive acids that can harm the power generation equipment.
- Concentration Level All levels of siloxanes have a cumulative negative impact on power generation, heat transfer, and catalyst systems. For this reason, it is important to incorporate a testing plan into the overall SAG™ siloxane removal process

## **The Siloxanes**

There are hundreds and perhaps thousands of different siloxane compounds. The most prevalent linear species in waste biogas are pentamethyldisiloxane, hexamethyldisiloxane (MM), octamethyltrisiloxane (MDM), and decamethyltetrasiloxane (MD2M). These all have the chemical structure of  $-(CH_3)_2SiO-$ . Among the cyclical species, hexamethyltrisiloxane (D3), octamethyl-tetrasiloxane (D4), decamethylpentasiloxane (D5), and dodecamethylhexasiloxane (D6) are most prevalent. Cyclical siloxanes have the same basic structure as the linear siloxanes, but have 2 less methyl groups than their counterpart linear siloxanes possessing the same number of silicon atoms. Siloxanes are characterized by relatively high molecular weights (ranging from 162.4 for MM to 444.9 for D6), high boiling points (100.5 °C for MM to 211 °C for D5) and low vapor pressures (limited information available). Nonetheless, these compounds are sufficiently volatile to become incorporated in biogas.

## **Deposits from Siloxanes**

During combustion of biogas containing siloxanes, silicon is released and can combine with free oxygen or various other elements in the combustion gas. Deposits are formed containing mostly silica and silicates ( $SiO_2$  and  $SiO_3$ ), but can also contain calcium, copper, sodium, sulfur, and zinc. Most deposits caused by combustion of siloxanes are off-white to light brown in color and are of varying texture, some very smooth with a powdery-looking surface, while others are coarse and grainy. These deposits can ultimately build to a surface thickness of several millimeters and are difficult to remove by chemical or mechanical means. (ADD BOILER PICTURE). The propensity for silica/silicate deposition will vary based on flame front, heated surface area, rotation/tip speed, post combustion equipment, heat recovery and catalyst.

The damage inflicted by the siloxane combustion byproducts and deposits can be profound. Reciprocating piston engines experience fouling in the combustion chamber, on the valves, valve seats, piston crowns and cylinder walls. (ADD ENGINE PICTURE) Sometimes deposits collect under the exhaust valves resulting in blowby and burnt valves. This phenomenon reduces compression and engine efficiency. In gas turbines, deposits from siloxane combustion form in the hottest areas, mainly on the first few rows of nozzles and blades. Prolonged operation of gas turbines where siloxanes are present in the biogas can lead to severe erosion of the turbine blades

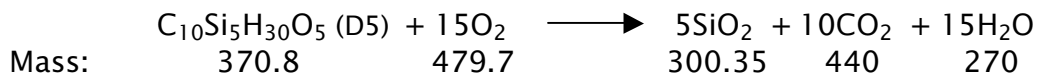
and a sharp drop in operating efficiency. Also, turndown of the turbine may be necessary to reduce heat.

Because of the difficulty in removing the silicon-based deposits and the cost to overhaul reciprocating piston engines and turbines, many manufacturers are considering removal of siloxanes from the biogas before it enters their equipment a requirement. SAG™ Filters by AFT are a low cost and non mechanical method of solving the problem

Catalysts are also being looked at for a number of different locations which have regulatory concerns. Siloxane as reduced silicon dioxide coats the catalyst and creates an impermeable glass. This reduces the efficiency of the catalyst for removal of formaldehyde and other byproducts from combustion. AFT has pioneered the use of specific SAG™ Graphites to protect catalysts (the oldest installation has been operating 24/7 for the past six years).

### Quantifying the Problem

Although there is no way to determine exactly how much of the siloxane combustion byproducts remain as deposits in engines and turbines, it is estimated that at least 0.1% to 0.5% is not expelled in the exhaust gases. Using this assumption, calculations can be made to determine the mass of the deposits that remain. In an engine that burns 140 SCFM (at 75 psig) of biogas containing 1 ppm v/v (15.7mg/m<sup>3</sup>) “siloxanes as D5,” a total of 0.0433 lb/hour of siloxanes enters the engine. Assuming complete stoichiometric combustion, the 0.0433 lb/hour D5 (decamethylcyclopentasiloxane) would be converted to 0.022 lb/hour silicon dioxide by the following reaction:



In one year’s time of continuous operation, the total mass of siloxanes entering the engine will be 192.7 lb. Assuming all of this becomes converted to SiO<sub>2</sub>, the total mass of SiO<sub>2</sub> created during combustion is 97.8 lb/year. (Show sand bag picture) Assuming 0.1 % to 0.5% is not expelled, this leaves a mass of approximately 0.1 lb. to 0.5 lb. per year to be deposited on the engine internals. This is more than sufficient to cause enough damage to an engine to require an overhaul at 5,000 hours or less, of operation. To completely overhaul a 1 MW engine to correct the damage inflicted by silicon-based deposits can cost \$60,000 and upward.

Microturbines experience similar problems from scaling, with the additional problem of severe erosion from scouring by small particles of silicon-based solids. This erosion can be so harsh on the impeller to cause failure of the turbine to operate. The heat recuperator section of the turbine is also impacted

Deposits from siloxane combustion by-products can also severely damage selective catalytic reactor (SCR) catalysts. Fouling of the catalyst’s surface by silicon-based deposits inhibits the reduction of NO<sub>x</sub> and hence failure of the process to meet air emission compliance standards. SCR catalysts can be precious metal-based and are quite expensive to replace. A new SCR catalyst bed can cost over \$200,000. Fouling

of SCR catalysts can occur in as little as a day or two to several weeks or months, depending on the concentration of siloxanes in the gas stream and other factors.

Boilers that burn biogas from landfills also suffer from siloxane contamination. Deposits on the tubes reduce heat transfer, thereby reducing the overall efficiency of the boiler. (ADD OTHER BOILER PICTURES) When the deposits become too thick, the tubes must either be cleaned or replaced. Frequency of cleaning or replacement is dependent on the concentration of siloxanes in the gas.

## Measurement of Biogas Contaminants

Before a SAG™ siloxane removal system can be designed, it is necessary to know what is in the biogas stream. There are three primary analyses that provide the necessary information. These are the EPA TO-14 test for volatile organics, the ASTM Procedure D-5504 GC/SCD for sulfur species, and SIL GC/MS analysis for individual siloxane species. All three tests are needed because all three groups of contaminants have an impact on the size and operating cost of the siloxane removal equipment.

The EPA TO-14 test measures for the following 60 contaminants:

Freon 12	1,1,2,2-Tetrachloroethane
Freon 114	1,3,5-Trimethylbenzene
Chloromethane	1,2,4-Trimethylbenzene
Vinyl Chloride	1,3-Dichlorobenzene
Bromomethane	1,4-Dichlorobenzene
Chloroethane	Chlorotoluene
Freon 11	1,2-Dichlorobenzene
1,1-Dichloroethene	1,2,4-Trichlorobenzene
Freon 113	Hexachlorobutadiene
Methylene Chloride	Propylene
1,1-Dichloroethane	1,3-Butadiene
cis-1,2-Dichloroethene	Acetone
Chloroform	Carbon Disulfide
1,1,1-Trichloroethane	2-Propanol
Carbon Tetrachloride	trans-1,2-Dichloroethane
Benzene	Vinyl Acetate
1,2-Dichloroethane	2-Butanone (Methyl Ethyl Ketone)
Trichloroethene	Hexane
1,2-Dichloropropane	Tetrahydrofuran
cis-1,3-Dichloropropene	Cyclohexane
Toluene	1,4-dioxane
Trans-1,3-Dichloropropene	Bromodichloromethane
1,1,2-Trichloroethane	4-methyl-2-pentanone (Methyl isobutyl ketone)
Tetrachloroethene	2-Hexanone
Ethylene Bromide	Dibromochloromethane
Chlorobenzene	Bromoform
Ethyl Benzene	4-Ethyltoluene

Meta-, Paraxylene  
Orthoxylene  
Styrene

Ethanol  
Methyl tert-Butyl Ether  
Heptane

A sample of the gas to be analyzed is collected in a Tedlar bag and submitted to the laboratory for analysis by GC/MS. All of the above species have been identified in landfill gas. Digester gas typically has about 30 of these species with the individual species and concentrations varying widely among applications.

The ASTM Procedure D-5504 GC/SCD measure for the following sulfur-containing species:

Butyl Mercaptan	2-Ethyl Thiophene
tert-Butyl Mercaptan	Hydrogen Sulfide
Carbon Disulfide	Isobutyl Mercaptan
Carbonyl sulfide	Isopropyl Mercaptan
Diethyl Sulfide	Methyl Mercaptan
Dimethyl Disulfide	3-Methyl Thiophene
Dimethyl Sulfide	n-Propyl Mercaptan
2,5-Dimethyl Thiophene	Tetrahydrothiophene
Ethyl Mercaptan	Thiophene
Ethyl Methyl Sulfide	

The same sample collection procedure is used for both the TO-14 and ASTM D-5504 tests. Usually, both analyses can be run from the same bag sample. Normally, hydrogen sulfide is present in all landfill gas with higher quantities from landfills receiving construction wastes.

Collection of municipal biogas for siloxanes analysis can be done by either the vacuum canister or by liquid solvent impinger methods. The experience of the author is that the impinger method is more accurate and has more reproducible results at much lower detection limits.

The SIL 1 Field Test Kit supplied by AFT uses this impinger method. The method involves the use of two midjet impingers containing a specific volume of an analytical grade solvent, like methanol or hexane, usually 15 ml, operated in series. Through these impingers is bubbled a small slip stream of the biogas through a rotameter for a specified period of time. The siloxanes in the biogas are absorbed into the solvent. The impingers are packed in a specialized container containing frozen gel packs and shipped overnight to the laboratory for subsequent analysis by GC/MS. Each of the siloxane species present and its concentration is measured and reported in  $\mu\text{g}$  (micrograms) per liter of gas. The results from each impinger are added to obtain the total weight of the siloxane species. By knowing the weight or mass of the siloxanes and the volume of gas that was passed through the impingers, the initial concentration of each siloxane in the biogas can be determined.

This data serves as the backbone for the development of a SAG<sup>TM</sup> Siloxane Removal System design by AFT.

The specific siloxanes most often encountered by the author in biogas are pentamethyldisiloxane, MM, MDM, D4 and D5. Of these, MM, D4 and D5 are usually always present. This phenomenon has been observed almost without exception in landfill and digester biogas in the US, Canada, and Europe.

Below are the siloxane species and their detection limit by GC/MS when the samples are collected by the impinger method using methanol as the solvent:

Table 1  
Siloxane Species

Siloxane Species	SIL 1 Method Reporting Limit	Final Reporting Limit, $\mu\text{g/L}$ <sup>1</sup>	Final Reporting Limit, ppb v/v
1,1,3,3-Tetramethyldisiloxane <sup>1</sup>	---	---	---
Pentamethyldisiloxane	1 $\mu\text{g/mL}$	0.3 $\mu\text{g/L}$	48.78
Hexamethyldisiloxane (MM)	1 $\mu\text{g/mL}$	0.3 $\mu\text{g/L}$	44.58
Octamethyltrisiloxane (MDM)	1 $\mu\text{g/mL}$	0.3 $\mu\text{g/L}$	30.61
Hexamethylcyclotrisiloxane (D3) <sup>2</sup>	---	---	---
Octamethylcyclotetrasiloxane (D4)	1 $\mu\text{g/mL}$	0.3 $\mu\text{g/L}$	24.41
Decamethylcyclopentasiloxane (D5)	1 $\mu\text{g/mL}$	0.3 $\mu\text{g/L}$	19.53
Dodecamethylcyclohexasiloxane (D6)*	1 $\mu\text{g/mL}$	0.3 $\mu\text{g/L}$	16.27

(Table 1 presents the new reporting limits for the targeted species in the Air Toxics / AFT SIL 1 Method. The second column provides the method reporting limit expressed in (g/L (i.e., mass of compound detected per unit volume of methanol). The third column provides an example of a final reporting limit concentration expressed in (g /L (i.e., mass of compound detected per volume of gas sampled). The fourth column represents the final reporting limit in parts per billion by volume. <sup>1</sup>Tetramethyldisiloxane decomposes rapidly and reliable analysis cannot be performed. <sup>2</sup>Hexamethylcyclotrisiloxane (D3) appears to be somewhat unstable and is believed to convert to other heavier compounds, perhaps D4 and/or D5. Thus an accurate analysis cannot be performed for D3.

### Removal of Siloxanes from Biogas

AFT has developed the SAGTM Filter System method of siloxane removal over the past seven years. It has proven to be the most positive removal method used whether the gas is saturated and processed or chilled, then processed. The SAGTM Process uses a novel form of polymorphous graphite developed by AFT to remove siloxanes from methane containing many types of organics. The SAGTM Media uses a novel application of physical sieving to remove the siloxanes in the presence of other organics in the gas, thereby allowing the beneficial fuel constituents to pass through.

The technology consists of porous pelletized or granular media contained in a vessel sized by the gas flow, pressure, temperature, siloxanes and organic species. There are several types (approximately 270) of SAG<sup>TM</sup> media that can be loaded into the vessels. The siloxane removal media has a preferential affinity for siloxanes over most other contaminants in the gas. Additional types of SAG<sup>TM</sup> media have affinities for other species and can be incorporated into the same vessel(s). The SAG<sup>TM</sup> media loaded into the vessels corresponds to the gas stream analysis characteristics and removal

requirements. A properly engineered SAG™ system can economically reduce siloxanes to non-detectable levels for extended periods of time.

AFT provides biogas chilling where it is economically justifiable to reducing high levels of organic contaminants ahead of the SAG™ system.. Usually, temperatures of 40 °F or lower are required to remove at least half of the condensable siloxanes and other harmful species. Chilling requires energy, which robs the yield of power generated from the gas. Nonetheless, chilling is a viable option as one of the steps in removing siloxanes from biogas where the concentrations are very high. Chilling alone, however, will not reduce the siloxanes to the level required by equipment manufacturers to prevent cumulative damage to power generation and heat transfer equipment.

### Economics

Earlier, it was mentioned that an overhaul of a 1 MW generator reciprocating engine could cost approximately \$60,000. If this is done on an annual basis, the annualized cost is approximately \$0.164 per kWh. This cost would remain the same, year after year. A SAG™ System for a 1 MW generator reciprocating engine would cost approximately \$0.042 per kWh on an annualized basis the first year, then approximately \$0.012 per kWh each year. There is an additional financial benefit associated with longer oil change intervals from 500 hours to 2,000 hours. Finally, of primary concern is the cost to produce electricity every time a generator is out of service. As more data from operations become available, it will be demonstrated that the Internal Rate of Return for biogas to electricity projects benefit from better removal of siloxanes.

### Conclusion

- Each Landfill gas is a unique blend of organic and inorganic compounds that can have a negative cumulative impact on power generation. Removing the most problematic of these (the siloxanes) will have a positive and immediate impact on bottom line operating costs. The financial benefits will vary depending on each individual landfill gas.
- Over the last eight years, AFT has pioneered a low cost method of analyzing and modeling the gas to determine the best treatment options for each site. The SIL -1Kit and GCMS procedure is now used on over 400 samples per year at sites across the country on low and high pressure gas streams.
- AFT was the first company to invent a reasonable method for identifying and removing siloxanes in mixed contaminant landfill gas with SAG™ Graphite media and SAG™ Systems tailored to each specific site.
- The AFT SAG™ Gas Management approach looks at all gas contaminants and available treatment options to manage gas quality. These may include compression, chilling, drying, filtration, separation, sulfur removal or other processes. Each set of our recommendations is based on years of experience in gas purification.
- Each SAG™ System is designed to remove siloxanes to warranted levels 24/7.
- AFT continues to provide testing and analysis of the landfill gas after the SAG™ System has been installed and started up. The AFT approach to Gas Quality

Management assures the lowest cost operation of the SAG™ system and power generation equipment for each operator.

- Each SAG™ System is backed by a written Process Guarantee on gas quality with each service agreement. AFT partners with the operator to manage the gas quality and to assure complete success of the operation.

Applied Filter Technology applies its considerable experience in biogas purification to provide the results demanded by generation equipment manufacturers. Further, AFT is committed to the successful development and commercialization of landfill gas as a clean fuel for today in electrical power generation, heat production, vehicle fueling, and pipeline feed.