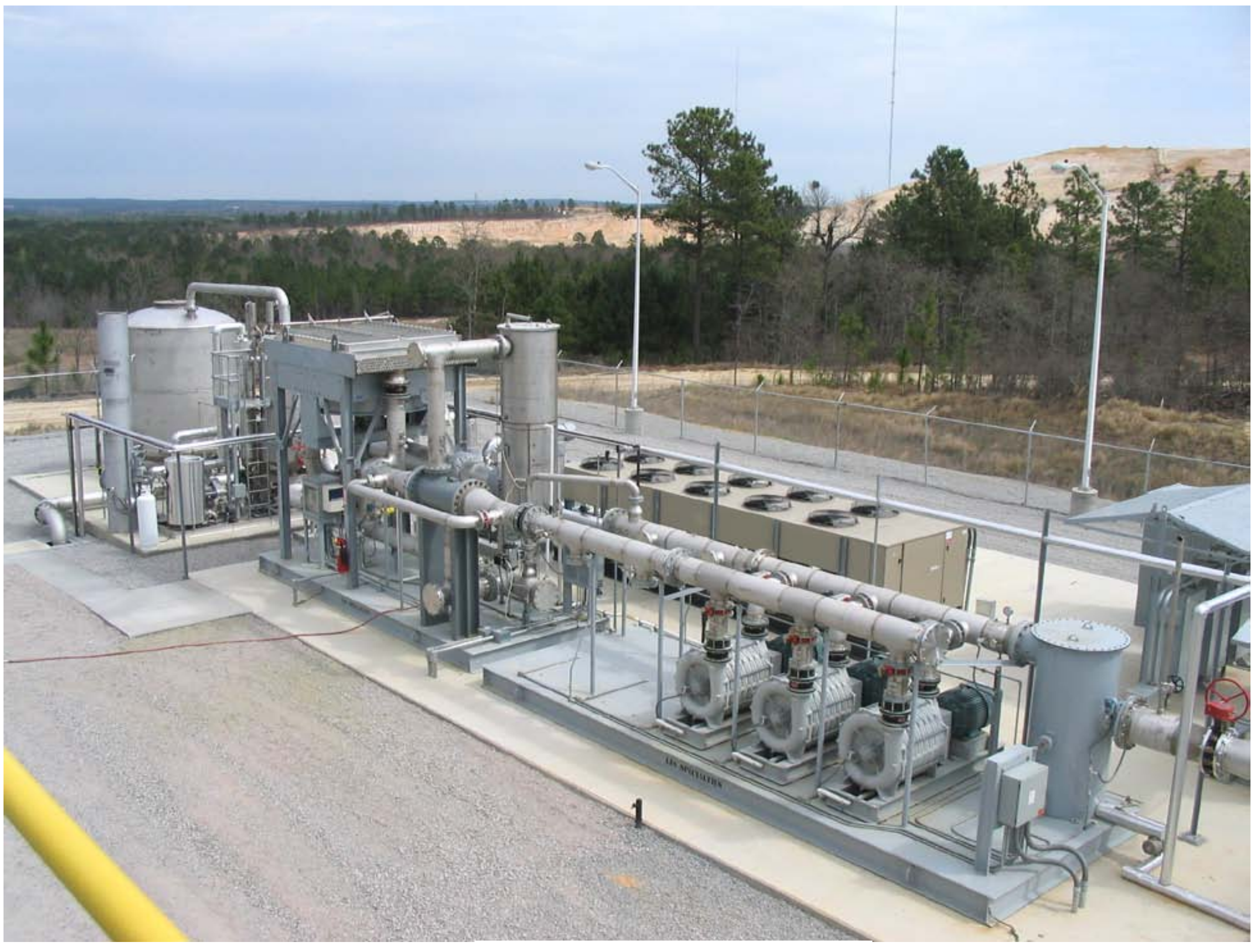
GUARANTEED REMOVAL OF SILOXANES FROM DIGESTER AND LANDFILL GAS



Richland, SC Landfill – 2500 SCFM

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July 13, 2007

With the continued threat of global warming and oil shortages, the quest for an alternative clean, renewable energy has skyrocketed. Hydrogen is promising but the cost to harness it and convert machines to use it is astronomical. Biodiesel and methanol are other alternatives, but their supply falls far short of the demand. Methane gas collected from waste water treatment plants (WWTP) and landfills has huge potential as an energy source. However, 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 and digester gas has been developed by Applied Filter Technology. The SAG™ Process has been tested on a number of sites over the past eleven years and it is now operating at landfills and digesters throughout the world.

The company has perfected a low cost method for analyzing the siloxanes at the sites with the SIL-2 Field Test Kit. This is a very simple procedure involving filling Tedlar bags and sending them back to AFT for gas analysis. With the data received from the gas analysis, a low cost method for removing siloxanes with SAG™ Polymorphous Porous Graphite Filters is employed. 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.

History of Siloxanes

For some time it has been known that siloxanes existed in landfill and anaerobic digester gas in low, medium and high molecular weight. If removed, the biogas can be upgraded for injection into natural gas pipelines or used for other purposes, such as firing boilers or the generation of electricity. AFT has been involved for more than eleven years in projects which 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 (exhaust) catalyst in power generation.

Early on (dating back to the early 1970s), 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; however, it was 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 biogas. But once again, biogas contaminants have become an issue. One group of contaminants in biogas has proved to be the most problematic for internal combustion engines: siloxanes. Siloxanes (or silicones, as they are sometimes called) are either linear or cyclical organic compounds comprised of silicon, carbon, hydrogen and oxygen. Siloxanes are prevalent in personal care products such as cosmetics, shampoos, deodorants, detergents and hairsprays. They are also commonly used in pharmaceuticals, inks, adhesives, lubricants and heat transfer fluids. Through the discard these containers, 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. These siloxanes are mainly a result of home laundry products and clothing as well as from industrial sources. Therefore, the siloxanes become entrained in the biogas by anaerobic digesters.

The use of landfill or digester biogas containing siloxanes in power generation engines has resulted in significant 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.

Most Common Siloxanes

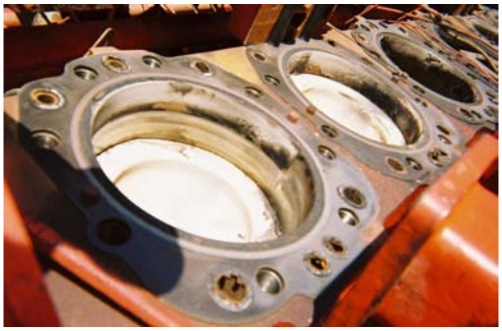
There are literally hundreds of different siloxane compounds, though only a handful are present in biogas. These may be broken down in to two categories: linear and cylical. The most prevalent linear species in waste biogas are pentamethyldisiloxane, hexamethyldisiloxane (MM), octamethyltrisiloxane (MDM) and decamethyltetrasiloxane (MD2M). These all have the chemical structure of $(CH_3)_2SiO$.

Among the cyclical species present in waste biogas, the most common are hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4), decamethylcylcopentasiloxane (D5) and dodecamethylcylcohexasiloxane (D6). Cyclical siloxanes have the same basic structure as linear siloxanes, but have 2 less methyl groups than their linear siloxane counterparts possessing the same number of silicon atoms.

Siloxanes are generally characterized by high molecular weights (162.4 for MM to 444.9 for D6), high boiling points (100.5 °C for MM to 245 °C for D6) and low vapor pressures. Therefore, these compounds are sufficiently volatile to become incorporated in biogas.

Deposits from Siloxanes

During combustion of waste biogas containing siloxanes, silicon is released and can combine with oxygen or various other elements in the combustion gas. Deposits are then formed containing silica and silicates (SiO_2 and SiO_3), though calcium, copper, sodium, sulfur, and zinc may also form. 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. Nevertheless, these deposits manefest themselves in the form of an off-white powdery-looking substance, either smooth or coarse in texture. They can ultimately build to a surface thickness of several millimeters and are extremely difficult to remove by either chemical or mechanical means.



The damage inflicted by the siloxane combustion by-product and deposits can be profound. Reciprocating piston engines experience fouling in the combustion chamber, on the valves, valve seats, piston crowns and cylinder walls. Deposits can even collect under the exhaust valves resulting in blowby and burnt valves. This phenomenon dramatically 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. In addition, 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 piston engines and turbines, it goes without saying that many manufacturers are considering the removal of siloxanes from the biogas before it enters their equipment. 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. Siloxanes, as reduced silicon dioxide, coat the catalyst and create an impermiable glass. This dramatically reduces the efficiency of the catlayst for removal of formaldehyde and other by-product 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 11 years).

Quantifying the Problem

Although there is no way to determine *precisely* how much of the siloxane combustion by-product remains as deposits in engines and turbines, it is estimated that at least 0.1% to 0.5% is not expelled in the exhaust gas. That may seem insignificant, but using this assumption, calculations can be made to determine the mass of the deposits that remain.

Consider an engine that burns a relatively small 140 SCFM (at 75 psig) of biogas containing 1 ppmv (15.7mg/m^3) "siloxanes as D5." A total of 0.0433 lb/hour of siloxanes enter the engine. Assuming complete stoichiometric combustion, the 0.0433 lb/hour D5 would be converted to 0.022 lb/hour silicon dioxide by the following reaction:

$C_{10}Si_5H_{30}O_5$ (D5) + $15O_2$ $\longrightarrow$ $5SiO_2$ + $10CO_2$ + $15H_2O$

Mass:	370.8	240	188.1	440	270

In one year's time of continuous operation, the total mass of siloxanes entering the engine will be 192.7 lb. Further, assuming that all of this becomes converted to SiO_2, the total mass of SiO_2 created during combustion is 97.8 lb/year. Therefore, estimating that 0.1 % to 0.5% is not expelled leaves a mass of approximately 1.5 ounces to 8 ounces 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 $150,000 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 impact the impeller enough to cause complete failure of the turbine. 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_x and hence failure of the process to meet air emission compliance standards. SCR catalysts are often precious metal based and are very expensive to replace. (A new SCR catalyst bed can cost in excess of $500,000.) Fouling of SCR catalysts can occur in as little as a day or two to several 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. 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 constituents that AFT tests for in order to provide the necessary information. These are the volatile organic compounds (VOCs), sulfur species and 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 procedure for sampling the gas is very simple: a sample of the gas to be analyzed is collected in a Tedlar bag and submitted to AFT's laboratory for VOC analysis. There are more than 60 species that 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 same sampling procedure is used for both the sulfur and siloxane tests. Usually, both analyses can be run from the same bag sample. Generally, hydrogen sulfide (sulfur) 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 Tedlar bag or by liquid solvent impinger methods. The experience of AFT is that the impinger method is less accurate and has less reproducible results at lower detection limits than that of Tedlar bags.

The SIL-2 Field Test Kit supplied by AFT uses the Tedlar bag method. Personnel simply fill the bags with a small gas sample and send it to AFT's lab for analysis. This data serves as the backbone for the development of a SAG™ Siloxane Removal System design by AFT.

Removal of Siloxanes from Biogas

AFT has developed the SAG™ Filter System method of siloxane removal over the past eleven years. It has proven to be the most effective removal method ever used, regardless whether the gas is saturated and processed or chilled, then processed. The SAG™ Process uses a novel form of polymorphous graphite developed by AFT to remove siloxanes from methane. The SAG™ Media uses an innovated 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 specifically sized for the gas flow, pressure, temperature, siloxanes and organic species. There are many types of SAG™ media (approximately 120) 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™ media have affinities for other species and can be incorporated into the same vessel(s). The SAG™ 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 would cost approximately $150,000. If this is done on a yearly basis, the annualized cost is approximately 4.5 cents per kwH just for the engine. This cost would remain the same, year after year. Effective removal of siloxanes and other components in the gas can take this kind of maintenance cost from yearly to every two years or longer. A significant cost savings will occur in both minor and major maintenance each year that the engine work can be extended.

There is an additional financial benefit associated with longer oil change intervals from 500 hours to 2,000 hours or longer. We have seen the benefit of cleaner oil with less silica occurring within the first few months of operation on an existing engine. Keep in mind that an engine with silica dioxide in the heated areas will take time to slough the silica unless the engine starts as a new or rebuilt unit.

In addition, and of primary concern, is the lost power generation revenue from every hour a unit is out of service. The production loss adds up very quickly. As more data from operations becomes available, we will be able to demonstrate the financial benefit from better removal of siloxanes in a variety of landfills.

For a 1 megawatt engine operating on landfill gas containing 1 ppmv of siloxanes (about 98 pounds per year of silica dioxide), the fully burdened operations cost could be between 2 to 3 cents per KwH. This figure includes oil changes every 500 hours, upper head rebuild once per year and two weeks of lost production at 3 cents per KwH. This also assumes starting out each year with a clean engine, so the actual total cost of operation could be much higher.

The cost of installing and operating SAG Technology on the same engine and siloxane level is 2/10 to 3/10 of a cent per KwH. The maintenance and power production benefit associated with cleaner gas going to the engine is the difference between these two sets of numbers and can be as high as 2 cents per KwH. We have seen an *average* tripling of oil life, a doubling of engine run life to downtime engine maintenance, and significant improvement in online power production time.

Conclusion

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

Summary

- 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 be significant.
- Over the last eleven 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-2 Kit procedure is now used on over 400 samples per year at sites across the country on low and high pressure gas streams for engines, boilers and turbines.

- 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 tailored to each individual site and is based on years of experience in gas purification.
- Each SAG™ System is designed to remove siloxanes to warranted levels 24 hours a day, 7 days a week. We are the only company that provides turnkey solutions and warranted performance with patented proven technology.
- AFT continues to provide testing and analysis of the landfill/digester gas long 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.

Dublin San Ramon, CA 250 SCFM