

Siloxanes in Landfill and Digester Gas Update

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ABSTRACT

Siloxanes are a family of man-made organic compounds that contain silicon, oxygen and methyl groups. Siloxanes are used in the manufacture of personal hygiene, health care and industrial products. As a consequence of their widespread use, siloxanes are found in wastewater and in solid waste deposited in landfills. At wastewater treatment plants and landfills, low molecular weight siloxanes volatilize into digester gas and landfill gas. When this gas is combusted to generate power (such as in gas turbines, boilers or internal combustion engines), siloxanes are converted to silicon dioxide (SiO₂), which can deposit in the combustion and/or exhaust stages of the equipment.

The Los Angeles County Sanitation Districts (Districts) have collected siloxane data from their wastewater treatment plants and landfills, plus other facilities, and conducted pilot testing on various methods of siloxane removal. The Districts reported on the findings of this program at the SWANA 2002 Landfill Gas Symposium¹.

The landfill gas data presented previously has been updated to include additional data provided by SCS and other sources. This paper will focus on the measurement of siloxanes, the presence of siloxanes in landfill gas, the different siloxane removal systems available, and the cost of siloxane removal.

INTRODUCTION

Digester and landfill gases are widely used as fuel to produce electricity, drive pumps and fire boilers. Unlike natural gas, these gases are normally saturated with moisture, and carry varying quantities of compounds that contain sulfur, chlorine, and silicon. This, however, has not deterred the successful use of both digester and landfill gases on a large number of biogas utilization projects. In general, combustion turbines, reciprocating

engines, and boilers have operated with no provisions for removal of these contaminants.

Evidence of siloxanes in biogas is found in the form of a white powder in gas turbine hot section components, as a light coating on various types of heat exchangers, in deposits on combustion surfaces in reciprocating engines, and as a light coating on post-combustion catalysts. The white powder is primarily silicon dioxide (SiO₂), a product of siloxane combustion. Microturbine and catalyst failures have focused industry-wide attention on siloxanes. Manufacturers of combustion turbines and reciprocating engines are expressing an increasing desire for siloxane control -- despite almost two decades of successful experience without such controls. There is no doubt that some maintenance cost benefit can be realized by siloxane removal (and through the incidental removal of other biogas contaminants that will occur during siloxane removal); however, it does not currently appear that siloxane removal is cost effective in most cases.

Common volatile siloxanes are listed in Table 1. Due to the length of the names of the various siloxanes, abbreviations are commonly used to identify the compounds. Siloxanes that are cyclic in structure have a single abbreviation of D. Siloxanes that have a linear structure have two abbreviations using either an L or M nomenclature. Table 1 also identifies the molecular weight, vapor pressure, boiling point, chemical formula, and water solubility of these compounds.

SAMPLING AND ANALYSIS OF SILOXANES

A major obstacle to understanding siloxanes continues to be difficulty in the accurate measurement of siloxanes. The individual siloxane compounds are commonly near or below their limits of detection in raw biogas samples. The siloxanes in digester gas appear to be predominately D₄ and D₅, representing over 90 percent of the total.

**TABLE 1
SELECTED CYCLIC AND LINEAR ORGANOSILOXANE PROPERTIES**

Name	Formula	MW	Vapor Pressure mmHg 77° F	Abbreviations	Boiling Point ° F	Water Solubility (mg/l) 25° C
Hexamethylcyclotrisiloxane	C ₁₂ H ₁₈ O ₃ Si ₃	222	10	D ₃	275	1.56
Octamethylcyclotetrasiloxane	C ₈ H ₂₄ O ₄ Si ₄	297	1.3	D ₄	348	0.056
Decamethylcyclopentasiloxane	C ₁₀ H ₃₀ O ₅ Si ₅	371	0.4	D ₅	412	0.017
Dodecamethylcyclohexasiloxane	C ₁₂ H ₃₆ O ₆ Si ₆	445	0.02	D ₆	473	0.005
Hexamethyldisiloxane	C ₆ H ₁₈ Si ₂ O	162	31	L ₂ , MM	224	0.93
Octamethyltrisiloxane	C ₈ H ₂₄ Si ₃ O ₂	236	3.9	L ₃ , MDM		0.035
Decamethyltetrasiloxane	C ₁₀ H ₃₀ Si ₄ O ₃	310	0.55	L ₄ , MD ₂ M		
Dodecamethylpentasiloxane	C ₁₂ H ₃₆ Si ₅ O ₄	384	0.07	L ₅ , MD ₃ M		

Siloxane concentrations are generally higher in digester gas than in landfill gas. As a result, it is somewhat easier to reliably quantify siloxanes in digester gas. Landfill gas may contain significant quantities of other siloxane compounds such as D₃ and D₆, plus L₂ through L₅. D₄ and D₅ may represent only slightly more than a majority of the siloxanes in some landfill gases to over 90 percent of the total in others. Infrequently siloxanes not listed on Table 1, such as trimethylsilanol, are found.

The most common commercially available analysis for siloxane involves collecting a sample by passing the sample through midjet methanol impingers followed by determination of the captured siloxanes by GC/MS. The method that is employed by the Districts involves sample collection in a metal canister followed by analysis by GC/MS. At least one contract laboratory allows collection of the sample with a Tedlar bag and subsequent analysis using GC/MS. The above methods are discussed in more detail below.

Two other test methods used in the past involved collection of the sample in carbon tubes, and a method, preferred by Caterpillar, that used a mineral oil. Neither of these methods are in use presently.

Methanol Impinger - GC/MS

ESS Laboratories (Cranston, Rhode Island) and Air Toxics (Folsom, California) use a procedure where the sample is drawn through two methanol filled, chilled impinger tubes in series. A GC/MS is used to identify siloxanes. Air Toxics currently targets five of the compounds in Table 1 (L₂, L₃, D₄, D₅, and D₆).

Air Toxics recommends the use of midjet impingers with 6 ml of methanol in each. The sample is drawn at a rate of 112 ml/min for 3 hours (producing the equivalent of a 20 liter sample). The concentration of siloxane in

the methanol, in ug/ml, and the ppmv in the gas can be calculated from the volume of methanol and the volume of the gas quantity passed through the impingers. The stated reporting limit is 16 to 49 ppbv for individual siloxanes, but in practice limits of detection vary from 19 ppbv to 189 ppbv.

ESS uses impingers containing 20 ml of methanol with a sampling rate of 1 liter/min for 20 minutes (20 liter sample). This procedure produced reporting limits that generally ranged from 500 to 1,000 ppbv for tests conducted by the Districts on landfill gas. In limited side-by-side testing, the Districts and ESS results were in general agreement.

ESS is also able to measure total silica. In side-by-side testing on the Districts' landfill gas, the total reported silica was 2 to 5 times the valued measured by the Districts' method. Additional testing is being conducted to further define the usefulness of total silica testing.

Metal Canister – GC/MS

The Districts have developed a sampling procedure that utilizes metal canisters to collect samples, which are then analyzed in one of the Districts' in-house laboratories. Samples are collected in a 6-liter metal Summa canister that is then analyzed by a GC/MS after being pressurized for 24 hours. The Districts currently target all eight of the siloxanes listed on Table 1. This procedure has been compared with the methanol impinger procedure with mixed results. In early 2003 Air Toxics conducted side-by-side testing of digester gas involving multiple samples². Air Toxics results agreed with the Districts' results except for D₄ and D₅. For these siloxanes, Air Toxics reported values three times the Districts' results. In subsequent side-by-side testing on landfill gas, the Districts identified more polymers than Air Toxics with concentrations (including D₄ and D₅) about 50% to 80% higher than Air Toxics.

In May of 2003 the Districts obtained a new GC/MS (Leco Pegasus III Time of Flight) that has consistently provided reporting limits in the 20 to 40 ppb range.

Tedlar Bag - GC/MS

AtmAA, Inc. (Calabasas, California) can perform what they call a "semi-quantitative measurement of volatile organic silicon components" by collecting a gas sample in a Tedlar bag for subsequent GC/MS analysis. This method by AtmAA is not considered accurate and is of dubious value. A second lab, Analytical Solutions (Willowbrook, Illinois), uses a similar method to determine siloxane polymers as well as total organic silica by atomic emission detection. The Districts are working with Analytical Solutions to verify the procedure.

Conclusions

Different laboratories and different researchers use different sampling techniques and do not use a consistent set of target compounds. The limits of detection vary at an individual laboratory over time and between laboratories. The reporting limits at commercial labs can be as low 20 ppb but can be as high as ten times this value for a single polymer.

In addition to problems with accuracy and detection limits, the impinger sampling procedure is very labor intensive. Three hours to obtain a single sample is excessive where duplicate samples are required for at least two and sometimes five locations. This is the reason the Districts developed a procedure that requires only a few minutes to obtain a sample. The Districts will continue to work with interested parties and labs to develop a lower cost, less time consuming, and more accurate detection method.

QUANTITY OF SILOXANES IN BIOGAS

Siloxane data is expressed in ppmv, mg/m³ and mg Si/mmBtu. While the latter expression is not commonly used, it is actually the most useful expression of siloxane data. It accounts for the varying fraction of the weight that silicon contributes to the molecular weight of each form of siloxane and adjusts for the varying methane content (energy value) of the fuel. While the methane content of digester gas is generally within a fairly narrow range (i.e., 57 percent to 64 percent), landfill gas is quite variable (i.e., 35 percent to 57 percent). Expression in terms of mg Si/mmBtu allows the true loading rate of

silicon, the deleterious precursor, to be tracked as a function of fuel consumption. Expression of the data as ppmv is useful since this is the most common way gaseous contaminants are reported in the United States, and the data is expressed in units that are easily understood. Data presented in this paper are in mg/m³ because different polymers can be directly added to obtain a total siloxane quantity as well as an estimate of the total Si.

Figure 1 provides siloxane data from twenty-eight landfills. The landfills represented in Figure 1 cover open and closed landfills, landfills in arid climates (10 inches precipitation) and wet climates (45 inches precipitation), and landfills containing relatively old and new waste. The data has been normalized to 50% methane. The first letter of the site name indicates the type of data collection as follows:

D	Districts method
S	SCS data collected in impingers and analyzed by Air Toxics
C	Samples collected by CAT as total Si reported as siloxane
G	Samples collected in Carbon tubes

A few generalizations can be made about the data:

- Landfills with older average waste ages generally have lower siloxane levels. It may be that this is due to the gradual exhaustion of siloxane over time or it may be because there was less siloxane in the waste to begin with since the use of siloxane has increased in recent years
- Active landfills generally have higher siloxane levels than closed landfills. This finding may simply be an alternative manifestation of the above finding;
- D₃, D₄, D₅, L₂ and L₃ are the only siloxanes generally observed above detection limits at landfills. On an average basis, D₄ is the largest contributor to total siloxane (about 60 percent of total), followed by L₂, D₅ and L₃ in that order.
- In general, landfill gas contains L₂ and L₃ and digester gas does not. One theory explaining this difference between the two biogases is the relative solubility. L₂ is much more water-soluble than D₄ and D₅. L₃ is more water-soluble than D₅ and is comparable to D₄.

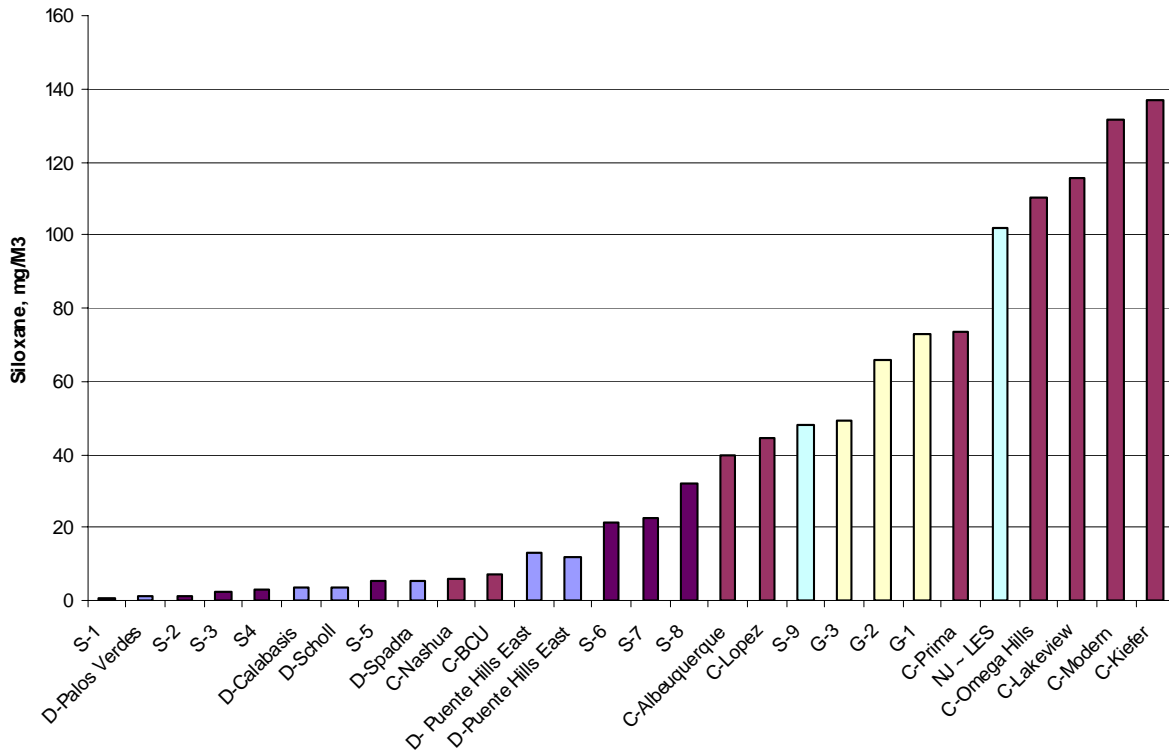
WHY SILOXANE REMOVAL?

As noted in the introduction, the presence of siloxanes in biogas has been known for many years. Rather than removing siloxanes, most chose to accept the increased

advantages or economic returns that may justify the cost and associated with siloxane removal.

In a more disturbing trend, manufacturers of technologies with decades of successful service in the

Figure 1, Siloxane in Landfill Gas



maintenance costs associated with the use of biogas since the increase is being offset by the use of low cost or no cost fuel.

Over the past 20 years there has periodically been a desire to employ a post-combustion oxidation catalyst and/or selective catalytic reduction to reduce air emissions from biogas fueled power equipment. This interest was primarily motivated by air permitting barriers. The result of the test programs was a failure of the catalyst after a few days of operation and in some cases only hours of operation. It is believed that the principal reason for these failures was siloxane.

As discussed below, relatively new technologies are available for biogas fueled power generation (e.g., microturbines and fuel cells). The suppliers of this equipment feel that these technologies may not be able to tolerate siloxanes. These technologies offer performance

biogas markets (e.g., reciprocating engines and combustion turbines) now feel obligated to impose siloxane standards where they have not been imposed before.

Until recently the inability to measure siloxanes reliably made the development of removal technologies virtually impossible. Although reliable siloxane detection is still problematic, experimentation and testing on siloxane removal is now possible.

Microturbines

Capstone and Ingersoll-Rand offer microturbines in the 30 to 250 kW ranges. The principal advantage of microturbines is their low air emissions. They also can operate with relatively low heating value fuels. One disadvantage of microturbines is a relatively low efficiency (30 percent). Low efficiency increases power production cost when using high priced fuels such as

natural gas or diesel but is less important with low cost biogas. Biogas fuel applications may represent the best market for microturbines.

Capstone has experienced siloxane induced turbine failures at multiple sites. As a result, Capstone has established a fuel specification that requires less than 5 ppbv ($\sim .03 \text{ mg/m}^3$) of siloxane. A 100 percent effective siloxane removal system is, therefore, required by Capstone for all biogas applications. In actual practice, Capstone turbines are tolerant of limited amounts of siloxane and have operated continuously for many months on biogas prior to failure. The prolonged exposure to untreated biogas results in a progressive loss of performance due to silica buildup in the combustor and recuperator. Ultimately the silica will build up to a larger mass that breaks off and causes the turbine wheel to seize. Once silica buildup has affected performance or caused a seizure, the power unit must be replaced to restore full performance.

Ingersoll-Rand has not confirmed a problem with siloxanes, but maintains an official fuel restriction of 10 ppbv of siloxane. Ingersoll-Rand requires siloxane removal on new installations, while accumulating operational hours on two facilities that fire untreated landfill gas. The testing may determine that siloxane removal is not needed, may be selectively needed, or may be required.

Gas Turbines

Solar Turbines has extensive experience with biogas dating back to a Centaur unit that the Districts started up in 1984 that is still in continuous operation. Over 35 turbines at landfills, plus other turbines operating on digester gas, followed this initial installation. Unfortunately, Solar encountered problems a few years ago with silica buildup on their new Taurus units. Solar's solution was a de-rating of this model and the re-evaluation of their fuel specification. The result was a Product Information Letter³ dated April 25, 2003 which called for a "zero" tolerance for siloxane. A maximum allowable concentration of approximately 87 ppbv ($\sim .1 \text{ mg/m}^3$) was established since this value was incorrectly judged the "lowest detectable concentration."

The principal problem reported by Solar was accumulation of deposits on turbine nozzles (blades). It should be noted that the turbine blades on a microturbine are relatively crude, compared to a larger combustion turbine, and microturbines should be more tolerant to impurities in biogas.

Internal Combustion Engines

There is extensive experience with internal combustion (IC) engines operating on biogas. In the few evaluations undertaken to date, the expected cost of siloxane removal has exceeded the increased engine maintenance caused by SiO_2 deposits. In spite of the success of IC engines in biogas applications, IC engine manufacturers now impose siloxane fuel restrictions. The current limits of four IC Engine manufacturers are presented in Table 2. The limits seem to be somewhat arbitrary since the engine operation and maintenance would not change with siloxane levels slightly above or below the limit. In fact, IC engines appear to operate over a very broad concentration of siloxanes with a general, but undefined, trend of increasing maintenance with increasing levels of siloxane.

Catalysts

In IC engine or turbine applications where selective catalytic reduction or oxidation catalysts are being considered or required for emission control, siloxane removal is a necessity. There are numerous examples where SiO_2 deposits from siloxane have resulted in catalyst deactivation in hours or days. The inability to continuously monitor siloxanes coupled with their rapid destructive effect makes this a difficult application. Other constituents in the biogas are present that can foul the catalyst, and this further complicates the study of siloxane impact. Sorge⁴ very recently reported on a failed attempt to use a catalyst on landfill gas.

Fuel Cells

Fuel cells use catalysts to convert methane in biogas to hydrogen and therefore, require high quality biogas, perhaps as clean as applications using selective catalytic reduction or oxidation catalysts. Standards governing fuel cells are still under development. One fuel cell manufacturer has called for a siloxane limit of 100 ppbv.

SILOXANE REMOVAL TECHNOLOGIES

Although there is an increasing list of possible siloxane removal technologies, carbon adsorption is still the only proven method now in commercial operation. The following provides a discussion of the capabilities of this technology and other potential removal technologies.

**TABLE 2,
MANUFACTURER SILOXANE LIMITS**

Engine Manufacturer	Siloxane, mg/m ³ in Landfill Gas
Caterpillar	28
Jenbacher	10
Waukesha	25
Deutz	5
Solar Turbines	0.1
IR Microturbines	0.06
Capstone Microturbines	0.03

Carbon Adsorption

Activated carbon has been widely used for the removal of a variety of substances from air and gas for decades. In 2001, the Districts conducted extensive testing of various types/grades of carbon including coconut shell and graphite on compressed and dried digester gas (365 psig, 40° F dew point). The results indicated that carbon under these conditions could adsorb approximately 1.0 percent to 1.5 percent siloxanes by weight or 10,000 to 15,000 mg siloxanes per kilogram of carbon. Adsorption capacity is defined as the point where siloxane breakthrough can be detected. If the process is allowed to continue, siloxanes will continue to be removed, but the siloxane exit quantity will continue to rise. Wheel¹ previously reported on details of this test program.

Laboratory experiments by Schweigkofler⁵ in Munich confirmed loadings, at breakthrough, of greater than one percent for charcoal and silica gel, but noted that relative humidity could have a significant effect on loading.

After a year of operation at the Calabasas microturbine facility, the Districts have experienced a loading of approximately 0.4 percent on coconut shell and on graphite activated carbon. The conditions at Calabasas are a gas at a dew point of 40° F and a pressure of 75 psig.

In a similar application to Calabasas, Sorge⁴ obtained 0.6 percent loading on graphite. This was a low pressure application with a chiller to reduce the dew point to 40° F prior to the activated carbon. This application used a graphite-based activated carbon for siloxane removal. L₂ was the first siloxane form to break through. The most disturbing observation was that the concentration of L₂ at the discharge of the removal device was much higher than the inlet concentration. It is speculated that

previously adsorbed L₂ was being bumped off by other compounds.

The same L₂ phenomena (higher L₂ at exit of carbon treatment than in the inlet L₂) was observed at Calabasas, and it was first speculated that the high L₂ was due to the release of previously accumulated L₂. At Calabasas, the carbon system was run for several weeks after L₂ breakthrough on one occasion. More L₂ was discharged than could have been accounted for by the total L₂ captured prior to breakthrough. This indicates that this phenomenon needs further research.

It is important to note that all the loading data presented above is for carbon following a chiller that produces a 40° F dew point gas prior to reheat above the dew point. Chilling of biogas prior to treatment with activated carbon benefits the life of activated carbon in two ways. First, the chiller can be expected to remove some of the siloxanes. Second, the adsorption loading of the carbon is influenced by the relative humidity and temperature of a gas.

Refrigeration

The Districts have documented a 50 percent removal of total siloxane at a full scale digester gas compression/chiller facility. The gas is chilled to 40° F and is at a pressure of 365 psig.

A compressor/chiller facility has been in operation at the Calabasas Landfill microturbine facility for over a year. Long-term siloxane removal averaged 32 percent. Removal rates were actually somewhat higher since the chilled gas was often reported at limits of detection. At Calabasas, the greatest percentage removal was seen on D₄.

Limited data from two installations similar to Calabasas had siloxane removals of 15 percent and 49 percent. The operable siloxane removal mechanism is not specifically known. It is probably largely a scrubbing effect with gaseous siloxane compounds being dissolved into the condensate being formed, rather than condensation of the siloxane compounds themselves.

Advanced Refrigeration

The Districts previously reported¹ on bench-scale research on the benefits of advanced refrigeration on siloxane removal. A 95 percent removal of total siloxane was seen at a temperature of -20° F. At least two firms are attempting to commercialize this process for biogas siloxane removal. Commercialization requires overcoming problems associated with icing. IR will place a commercial unit in operation during the second quarter

of 2004 at the Districts' Lancaster wastewater treatment plant to condition digester gas prior to a 250 kW microturbine.

Liquid Absorption

The methanol impinger sampling concept is predicated on the notion that siloxane can be completely removed by liquid absorption. If liquid absorption of siloxane works on a micro-scale, it should work on a large scale.

The Mountain Gate Landfill has a gas processing plant that uses liquid absorption and activated carbon polishing for removal of hydrogen sulfide, volatile organic compound and siloxane. A continuously regenerable solvent is used in a counter current tray tower. This solvent is Selexol, a dimethylether of polyethylene glycol. About 99 percent of the siloxane is removed in the tray tower with the remainder removed by carbon. The plant currently has a throughput of about 1,500 scfm, and liquid absorption may be cost effective for large installations.

Researchers have conducted testing using other liquids, including carbon dioxide.

Silica Gel

Schweigkofler⁵ conducted siloxane removal experiments on several organic and inorganic adsorption materials including polymer beads. Schweigkofler found silica gel to have a higher affinity for L₂ than carbon. The Districts obtained a 50% increase in removal capacity as compared to carbon on digester gas. Silica gel may prove to be a better adsorbent in landfill gas applications than activated carbon because of the reported greater affinity for L₂. The Calabasas Landfill microturbine removal system has been loaded with silica gel in the first vessel and carbon in the second to verify the experimental test results.

REMOVAL ECONOMICS

Activated carbon

Two costs must be considered -- initial capital cost and ongoing replacement cost of the activated carbon. The capital cost includes the cost of the vessels and piping associated with holding the activated carbon, and the cost of the initial change of the activated carbon. The capital cost is a function of the somewhat arbitrary selection of the desired frequency of activated carbon changeout (e.g., three months versus six months). On a life cycle basis, the cost of the vessels becomes increasingly less important. The cost of the activated carbon replacement dominates the cost of siloxane removal.

The two factors governing activated carbon exhaustion are siloxane mass loading rate and the activated carbon's siloxane adsorption capacity. The siloxane mass loading rate is a function of gas flow rate (scfm or m³/min) and siloxane concentration (ppmv or mg/m³). The siloxane mass loading rate can be expressed in units of lbs/day, grams/day or other expressions of the accumulation rate.

The adsorption capacity can be expressed as a weight to weight ratio -- lb siloxane absorbed per lb of activated carbon, or mg of siloxane absorbed per gram of activated carbon. The adsorption capacity is generally defined as the mass loading to the point of initial detection of siloxane at the outlet of the treatment vessel (breakthrough). Some applications, such as microturbines, call for a non-detect level of siloxane. Mass loading to the point of breakthrough is in agreement with this requirement. Other applications, such as reciprocating engines, sometimes call for siloxane limitations over limits of detection. In such applications, residual adsorption capacity exists beyond breakthrough. Outlet siloxane concentrations generally increase rapidly after breakthrough and this additional capacity is very limited. A mass loading rate, based on breakthrough, can also be used to approximate the requirements of the more tolerant applications.

Activated carbon's siloxane adsorption capacity is affected by several factors including:

- Siloxane speciation (the relative concentration of the various forms of siloxane that are present);
- The presence of other compounds in the gas that may compete with siloxane for activated carbon "pore space;"
- Gas physical condition (moisture content, temperature, and relative humidity); and
- Activated carbon type.

It is the authors' observation that adsorption capacity varies with the type of siloxane being removed. The lighter, straight molecular forms, particularly L₂, break through sooner than the heavier, cyclic molecular forms. A gas with no L₂, or little L₂, would have a much higher adsorption capacity than a gas having more L₂. A similar phenomenon is seen in activated carbon's removal of more "traditional" organic compounds. Vinyl chloride, for example, is much more difficult to remove with activated carbon than carbon tetrachloride.

Landfill gas and digester gas contain a number of compounds, other than siloxanes, that activated carbon will remove, including hydrogen sulfide and a group of

compounds known as volatile organic compounds. In general, the concentration of volatile organic compounds in landfill gas is significantly higher than in digester gas. Hydrogen sulfide in digester gas can vary from 25 ppmv to over 1,000 ppmv, while hydrogen sulfide in landfill gas usually varies from 10 ppmv to over 100 ppmv. When siloxane adsorption capacity is determined on a pilot-scale or full-scale basis with landfill gas and digester gas, at least some of the pore space is being consumed by compounds other than siloxane. Hydrogen sulfide appears to present the greatest problem since its concentration is generally relatively high. One strategy to extend activated carbon life may include use of potassium permanganate or sodium hydroxide impregnated activated carbon in the first vessel, or in a layer in a single vessel where the biogas first contacts the activated carbon. Impregnated activated carbon can remove ten times as much hydrogen sulfide than unimpregnated activated carbon. If the hydrogen sulfide concentration is very high, it may be more cost-effective to use a pretreatment step such as SulfaTreat or an iron sponge.

As a general statement, the performance of activated carbon is affected by gas temperature and moisture. Activated carbon performs better on a dry, cool/warm gas than on a wet, hot gas. Biogas processing schemes that incorporate a refrigeration-based moisture removal process prior to the activated carbon step should be expected to experience longer carbon life. In addition, refrigeration will generally achieve some siloxane removal and reduce the mass load of siloxane to the activated carbon.

Several types and grades of activated carbon are commercially available. Activated carbon is manufactured for commercial use predominately from one of two feed stocks -- coconut shells and bituminous coal. Depending on the manufacturer, there is some variability in size and shape of the granules or pellets. It is reasonable to assume that one type of activated carbon may be more effective than another under theoretical and, perhaps, under practical conditions. It is the authors' opinion that this difference in performance is yet to be demonstrated in actual practice. It is difficult to quantify the performance of various grades of activated carbon when so many other variables are changing, and given current limits of detection for siloxanes.

As can be inferred by the above discussion, the siloxane adsorption capacity has the potential to vary greatly from site to site. Based on available information on landfill gas, adsorption capacity of activated carbon can vary substantially. Two examples of operating costs are the Calabasas Landfill microturbines and the experimental

work of Waukesha⁴. Both of these removal systems chilled landfill gas to 40° F prior to carbon absorption.

	Calabasas	Waukesha
Capital Cost, \$/kw	85	82
Siloxane inlet		
Concentration, mg/m ³	2	34
Carbon Cost, cents/kwh	.3	1.5

For the Calabasas case with a very low siloxane concentration the cost of removal are acceptable. For the Waukesha case that is more representative of expected siloxane concentrations the operating costs are excessive.

Districts pilot testing with digester gas suggests a siloxane loading for carbon that is approximately 3 times the .6% mass loading experienced by Waukesha but this is expected with the L₂ present in landfill gas. If, in fact, the Waukesha loading is typical, siloxane removal would be cost prohibitive for most landfill gas applications.

CONCLUSIONS

It appears that microturbine and engine manufacturers are setting and tightening siloxane standards. The equipment manufacturers should proceed with caution. While siloxane removal may reduce the cost of maintenance of their equipment, the total cost of plant operation/maintenance may increase. Decisions to proceed or not proceed with projects are based on the total cost of plant operation/maintenance.

Siloxane sampling and analysis methods vary from one laboratory to another. Limits of detection are highly variable, both from one laboratory to another, and temporarily at the same laboratory. As a minimum, the industry needs to reach a consensus on a sampling methodology and a target compound list.

Siloxane levels vary greatly from one landfill to another. While there seems to be some relationship to waste age, higher waste ages do not guarantee lower siloxane levels.

References

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