SILOXANES AND LANDFILL GAS UTILIZATION
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Siloxanes are volatile organic silicon compounds (VOSCs), which are present at the parts per million volumetric (ppmv) level is landfill gas (LFG). Siloxanes are not the only VOSCs present in LFG. Two other groups of VOSCs are present – silanes and silanols. VOSCs are man-made organic compounds that consist solely of carbon, oxygen, hydrogen and silicon. When VOSCs burn, they primarily form carbon dioxide, water and silicon dioxide. Silicon dioxide is commonly known as silica. Silica is a solid at combustion gas temperatures, and silica will form deposits inside energy utilization equipment. The silica deposits cause maintenance and operational problems. A discussion of siloxanes and LFG utilization must begin with two clarifications. First, the LFG silicon problem is not as a siloxane problem, but rather is a VOSC problem. Second, the problems resulting from VOSCs are not due to the VOSCs themselves, but due to a product of VOSC combustion – silica.

SCS Engineers (SCS) has found fourteen different VOSCs to be present in samples of LFG drawn from over 100 landfills over the last thirteen years. Table 1 identifies what SCS found to be the most commonly occurring VOSCs. In the short form notations for siloxane compounds, "D" represents ring compounds, while "L" represents linear compounds. The numeric subscript attached to the "D" or "L" indicates the number of silicon atoms present in the compound.

Table 1
VOSCs Commonly Present in Landfill Gas

Formal Name	Short Form	Formula
Hexamethylcyclotrisiloxane	D_3	$Si_3\text{-}O_3\text{-}(CH_3)_6$
Octamethylcyclotetrasiloxane	D_4	$Si_4\text{-}O_4\text{-}(CH_3)_8$
Decamethylcyclopentasiloxane	D_5	$Si_5\text{-}O_5\text{-}(CH_3)_{10}$
Hexamethyldisiloxane	L_2	$Si_2\text{-}O\text{-}(CH_3)_6$
Octamethyltrisiloxane	L_3	$Si_3\text{-}O_2\text{-}(CH_3)_8$
Trimethylsilanol	MOH	$Si\text{-}(CH_3)_3\text{-}OH$

Table 2 identifies the properties of the VOSCs listed on Table 1. The molecular weight, silicon percentage (silicon mass divided by total compound mass), vapor pressure, boiling point and water solubility varies greatly among the VOSCs. While it is convenient to simply think of VOSCs as the total amount of VOSCs present, the types and amounts of VOSCs present are

important. The varying physical properties of the VOSCs, particularly their water solubility and their vapor pressure, will affect the efficacy of VOSC removal technologies.

Table 2
Properties of Selected VOSCs

Compound	MW	% Silicon	Vapor Pressure mmHg	Boiling Point (º F)	Water Solubility (mg/l)
D_3	222	38.0%	10	273	1.560
D_4	297	37.8%	1.3	347	0.056
D_5	371	37.9%	0.4	410	0.017
L_2	162	33.4%	42	214	0.930
L_3	236	35.7%	3.9	306	0.034
MOH	90	31.2%	15.8	210	0.0004

Because of the widely varying molecular weights of VOSCs, it is not possible to combine and compare laboratory data when reported on a ppmv basis. One ppmv of D_5 contains over four times the mass of one ppmv of MOH. Thus, it is not meaningful to report the total VOSCs in LFG at a landfill for a single sampling event, or to compare the results from a sampling event to prior sampling events at the same landfill, or to compare the results at one landfill to another landfill on a ppmv basis. Laboratory results should be expressed on a mass basis, for example, as milligrams per cubic meter (mg/m^3). A subtler consideration related to mass is the variability of the percentage silicon within the VOSC molecule. As can be seen on Table 2, the fraction of the VOSC molecule that is actually silicon varies from a low of 31.2 percent (for MOH) to a high of 38.0 percent (for D_3). Since silicon, rather than the VOSC as a whole, is the precursor to silica formation, the quantity of silicon delivered to the energy production equipment is what is relevant. D_3 would, for example, deliver 22 percent more silicon than MOH for the same reported mg/m^3 concentration. To address this concern, VOSCs are more precisely reported on the basis of their silicon mass only, in the form of milligrams silicon per cubic meter ($mg\ Si/m^3$). In being even more definitive, VOSCs can be reported on the basis of pounds of silicon per million British thermal units (lbs Si/mmBtu) or micrograms of silicon per British thermal unit (µg Si/Btu). If an LFG has a higher methane content, then less LFG on a volume basis must be delivered to the energy production equipment to produce the same amount of energy output, reducing the accumulation of silica deposits on the equipment. An LFG with a methane content of 53 percent would deliver 11 percent less silica than an LFG with a methane content of 47 percent.

There are two important takeaways from the above discussion. First, VOSCs must be reported on a mass basis (e.g., mg/m^3) rather than on a concentration basis (ppmv). Second, reporting the total quantity of VOSCs present in an LFG at a landfill is acceptable; however, the total VOSC quantity is only a relative indication of the differences between landfills and an indication of changes at a landfill over time. Because of the different properties of the individual VOSCs, it is necessary to characterize and study VOSC type and quantity if VOSC removal treatment is being considered. Reporting on an $mg\ Si/m^3$ basis is preferable to reporting on an mg/m^3 basis and is recommended.

SCS is often asked what VOSCs SCS has encountered in its sampling of LFG. SCS has seen the following in its VOSC sampling:

- VOSCs have varied from 1.5 mg Si/m^3 to 60 mg Si/m^3. The lowest values were seen at landfills that closed in the 1980s or earlier;

- The most commonly found VOSCs were D_4 (found 90 percent of the time); D_5 (found 83 percent of the time); and MOH (found 77 percent of the time);

- The next most frequently found VOSCs were L_2 (found 45 percent of the time) and D_3 (found 20 percent of the time); and

- Ten other VOSCs were found (each found no more than seven percent of the time).

VOSCs are now found in a wide range of personal health and beauty products. They are used as an aid in manufacturing industrial products, and are used as a solvent in dry cleaning. VOSCs enter the landfill with waste and they slowly volatize into the LFG. The use of VOSCs has risen significantly over the last two decades, which largely explains the finding that LFG from old, closed landfills have low LFG VOSC concentrations. As VOSC use increases, it is expected the LFG VOSC concentrations will continue to increase.

VOSCs are currently sampled with and analyzed by many different methods in the LFG industry. As a consequence, reported VOSC results vary significantly, and the results are not directly or indirectly comparable. VOSC samples are collected by four methods:

- Capture of an LFG sample in a Tedlar bag;

- Capture of the VOSC compounds in methanol by bubbling the LFG through small methanol vials (impingers);

- Capture of the VOSC compounds in mineral oil by bubbling the LFG through bottles containing oil; and

- Capture of the VOSC compounds on activated carbon in sample tubes.

Arguments can be made for and against each of these methods, but what is inarguable is that VOSC capture will differ under each method. Some of the pros and cons for the sampling methods are related to: the likeliness of total VOSC capture; complexities governing sample shipment; time required to conduct sampling; representativeness of the sample collected; and the need for a special sampling apparatus to support the sampling event.

Laboratories analyze for as few as five, and as many as twenty-two individual VOSCs. Obviously, the shorter the VOSC target list, the more likely it is that the total quantity of VOSCs will be underreported. Of particular concern is that several laboratories leave MOH off of their target list. MOH occurs very frequently in LFG, and usually represents an important fraction of the total mass of the VOSCs in an LFG sample. Of the laboratories that SCS is aware of, all but

two use a gas chromatograph with a mass spectrometer (GC/MS) to identify and quantify VOSCs. One uses a gas chromatograph with an atomic emission detector (GC/AED). One uses a gas chromatograph with an inductively coupled plasma (GC/ICP) detector. The latter laboratory reports total silicon in the LFG and thus may over-report VOSC content. Each combined sampling and analysis method has different limits of detection. At some laboratories, the limits of detection are relatively high. Laboratories report results as ppmv or as mg/m^3 or mg Si/m^3 at actual or 100 percent methane. The difference in reporting units, unlike the other sampling and analysis issues, is easily rectified. When a laboratory reports its results only on a ppmv basis, the results can be converted to an mg/m^3 basis, using the molecular weights of the individual VOSCs, as long as the ppmvs of the individual VOSCs were reported by the laboratory.

When VOSC data is being collected to confirm conformance with the requirements of a specific equipment manufacturer's VOSC limits, then it is necessary to employ the methods specified by the equipment manufacturer; otherwise, the methods employed can be selected based on the LFG user's assessment of the best method. Whatever method is chosen, the method should consistently be employed over time and be consistently employed at the user's multiple sites to assure data comparability. For a number of reasons, the least desirable methodology is mineral oil capture coupled with GC/ICP. Bag sampling appears to be favored over other methods because of ease of sampling, and because of the assurance of total VOSC capture. Laboratories providing an extended VOSC target list and lower limits of detection would appear to be favored, unless an application requires only a rough assessment of VOSC concentration.

VOSCs adversely affect LFG utilization equipment by the same mechanism. When burned, VOSCs form silica. Microparticles of silica accumulate to form deposits on the interior components of fuel burning equipment. The deposits grow over time. Reciprocating engines are the most commonly employed LFG utilization technology. Deposits form within the engine's combustion chamber on heads and pistons. The deposits will result in increased carbon dioxide emissions and ultimately in detonation-caused shutdowns. The deposits must be manually removed through a painstaking process known as decoking. When required, decoking events are in addition to normally scheduled engine overhauls. Chips of silica can also become dislodged, causing individual valves to be torched, necessitating replacement of a head before expiration of its normal life. Silica deposits will accumulate on spark plugs, increasing the frequency of their replacement. Silica will also find its way into the engine oil, increasing the frequency of oil changes, since silicon oil concentration is a parameter triggering oil changes.

A few air districts in California are now requiring the addition of post-combustion air emission control systems on reciprocating engines. The catalysts used in these systems are rapidly fouled by silica deposits. Engines equipped with post-combustion catalytic air emission controls require close to 100 percent LFG VOSC removal.

Reciprocating engine manufacturers have established what they feel are acceptable limits for LFG VOSC content, or have established a limit on the rate of silicon accumulation in engine oil – the latter being a surrogate for LFG VOSC concentration. Exceeding these limits would void the manufacturer's warranty, or void obligations under fixed price long-term maintenance service agreements. It should be mentioned, however, that engines are often operated at VOSC

levels beyond the limits set by engine manufacturers, with only the consequence of acceptably higher maintenance costs.

Since the introduction of microturbines to the LFG market in 2001, it has been known that microturbines are very sensitive to silica deposits. The recuperator, a heat exchanger which preheats the combustion air with exhaust gas, for efficiency enhancement, is the most sensitive microturbine component. Silica deposition in the recuperator exhaust gas path chokes the flow of exhaust and decrease power output. Silica deposits have also accumulated on burner nozzles and on turbine wheels. Microturbine manufacturers have called for close to 100 percent VOSC removal.

Combustion turbines have experienced the accumulation of silica deposits on fuel nozzles and turbine blades, which has led to either the concern, or the actual experience, that the interval between major overhauls is reduced and/or that turbine output and efficiency would suffer. Again, turbine manufacturers have set LFG VOSC limits (varying based on whether or not the machine incorporates a recuperator). The established limits must not be exceeded in order to preserve the manufacturer's warranty or fixed price long-term service agreements.

Direct use of LFG as a substitute for natural gas is common in the LFG utilization industry. LFG can be used as a boiler fuel, in industrial furnaces or dryers, or for off-site electric power generation. Boilers have sometimes experienced silica deposits on tubes on their economizer section, but in the author's experience not in their evaporator section. The silica deposits are more problematic when the evaporator section is equipped with finned tubes. The consequence of the silica deposits are reduced boiler efficiency and reduced steam production. It is often reported that the silica deposits can be removed without too much difficulty through the use of compressed air or hydroblasting. The sensitivity of LFG uses other than boilers to silica deposits must be considered on a case-by-case basis.

Conversion of LFG to pipeline quality gas does not involve combustion; hence, one would assume that VOSCs would not be a concern. However, a few pipeline natural gas companies have imposed a VOSC (siloxane) limit on the delivery of biomethane into their pipelines. The limits are extremely stringent, and range from 0.1 to 0.4 mg Si/mg. The pipeline companies' intent is to insure that no class of fuel burning equipment (from residential furnaces to power generation equipment) operated by their customers would experience any adverse impact from the introduction of biomethane into their pipelines.

Reciprocating engines used in vehicles can be expected to experience the same types of adverse VOSC impacts as those experienced by reciprocating engines used in power generation; however, vehicle fuel users will have little tolerance for fuel-caused problems. Cummins, the major manufacturer of compressed natural gas (CNG) engines, had established a 3.0 ppmv limit for VOSCs (siloxanes) for biomethane fuel. Depending on the distribution of the type of VOSCs present, 3.0 ppmv is in the vicinity of 10 mg Si/m^3. It appears as if the Cummins limit is too high, and that a limit closer to the prevailing natural gas limits, a limit of say 0.4 to 1.0 mg Si/m^3, would be more appropriate for CNG processed from LFG.

Table 3 summarizes VOSC limits currently in use in the LFG utilization industry. The limits are expressed by equipment manufacturers and gas users in the form of ppmv, µ/Btu, mg/m^3 or mg Si/m^3. Table 3 converts all of the limits to mg Si/m^3 using a typical LFG VOSC distribution (when necessary).

Table 3
VOSC Limits for LFG Utilization

Technology	Limit mg Si/m^3
Reciprocating Engines	5 to 18
Vehicle Fuel	10
Combustion Turbines (without Recuperation)	5
Combustion Turbines (with Recuperation)	2.5
Microturbines	0.3
Pipeline Quality Gas	0.1 to 0.4

Note: All limits are cited at a 50% methane content equivalent except for pipeline quality gas and vehicle fuel.

VOSCs in LFG are gases within gases. VOSCs cannot be filtered out of LFG, since VOSCs are not in the form of particulates. Advanced physical operations, including condensation, absorption and/or adsorption, must be employed.

Conventional chilling, lowering LFG to a temperature in the vicinity of 40º F, is a marginally effective VOSC removal technology. It is believed that VOSCs are removed during conventional chilling primarily through absorption of the VOSCs into the condensing water, and to a much lesser extent, due to the direct condensing of VOSCs from a gas into a liquid. The effectiveness of conventional chilling is dependent on the amount of moisture in the LFG, the types of VOSCs present and the effectiveness of post-chilling moisture separation. SCS has results showing VOSC removal by conventional chilling varying from zero percent to 35 percent. Conventional chilling is commonly used on LFG utilization projects for the purpose of moisture removal, and VOSC removal is an incidental benefit. Lowering LFG temperature below 40º F will increase VOSC removal. Pilot-scale work by the Los Angeles County Sanitation Districts on biogas circa 2000 demonstrated a VOSC removal of about 95 percent at minus 13º F, when coupled with very effective moisture removal (a one-micron coalescing filter). Attempts at commercializing "advanced chilling" for VOSC removal have not been successful.

Non-regenerative, solid-media VOSC removal systems have been widely and successfully deployed over a wide range of conditions. Non-regenerative systems employ single-use media. The media adsorbs VOSCs onto its surface until the media's adsorption capacity is exhausted, as evidenced by the breakthrough of VOSCs in the LFG at the outlet of the media vessel. The media is then replaced with fresh media. Non-regenerative systems are usually employed in applications that have low or moderately sized flow rates and/or have relatively low untreated gas VOSC levels. Non-regenerative systems are also employed when very low treated gas

VOSC levels are required, because non-regenerative systems can be designed and operated to achieve the lowest VOSC level of all available technologies.

Activated carbon and silica gel are usually employed as media in non-regenerative systems. Media consumption varies based on the characteristics of the media employed, the types and quantities of VOSCs to be removed, the types and quantities of other volatile organic compounds (VOCs) and other compounds that are unavoidably co-removed, and the required treated VOSC level. Media consumption can range from 7,000 standard cubic feet (scf) of LFG per pound (lb) of media to 70,000 scf/lb of media. In raw LFG applications, the life of the media and its treatment efficacy is improved by chilling and reheating the LFG to reduce its moisture content. Relative humidity of the LFG should be limited to less than 50 percent and its temperature limited to less than 100º F. Non-regenerative systems always incorporate conventional chilling as an initial step. Non-regenerative systems are commonly used to treat LFG for use in microturbines, small reciprocating engine plants and to "polish gas" that has already received initial VOSC treatment. In polishing applications, SCS has provided systems that consistently deliver a product gas with a VOSC level as low as 0.04 mg Si/m^3.

Regenerative VOSC removal systems can rely on absorption or adsorption. In the absorption process, undesirable gases are preferentially dissolved, under pressure, into a solvent that circulates through a scrubber tower. In the LFG utilization industry, Selexol and Coastal AGR are solvents that are used to separate VOCs (including VOSCs) and carbon dioxide from LFG. In pipeline quality gas plants, the first of the two absorption stages is optimized to remove VOCs. A single stage of absorption can be employed when only VOSC removal is required. Spent solvent is continuously regenerated by depressurization and stripping with air or carbon dioxide. The VOC-laden stripper gas is sent to a thermal oxidizer for disposal. Single stage absorption for VOC removal, while practiced in the early years of the LFG utilization industry, is now highly unusual; however, SCS currently operates such a plant. The product gas is polished with non-regenerative activated carbon, and successfully supplies fuel to an off-site combustion turbine which is equipped with selective catalytic reduction and catalytic oxidization for air emissions control.

Regenerative solid-media VOSC removal systems incorporate provisions to allow their media to be regenerated on-site. Prior to the media in an online vessel being exhausted, it is taken offline and the media is regenerated through the application of heat supplied by the backflow of a hot gas. Once the media reaches a desired temperature, the temperature is held for a period of time, as backflow continues, and then the media is cooled by continuing to backflow unheated gas. The process of adsorption of VOCs (and VOSCs) at ambient temperature, and then driving off adsorbed VOCs (and VOSCs) at high temperature has led this process to be called temperature swing adsorption (TSA). The TSA vessels are generally sized to last one to two days between regenerations. Full regeneration cycles typically last between twelve to eighteen hours. Regeneration temperatures are generally in the range of 350º F to 450º F. Heat for regeneration is most commonly supplied by an inline electric heater. The gas used for backflow is carbon dioxide (when available at a pipeline quality gas plant), LFG or air. The media employed in these systems is activated carbon (when carbon dioxide or excess LFG is available), activated alumina, silica gel or proprietary blends of materials. Regenerative solid-media VOSC removal systems are commercially available. Vendors generally quote product gas VOSC guarantees of

2.5 mg Si/m^3 with the expectation that performance will be closer to 1.0 mg Si/m^3. While the media in these systems is regenerative, the media cannot be regenerated for an unlimited number of cycles. Media is typically replaced every one to two years.

Regenerative solid-media systems are most commonly used to treat LFG for combustion turbines and moderate to large sized reciprocating engine plants (when neither are equipped with catalytic air emission control equipment), and as components of pipeline quality gas plants. Regenerative solid-media systems are suitable for combustion turbine and reciprocating engine applications because they lower raw LFG VOSC levels to below maximum VOSC levels established by equipment manufacturers. When equipment manufacturer VOSC levels are not a concern, either because the manufacturer levels are not exceeded or because they are not rigorously enforced, the justifications for installation of a regenerative VOSC removal system (or a non-regenerative system) is reduced power generation equipment maintenance cost and increased power production. Cost versus benefit analyses must be undertaken on a case-by-case basis to determine if installation of a VOSC removal system is justified. In most cases, the investment does not appear to be justified. If the combustion turbines or reciprocating engines are equipped with catalytic air emission control equipment, it is almost certain that non-regenerative solid-media VOSC removal must be added after regenerative VOSC removal as a polishing step.

If a large direct use LFG utilization project requires VOSC removal, then a regenerative solid-media VOSC removal system, with or without non-regenerative system polishing (depending on the stringency of the application), is most likely to be more cost-effective than a non-regenerative system. For small LFG utilization applications, non-regenerative VOSC removal systems will be more cost-effective than regenerative systems. For moderately sized VOSC applications, it will be necessary to conduct a technical/financial study to determine whether a non-regenerative or a regenerative system is more cost-effective. Pipeline quality gas plants appear capable of meeting current pipeline VOSC limits. Non-regenerative activated carbon could be added as the final step at a pipeline quality gas plant to assure compliance with the more stringent limits.