



# Siloxanes in the Waste Stream

## Environmental and Financial Impacts

A look at the potential environmental and financial impacts for landfill owners and operators following the emergence of siloxane contaminants in landfill gas.

Siloxanes have emerged as common contaminants in landfill gas (LFG) and other biogas with potentially significant environmental and financial impacts for owners and operators of landfills and gas-to-energy (LFGTE) facilities. Siloxanes present in LFG can degrade the operating efficiency of LFGTE engines. Elevated siloxane concentrations can also potentially result in LFGTE facilities exceeding permitted emission limits for particulate matter (PM) and carbon monoxide (CO) and may also prevent landfills from demonstrating compliance with health-based guidelines for formaldehyde emissions. High siloxane concentrations can increase operating costs through the need for increased maintenance or replacement of equipment, and through fouling of post-combustion, catalytic emissions controls.

**Table 1.** Organosilicon compounds commonly detected in LFG.<sup>2</sup>

CAS No.	Compound Name and Abbreviation
1066-40-6	Trimethylsilanol (TMS)
107-46-0	Hexamethyldisiloxane (L2)
541-05-9	Hexamethylcyclotrisiloxane (D3)
107-51-7	Octamethyltrisiloxane (L3)
556-67-2	Octamethylcyclotetrasiloxane (D4)
141-62-8	Decamethyltetrasiloxane (L4)
541-02-6	Decamethylcyclopentasiloxane (D5)
141-63-9	Dodecamethylpentasiloxane (L5)
540-97-6	Dodecamethylcyclohexasiloxane (D6)

## The Background on Siloxanes

Siloxanes belong to a functional group of organosilicon compounds (containing carbon-silicon bonds) that also includes silanes and silanols. Siloxanes are volatile organic compounds (VOCs) that are built on silicon (Si) instead of carbon and are generally categorized by their physical structure, either cyclical (D) or branched chains (L), and the number of Si atoms in the molecule (e.g., L2 or D3). Table 1 shows the most common organosilicon compounds, predominantly siloxanes, found in LFG. Physical properties, such as boiling point and water solubility, vary among the species.

Siloxanes themselves are non-toxic, not known as a health hazard and not regulated by the U.S. Environmental Protection Agency (EPA). They are used extensively in household products and cosmetics for their smoothing or softening effect. A solid antiperspirant deodorant may contain as much as 50 percent siloxanes.<sup>1</sup> They are also a common component of many industrial products including plastics, adhesives,

and lubrications, and they are even found in some fat-free or reduced fat synthetic food products such as salad dressings or potato chips.

Due to their widespread use, siloxanes are a common component in a variety of waste streams, particularly wastewater treatment plant sludge, household municipal solid waste, and industrial waste. As these wastes degrade in a landfill, the warm temperatures and negative pressure differential allow the siloxanes to volatilize and enter the gas stream. Due to the variable nature of waste streams, siloxane concentrations in LFG can vary significantly over time and between sites; therefore, it is important to test the gas during the early planning stages of a beneficial-use project and at six-month intervals throughout the life of the project.

Currently, siloxanes are not subject to air quality regulations; however, some states such as Vermont are now requiring testing for siloxanes in LFG to quantify siloxane combustion-product emissions of silicon dioxide (SiO<sub>2</sub>), or silica, which is regulated as PM. Because siloxanes are not regulated air pollutants themselves, there are no promulgated methods for testing siloxanes in LFG. However, there are a variety of commercially available siloxane sampling, analysis, and monitoring methods used to evaluate LFG quality in support of beneficial-use projects.

Common sample collection methods include sorbent tube/vial and whole-air with subsequent analysis at an air analytical laboratory by gas chromatography/mass spectrometry (GC/MS). For the sorbent method, a predetermined volume of gas (typically 6 liters) is passed through a sorbent-filled plastic tube or glass vial at a uniform, low flow rate (typically 200 milliliters per minute) and the siloxanes stick to the sorbent media. Figure 1 shows a sorbent tube filled with a solid media for sampling siloxanes in LFG. Typically, the sorbent media is either activated carbon, methanol, or oil. The whole-air method is generally simpler and involves collecting a grab sample or a time-integrated sample in a Tedlar bag or Summa canister.

Each sample collection method has its pros and cons and there are several factors to consider including cost, hold times, reporting limits, and dangerous goods shipping requirements. In addition, the target analyte list, reporting limits, and reporting units can vary significantly between analytical laboratories.

Typically, the analyte list can vary from 5 to 22 organosilicon compounds depending on the analytical laboratory; however,



**Figure 1.** Sorbent Tube Filled with Solid Adsorbent Media for Sampling Siloxanes in LFG.

Photo Credit: Sanborn, Head & Associates, Inc.

the compounds most commonly found in LFG include D3, D4, D5, L2, L3, and TMS, with D4 and D5 being the most prevalent (Table 1).<sup>2</sup> Total organosilicon concentration in LFG can range from not detected to well over 100 mg/m<sup>3</sup>, with siloxanes generally accounting for 90 percent or more of the total concentration.

### Traditional Siloxane Concerns for Landfills

The impacts of siloxanes on LFGTE equipment (e.g., engines, turbines, boilers, etc.) have been well-documented over the last couple of decades as more and more projects have come online. There is now a longstanding recognition that siloxanes present in the LFG can degrade the operating efficiency of the LFGTE equipment, which decreases energy generation and increases CO emissions.<sup>3</sup>

During LFG combustion in the engine or boiler, the siloxane molecules break down and combine with oxygen and other elements present during combustion to form silica and silicates, which are chemically and physically similar to sand or glass. Silica deposits can form in the combustion chamber, exhaust manifold, turbine, and exhaust stack, and become thick, extremely hard, and difficult to remove.

In engines, deposits in the combustion chamber can be abrasive and cause premature degradation of the exhaust valve faces and seats. In addition, deposits on the valve seat can chip off and lead to valve guttering, which is when the combustion gases pass through a valve that is in the closed position and create a torch effect that can melt the valve. In turbines, deposits can cause bearing failure and wheel erosion, and reduce the effectiveness of heat recovery equipment.<sup>1</sup>

The overall result is a reduction in combustion efficiency and energy production, increased equipment maintenance, and difficulty in meeting stringent CO standards as combustion

efficiency degrades. Due to the significant damage that siloxanes can cause, engine and turbine manufacturers have set stringent limits on siloxane levels in LFG that, if exceeded, invalidate warranties. Caterpillar has set a silicon in gas limit of 0.60 µg Si/Btu for low energy fuel engines and requires gas treatment if the limit is exceeded.<sup>1</sup> Limits for turbine equipment are more stringent, typically ranging from one to two orders of magnitude less than engine limits, depending on the type of turbine.

### New Concerns and Regulatory Implications

Formaldehyde is a leading air toxic that is receiving increased regulatory attention. Like CO, formaldehyde is a product of incomplete combustion. Formaldehyde is emitted from LFG engines at rates that typically cause their ambient air impacts to exceed health-based maximum concentration guidelines for formaldehyde. For more detailed information about emerging health-risk concerns over formaldehyde emissions from LFG engines, see the Little and Zemba article appearing elsewhere in this issue of *EM*.

Principal control of formaldehyde emissions (and CO emissions) from LFG engines and other LFGTE equipment is achieved by maintaining good combustion efficiency. However, siloxanes present in the LFG fuel can actually increase those emissions when silica, formed from the siloxanes, deposits on engine cylinders and reduces combustion efficiency.<sup>4</sup> As discussed in the next section, siloxane removal systems (SRSs) are now deployed ahead of LFGTE equipment to remove siloxanes, which then preserves good combustion efficiency and the attendant reduced emissions of CO and formaldehyde. Besides formaldehyde control by maintaining good combustion efficiency, further reduction of formaldehyde emissions could be achieved in theory by means of post-combustion control using catalytic oxidation. However, it is presently uncertain as to whether that is achievable.

Besides the concerns for formaldehyde and CO emissions, the combustion of LFG containing elevated concentrations of siloxanes can also generate silica emissions, a form of PM, at levels that could exceed ambient air limits for silica set by some states, depending on the structure (e.g., crystalline, amorphous) and particle size of the SiO<sub>2</sub> emitted. Since emission rates of silica per se are not typically measured directly, some state agencies have elected to use total PM<sub>10</sub> emissions as a surrogate for silica emissions and require annual siloxane testing with the results being used to calculate annual PM emissions. While SRSs can be useful for controlling CO and formaldehyde emissions, regenerative SRSs generally achieve no net reduction in PM emissions for

reasons explained in the next section. For LFGTE facilities that have high levels of siloxanes in the LFG, silica emissions can account for a significant portion of the facility's permitted PM emission limit.

## Siloxane Treatment

An increasing number of LFGTE facilities are using SRSs ahead of the LFGTE equipment to reduce the potential for negative impacts associated with siloxanes in LFG. Removal of the siloxanes from the LFG fuel enables the LFG engine to maintain good combustion efficiency, thereby also restricting the formation and emission of CO and formaldehyde. These SRSs are demonstrated to be effective in this regard. However, as explained below, the SRSs currently used in larger-scale LFGTE projects do not reduce the substantial emissions of the silica PM that derive from those siloxanes. Nor are SRSs demonstrated as yet to be capable of reducing siloxanes in LFG sufficiently to enable efficient operation of a catalyst-based control system after the LFGTE equipment to further abate CO and formaldehyde emissions beyond the control achieved via good combustion efficiency.

Regenerative, siloxane-only removal systems are considered the industry standard for LFGTE projects, particularly projects that utilize LFG-fueled engines to generate electricity.<sup>5</sup> These SRSs are placed ahead of the LFGTE equipment and work by passing the landfill gas across the surface of engineered catalytic media designed to target and remove the siloxanes by causing the siloxanes to bond to the media surface.

Figure 2 shows a typical regenerative SRS with two treatment vessels, as installed at an LFGTE facility. The SRSs are called regenerative because the captured siloxanes can be stripped off the spent media and the media can be used again.



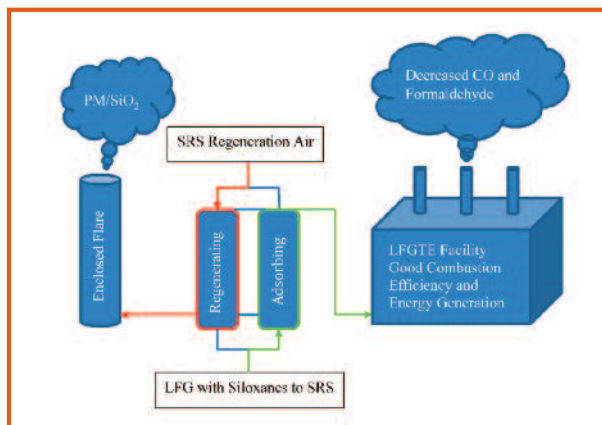
**Figure 2.** Regenerative Siloxane Removal System Installed at an LFGTE Facility.

*Photo Credit: Sanborn, Head & Associates, Inc.*

Typically, two or more media vessels are used in the control system so that at least one can always be online while the other is being regenerated. The media can normally be regenerated and reused for about two years. Regeneration is achieved through a process wherein heated air is directed across the media in the vessel, breaking the bond between the siloxanes and the media, transferring the siloxanes to the heated air. This heated air containing the siloxanes is typically then delivered to a flare or thermal oxidizer to destroy the conventional contaminants present in the gas prior to its being vented to the atmosphere. However, when the flare or thermal oxidizer destroys the siloxanes that are present, silica is emitted in the exhaust gas. Accordingly, overall emissions of PM formed from LFG siloxanes (i.e., silica particles) are not reduced. However, those silica PM emissions are at least transferred from the energy recovery engine (where they can otherwise degrade engine performance and increase emissions of CO and formaldehyde) to the flare, an emission source having greater plume rise and hence enabling better dispersion.

Figure 3 shows a typical process flow for a regenerative SRS installed at an LFGTE facility. Capital costs for a mid-size (i.e., 2,500 scfm) regenerative SRS are on the order of US\$1.5 million, with annual operating costs of approximately US\$0.5 million, and a payback period of three years or less, depending on the inlet siloxane level.<sup>6</sup> Costs can be recovered through reduced frequency of equipment maintenance, fewer engine rebuilds, and additional revenue from increased equipment availability and power generation.

While regenerative, catalytic SRSs are well-demonstrated to preserve good combustion efficiency, thus reducing emissions of formaldehyde and CO at LFGTE facilities, it is not yet established whether those SRSs can achieve sufficient siloxane



**Figure 3.** Typical Process Flow for a Regenerative SRS Installed at an LFGTE Facility.

removal to also enable further control of formaldehyde and CO emissions using a catalytic control system after the LFGTE equipment. This is because the siloxanes present in the LFG can also cause silica deposits on the downstream control catalysts that quickly render them ineffective for achieving additional formaldehyde and CO control.<sup>7</sup>

There are several landfill facilities throughout the United States that have installed catalytic treatment systems for additional control of formaldehyde and CO emissions; however, sufficient long-term performance data are not yet available to evaluate catalyst performance or longevity. In the absence of a demonstrated, downstream treatment system, formaldehyde emissions are controlled through good combustion practices, with CO emissions used as a surrogate to monitor engine combustion efficiency.

For smaller LFGTE projects, (i.e., LFG flow less than 1,000 standard cubic feet per minute [scfm]), activated carbon or other nonregenerative treatment systems for siloxane control may be more cost-effective.<sup>5</sup> A properly sized activated carbon system can remove siloxanes to the level required; however, the media life may be limited by the presence of moisture, non-methane organic compounds, and hydrogen sulfide which also compete for adsorption surface area. Non-regenerative systems may also be more suitable for facilities

where PM emissions are a concern because the siloxanes become trapped in the media and can be disposed of off-site rather than combusted on site and released as SiO<sub>2</sub>.

Conventional filtering systems will not remove siloxanes from LFG; however, refrigeration with condensation may remove a small percentage of the siloxanes. Higher removal efficiencies may be achieved using subzero refrigeration which involves reducing the temperature to -20 °F, but concerns over icing and cost-effectiveness have limited applications.

## Conclusion

The economic impacts from siloxanes present in LFG can be significant for landfill owners, LFGTE facility owners, and their operators if those siloxanes are allowed to reduce the operating efficiency of the LFGTE equipment. Such loss of operating efficiency can increase the emissions of key pollutants such as CO, PM, and formaldehyde, and hence, cause exceedances of permitted emission limits or air quality standards that result in expensive violations. The reduced operating efficiency also increases operating and maintenance costs, and increases downtime of the power generation equipment.

Facilities with elevated siloxanes levels in the LFG can likely realize cost savings through installation of an SRS to remove much of the siloxane from the LFG ahead of the LFGTE

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equipment. There are many variables to consider when performing a cost-benefit analysis for siloxane treatment; however, increased regulatory scrutiny of formaldehyde and PM emissions from LFGTE projects may necessitate installation of SRS equipment. This is particularly so if SRS technology is shown to not only remove siloxanes enough upstream

to preserve the operating efficiency of LFGTE equipment, but to also reliably remove those siloxanes with the very high efficiency required to enable use of a downstream oxidative catalyst to achieve further control of formaldehyde emissions. **em**

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