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VENTURE

VISION

Siloxanes in Landfill Gas

A topic receiving increased scrutiny in landfill gas is the occurrence of siloxanes and their impact; particularly on rotating equipment. Siloxanes are put in the crosshairs by transmission companies. But what are siloxanes? Why the fuss? What is the solution?

Siloxanes Defined

All biogas, whether from a landfill or an anaerobic digester, contains a class of trace organic compounds referred to as siloxanes. These siloxanes are generally grouped as volatile methylsiloxanes (VMSs) and linear poly dimethylsiloxanes (PDMs). The sources of the siloxanes in biogases are numerous, and increasing. For example, in the search for improved environmental cleaners, volatile methylsiloxane solvents have value because they are aroma-free, widely available from natural sources and are exempt from current VOC regulations. Other uses of siloxanes include: carrying agents in skin cream and stick deodorants, as well as shampoos, cosmetics, detergents, ink, lubricants, and adhesives. A solid antiperspirant may contain as much as 50% siloxanes (by weight).

As a consequence of their widespread and growing use, siloxanes are becoming increasingly prevalent in landfills and wastewater. In wastewater, hydrophobic siloxanes accumulate in the sewage sludge and under anaerobic digestion transfer to the biogas. Similarly, siloxanes in the anaerobic environment of a landfill, also transfer to the biogas.

Siloxane Behavior

Siloxanes have high vapor pressures and high Henry's Law constants, resulting in low water solubility's (See Table 1). As a result, siloxanes have an affinity for the vapor phase, and are easily transported in biogas.

See SILOXANES, page 3

Table 1: Various Siloxane Compounds and their Properties

Siloxane Compound	Abbreviation	Molecular Weight (g/mol)	Boiling Point (°C)	Melting Point (°C)	Vapor Pressure (kPa)
Hexamethylcyclotrisiloxane $C_{12}H_{18}O_3Si_3$	D3	222	134	64	1.14 @ 25 °C 1.83 @ 25 °C
Octamethylcyclotetrasiloxane $C_8H_{24}O_4Si_4$	D4	297	175	17.4	0.10 @ 20 °C 0.13 @ 25 °C 0.17 @ 25 °C 0.15 @ 28 °C 0.22 @ 32 °C
Decamethylcyclopentasiloxane $C_{10}H_30O_5Si_5$	D5	371	210	-44	0.05 @ 25 °C 0.02 @ 25 °C
Dodecamethylcyclohexasiloxane $C_{10}H_{36}O_6Si_6$	D6	445	245	-3	0.003 @ 25 °C
Hexamethyldisiloxane $C_6H_{18}Si_2O$	L2	162	100	-67	4.12 @ 25 °C
Octmethyltrisiloxane $C_8H_{24}Si_3O_2$	L3	237	153	-82	0.52 @ 25 °C
Decamethyltetrasiloxane $C_{10}H_{30}Si_4O_3$	L4	311	194	-68	0.073 @ 25 °C
Dodecamethylpentasiloxane $C_{12}H_{36}Si_5O_4$	L5	385	230	-81	0.009 @ 25 °C

McBean, E. A. 2008. Siloxanes in biogases from landfills and wastewater digesters. Canadian Journal of Civil Engineering, 35(4), 431-436. *In* Glus, P.H., Liang, K.Y., Li, R., and Pope, R. 1999. Recent advances in the removal of volatile methylsiloxanes from biogas at sewage treatment plants and landfills. *In* Proceedings of the US Air and Waste Management Association Conference, St. Louis, Mo. Air and Waste Management Association, Pittsburgh, Pa. Paper No. 330.

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In this Issue:

HEADS UP!

Proposed Rule: Mandatory Reporting of Greenhouse Gas Emissions (GHG Reporting)

On March 10, 2009 EPA Administrator Lisa Jackson signed a proposed rule requiring mandatory reporting of greenhouse gas GHG) emissions from large sources in the United States. The proposed rule announcement, published in the Federal Register April 10, 2009, calls for public comment from now until June 9, 2009.

Published under Docket ID No. EPA-HQ-OAR-2008-0508, the rule contains 818 pages of preamble and 593 pages of regulation; it is a lengthy read. The Environmental Protection Agency Web site features a growing population of additional information, FAQs, data sheets, etc. The detailed information can be viewed at www.epa.gov/climatechange/emissions/ghgrulemaking.html.

In summary, EPA proposes that suppliers of fossil fuels or industrial greenhouse gases, manufacturers of vehicles and engines, and facilities that emit 25,000 metric tons or more per year of GHG emissions submit reports to EPA on an ongoing, annual basis. Facilities and suppliers would begin collecting data on January 1, 2010. The first emissions report would be due on March 31, 2011, for emissions during 2010.

The reports would be submitted electronically, in a format to be specified by the Administrator after publication of the final rule. To the extent practicable, existing facility reporting programs will be adapted to include GHG emissions data.

Reporting would be at the facility level, except certain suppliers and vehicle and engine manufacturers would report at the corporate level. Each facility or supplier would also be obliged to retain five years of records and make them available to EPA upon request.

The gases covered by the proposed rule are carbon dioxide (CO2), methane (CH4), nitrous oxide (N2O), hydrofluorocarbons (HFC), perfluorocarbons (PFC), sulfur hexafluoride (SF6), and other fluorinated gases including nitrogen trifluoride (NF3) and hydrofluorinated ethers (HFE). The intent is to collect "accurate and comprehensive emissions data to inform future policy decisions."

The Regulatory Impact Analysis, posted March 26, also notes that the proposed rule is intended to address "inadequate or asymmetric information": meaning inconsistent, incomplete and uncoordinated data requirements between the state and Federal levels.

EPA estimates that 13,205 entities would be covered by the rule, emitting 3,870 MtCO2e per year, with an annual cost in the first year of $160 million and with an annualized cost of $127 million for subsequent years.

EPA anticipates no significant "impacts on the economy in general or on individual sectors or small entities within those sectors."

Further, EPA "expects the benefits of the proposed rule to be substantial."

The reporting process will be challenging; what follows will be more challenging. Get ready to: identify the direct and indirect sources of greenhouse gases, pull together utility bills, consider alternatives to "fossil" fuels such as landfill gas, give some thought to how to address joint ventures or entities over which you have some ownership of but no control, give some thought to how to address GHGs generated in the supply chain, and evaluate what this will mean to your organization.

See also Venture's Winter 2009 newsletter for information on tools for CO2 capture and basics of renewable energy credits and carbon credits.

Removal & On-Line Monitoring for Process Control

From SILOXANES, page 1

Siloxane Behavior cont'd.

The major siloxane issue faced by biogas users is that the high molecular weight volatile compounds convert to silicon oxides during combustion and form amorphous silica ash. These silicon oxides deposit firmly on cylinder heads, valves, and pistons of engines. The hard silicon residues abrade and rapidly wear gas engine surfaces. Because silicone oxide also acts as a thermal insulator, it contributes to the overheating of the engine parts.

Typically, for internal combustion engines, the slip liners become abraded and the piston crowns become worn. Problems include up to 75% reduction in engine head life, valve plugging, and spark plug fouling. Furthermore, siloxanes also have a deleterious effect on engine emissions control devices such as SCRs and SNCRs (which are now required in some states such as California).

Fig. 1

Impact on Warrantees

We are seeing a growing trend: Manufacturers of engines and turbines are qualifying their warrantees with stringent limits on siloxanes in the fuel supply. Whereas limits were between 5 to 35 mg/m^3, now, we are seeing limits stipulated under 5 mg/m^3. Additionally, some manufacturers have been decreasing the limits for silicon in the engine oil (i.e., 1 mg/L in the oil).

Photos:

Fig. 1:
This photo shows siloxane deposits on engine pistons.

Fig. 2:
This is a model of Venture's siloxane adsorption media testing vessel.

Fig. 3:
This is a 3D rendering of a Regenerative Selective Adsorption System for siloxanes, which is about to begin fabrication.

Siloxane Removal

The good news is that siloxanes can be removed from biogas; doing so cost effectively is the challenge. Venture has developed a siloxanes removal system for biogas. Depending on the product gas specification, biogas matrix and budget, either a single stage or a two stage system configuration can be used.

Venture recently completed field testing of various adsorption media at a customer's site using its custom-designed test apparatus. After evaluating removal effectiveness and performing desorption studies, a system using the recommended media was installed and recently commissioned. A more advanced system is ready for fabrication in another installation.

For optimum removal efficiency, Venture incorporates selective adsorption using a variety of media, followed by activated carbon adsorption. Selective adsorption upstream of carbon does several things:

1) it economically removes moisture from the raw landfill gas that competes for activated carbon surface area,
2) it removes a significant portion of the siloxanes (In many instances, it removes as much as 95%+ of total siloxanes), and
3) it reduces the size of the activated carbon system.

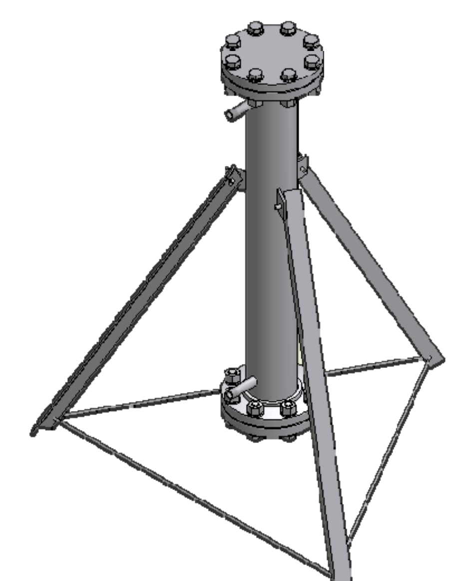

Fig. 2

Fig. 3

Siloxane Measurement & Control

Most adsorption processes are regenerated on-site with heat, including Venture's siloxane removal system. Currently, the regeneration sequences are time-based (controlled by PLC) from empirically derived siloxane breakthrough curves generated during the testing and study phase (or predicted using our ChemCAD process model). These regeneration time sequences are set conservatively (hours before anticipated breakthrough of the siloxanes) to prevent siloxane breakthrough.

The most widely used method for siloxane analysis of biogas is done via grab samples and off-site analysis using gas chromatography / mass spectrometry (GC/MS). A major drawback of the laboratory analyses is the time consuming and laborious procedure.

That is all about to change. For the past 6 months, Venture has been developing an on-line, real-time siloxane monitoring device. This new device (based on GC and GC/MS) will measure siloxane levels in treated biogas with digital output to a plant PLC. The siloxane monitoring system will also function as a process controller. By providing instantaneous and continuous siloxane measurements at the adsorber outlet, the sequence of regeneration (and even its duration) can be controlled based on concentration rather than time. This will save energy costs and can be used as a predictive maintenance tool for media replacements.

Field testing and verification of the new monitoring system is on-going. Full commercial availability and use is expected in July 2009. To learn more about these exciting developments, please contact Mr. Dave Moniot at 412-231-5890, ext. 301.

A Message from the Editor

VENTURE

Here's a different sort of message this quarter, brought to you by Venture's multi-talented Executive Assistant / Vision Creator Amanda Artzberger. Do you ever get bored designing, engineering and building projects for common geographic and atmospheric conditions? Take a moment and consider this task; you may end up re-appreciating your line or work, or re-consider your current location in the galaxy for...

Engineering on the Moon!

On March 6, 2009 NASA launched a telescope to find Earth-like planets in other solar systems. Of more interest to engineers is inhabiting the moon.

Vision for Space Exploration has spawned the creation of NASA's Innovative Partnerships Program. Through seed funds engineers' projects can be funded to advance NASA's technologies, including building bases and habitats on the moon.

Concrete made from moon dust and sulfur is discovered already. But how will NASA create structures in a place with 1/6 gravity and little atmosphere to burn away meteorites? That is where engineers and construction equipment designers will put their innovative minds to the test.

On the equipment end Caterpillar, one of 38 companies with IPP funds, is working with NASA to create machinery. Issues to be solved include: lunar dust, auto-greasing of parts, exchange diesel engine for electric, remote vs. autonomous operation, and material weight and strength.

Working in low gravity, zero-atmosphere environment offers challenges for the design and construction of structures on the moon. Design factors can be safely reduced but reliability is critical; thus, testing and analysis will increase accordingly. A factor to be considered is the loading associated with the violence of lift-offs.

Another factor is unnecessary weight that results from the use of standard structural shapes and materials. Commercial low Earth orbit launch costs are approximately $4,000/lb. and geosynchronous transfer orbit costs are approximately $10,000/lb.; imagine the costs to ship materials to the moon! Lightweight plastics offer benefits but may not be the solution. Plastics are vulnerable to off-gassing (for example: when plastics are heated emitting phthalates creating smells or odorless gases, which disrupt the delicate atmospheric balance within shuttles and stations; and result in loss of desirable material properties) and UV degradation (cracking and/or disintegration of the material after extended exposure to the UV). In addition to plastics some structural materials are being analyzed. These include lunar concrete, inflatable habitats and underground dwellings.

But when the design is figured out, the unusual nature of the construction will brings its own set of problems. The moon's temperatures range from 224 degrees to minus 243 degrees Fahrenheit. This will greatly affect the use of lubricants, coatings, and other materials.

Consider changing tire- lug nuts tightened to the standard 100 ft-lbs on *terra firma* will be harder to remove on *terra luna*. At 16.7% of earth's gravity, human weight won't be much help, and assistance may be needed to hold down the vehicle as you loosen the nuts (Without special tools, screws used in outer space are typically not torqued to more than 25 ft-lbs.).

After all this thought and planning, maybe exploration is more appealing than construction on the moon. The Google Lunar X PRIZE, or Moon 2.0, will award $30 million to the team that can safely land a robot on the moon, travel 500 meters, and send high definition images and other data to Earth. Someone has to explore the terrain before the atypical engineering and construction, right?

Venture News

Welcome New Employees

Kurt Albert
Paul Collins
Kevin Constantine
Allen Derringer
Bradley Malone
Robert McCarthy
Dale Parker
David Todd

Employee News

Congratulations

Congratulations and best wishes to Matt DeStefano and his wife Angela. They were married on April 25, 2009.

Happy Birthday

June
Bryan McCord
Kevin Constantine

July
Dave Moniot
Bill Slatosky
Luis Segarra