NEW TECHN0LOGY FOR REMOVAL OF SILOXANES IN DIGESTER GAS RESULTS IN LOWER MAINTENANCE COSTS AND AIR QUALITY BENEFITS IN POWER GENERATION EQUIPMENT

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“NEW TECHN0LOGY FOR REMOVAL OF SILOXANES IN DIGESTER GAS RESULTS IN LOWER MAINTENANCE COSTS AND AIR QUALITY BENEFITS IN POWER GENERATION EQUIPMENT”

For several decades, Wastewater treatment facilities have used digester-produced methane gas to generate heat for operations and power for onsite requirements. Its use today and into the future will become more important as costs for maintenance and fuel continue to rise. Further, fuel security issues and environmental air quality will also play a larger role in the production and use of digester gas as the costs for natural gas rise. Increasing the use of digester gas for operations and power generation at WWTP facilities can be pursued only if the costs associated with using this resource are lower than the purchase price of natural gas.

A major problem with the use of digester gas for heat and power production has been silicate deposits. The primary cause of silicate-based material deposition is the increased use of siloxanes in consumer and industrial products over the past thirty years. During combustion of biogas containing siloxanes, silicon is released and can combine with free oxygen or various other elements in the combustion gas. Deposits are formed containing mostly silica and silicates (SiO_2 and SiO_3), but can also contain calcium, copper, sodium, sulfur, and zinc. Most deposits caused by combustion of siloxanes are off-white to light brown in color and are of varying texture, some very smooth with a powdery-looking surface, while others are coarse and grainy. These deposits can ultimately build to a surface thickness of several millimeters and are difficult to remove by chemical or mechanical means. The propensity for silica/silicate deposits appears to vary based on flame front, heated surface area, rotation/tip speed, and post-combustion equipment such as heat recovery and catalysts. These deposits result in higher stack temperatures and poor heat transfer in heat exchangers. In power generation equipment, silicate -based material is deposited on pistons and in cylinder heads of reciprocating IC engines. In turbines, silicates can cause severe abrasion of impeller blades. These phenomena result in lower power production, reduced heat recuperation and sometimes catastrophic failure. All digester biogas contains siloxanes and unless removed before combustion, silicates will form and poison exhaust catalysts which impedes their ability to reduce CO and NO_x emissions.

The use of siloxanes is predicted to increase by at least 5% per year into the future because of their highly desirable product enhancement characteristics. Siloxanes are manufactured non-toxic additives which improve product properties in cosmetics, deodorants, etc. such as color dispersion, uniformity and ease of use. Siloxanes are released in digesters during biodegradation and heating and become incorporated in the biogas produced. Siloxanes are difficult to remove from biogas, and once oxidized to form silicates, they become strongly bonded to the heated metal surfaces in reciprocating engines, boilers and turbines requiring frequent and expensive maintenance. Below is a graphical representation of an analysis of a silicate-based deposit that caused the failure of a catalyst:

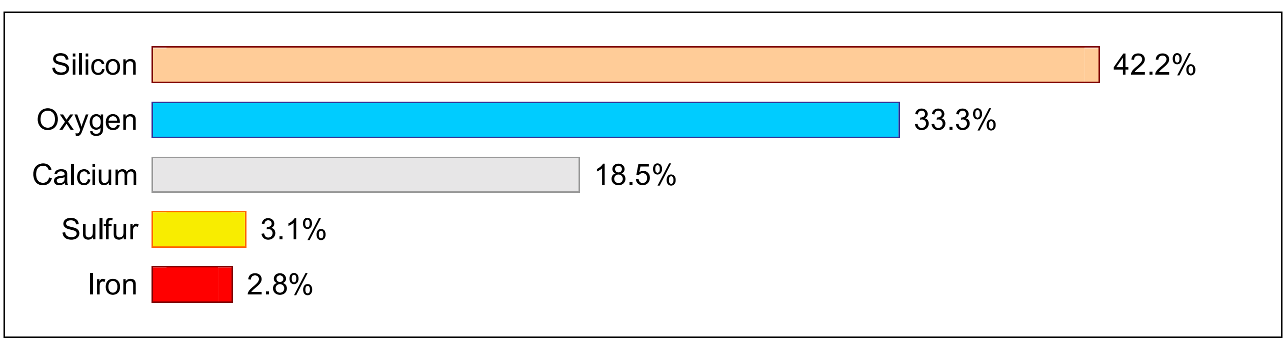


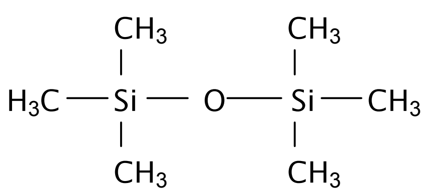
Figure 1 – Elemental Analysis of Silicate Deposit from Catalyst

The damage inflicted by the siloxane combustion byproducts and deposits can be profound. Reciprocating piston engines experience fouling in the combustion chamber, on the valves, valve seats, piston crowns and cylinder walls. Sometimes deposits collect under the exhaust valves resulting in blowby and burnt valves. This phenomenon 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. Also, turndown of the turbine may be necessary to reduce heat.

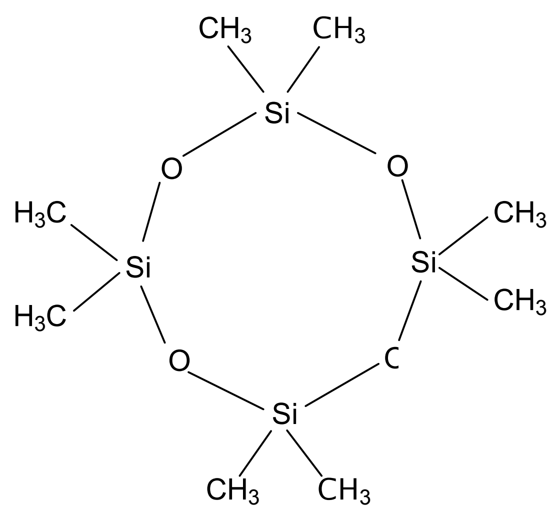
Because of the difficulty in removing the silicon-based deposits and the cost to overhaul reciprocating piston engines and turbines, many manufacturers are now requiring removal of siloxanes from the biogas before it enters their equipment.

INFORMATION ON SILOXANES

Siloxanes found in digester gas fall into two broad categories—linear and cyclical. The two most common linear siloxanes encountered are Hexamethyldisiloxane (called "MM") and Octamethyltrisiloxane (called "MDM"). The two most common cyclical siloxanes found in digester gas are Octamethylcyclotetrasiloxane (called "D4) and Decamethylcyclopentasiloxane (called "D5"). Below are the chemical structures of MM and D4:



<u>Siloxane "MM"</u>



<u>Siloxane "D4"</u>

Figure 2 – Molecular Structure of Siloxanes "MM" and "D4", Common in Digester Gas

Over the past two years, AFT has analyzed the biogas of 50 different municipal anaerobic digesters for siloxanes and other volatile silicon-containing organics. It should be noted that siloxanes were found in every one of the 50 digester gases analyzed. Following are the results of this study:

		Concentration		
		Range, ppbv		ppbv
Organic Silicon Species	Number of Hits	Low	High	Average
Butoxytrimethylsiloxane	1	---	---	920
Methoxytrimethylsilane	1	---	---	227
1,1,3,3-Tetramethyldisiloxane	1	---	---	85
Pentamethyldisiloxane	2	51	100	76
Hexamethyldisiloxane (MM)	10	46	2,260	847
Octamethyltrisiloxane (MDM)	12	32	465	183
Hexamethylcyclotrisiloxane (D3)	5	285	8,700	2,155
Octamethylcyclotetrasiloxane (D4)	46	33	20,144	2,456
Decamethylcyclopentasiloxane (D5)	47	102	18,129	3,422
Dodecamethylcyclohexasiloxane (D6)	3	37	765	352
Tetramethylsilane	1	---	---	170
Trimethylfluorosilane	1	---	---	610
Trimethylpropoxysilane	1	---	---	5,200

Figure 3 – Silicon-Containing Organics Found in 50 Digester Gas Streams

By examining Figure 3, it is apparent there can be other silicon-containing species in digester gas that are not siloxanes. Their combustion byproducts, however are the same as for the siloxanes and will inflict the same damage. There is virtually a 100% probability for siloxanes of one type or another, or other silicon-containing organics, of being in municipal digester gas. Further, there is a greater than 90% probability that the digester gas stream will contain either siloxane D4 or D5.

Quantifying the Damage from Siloxanes

Although there is no way to determine exactly how much of the siloxane combustion byproducts remain as deposits in engines and turbines, it is estimated that at least 0.1% to 0.5% is not expelled in the exhaust gases. Using this assumption, calculations can be made to determine the mass of the deposits that remain. In an engine that burns 140 SCFM (at 75 psig) of biogas containing just 1 ppmv or 1000 ppbv (this is less than one third of the typical average concentration found in digester gas) siloxane D5, a total of 0.008 lb/hour of siloxane enters the engine. Assuming complete stoichiometric combustion, the 0.008 lb/hour D5 (decamethylcyclopentasiloxane) would be converted to 0.065 lb/hour silicon dioxide by the following reactions (incomplete and complete combustion):

$$C_{10}Si_5H_{30}O_5\text{ (D5)} + 20O_2 \longrightarrow 5SiO_2 + 10CO_2 + 15H_2O$$

Mass: 370.8 693.6 300.35 439.9 270.1

Or

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

Mass: 370.8 479.7 300.35 280.0 270.1

In one year's time of continuous operation, the total mass of siloxane D5 alone entering the engine will be 71 lb. Assuming all of this becomes converted to SiO_2, the total mass of SiO_2 created during combustion is 57 lb/year. Assuming 0.1 % to 0.5% is not expelled, this leaves a mass of approximately 0.06 lb. to 0.29 lb.(27.2 g to 151.5 g) per year to be deposited on the engine internals. Even a small fraction of this amount is more than sufficient to cause enough damage to an engine to require an upper end 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 $60,000 and upward.

Catalysts are very susceptible to poisoning and fouling. Siloxanes form silicates which coat the catalyst and create an impermiable glass-like material. This reduces the efficiency of the catlayst for removal of formaldehyde and other byproducts from combustion. Catalyst beds can foul in as little time as a few days. Since there is no way to recover the fouled catalyst, it has to be replaced with new media. Replacement of catalyst media is costly. Also of concern is the growing body of evidence that there is a direct correlation between increases in CO emissions and the build-up of silicate-based deposits from combustion of siloxanes in generator engines.

REMOVAL OF SILOXANES FROM DIGESTER GAS

Applied Filter Technology developed a non-mechanical process to remove siloxanes from digester gas in 1996. The basis of this process is sequential removal of siloxanes and other contaminants in what is termed a “Selective Active Gradient™” or the shortened name, SAG™. The SAG™ Process utilizes gas sieving media called PMG™ or PolyMorphous Porous Graphite™. Siloxanes are removed and trapped by the PMG™, which requires easy periodic replacement. AFT utilizes over 270 different PMG™ media for removal of siloxanes in the SAG™ process.

The first installation of the SAG™ process on digester gas was at the Sacramento County MSD Carson Cogeneration facility in California in 1996. This system is for protection of an SCR catalyst and has been in constant operation for seven years with no catalyst failure. Below are some of the details about this operation:

– SCR Catalyst Protection

Total Gas Flow:	1600 SCFM to 2500 SCFM
Siloxane Contaminants:	Siloxanes MM, D4, and D5
The Major Problem Area:	Siloxanes fouling the SCR catalyst
System Size:	3 x 8 ft. diameter vessels, each containing 10,000 lb. of media (2 operate in series with one in standby)
Installed Cost:	$92,000
Annual O&M:	$40,000
Annual Cost Savings:	$2 Million in catalyst replacement and downtime charges

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Santa Margarita, CA – Microturbine Protection

In December of 2001, the City of Santa Margarita, CA installed a SAGTM system to protect their Microturbines. They have been operating continuously without reduction in power output from the microturbines. Following is a brief summary of this installation:

Total Gas Flow:	30 SCFM
Siloxane Contaminants:	Siloxanes MDM, D4, and D5
The Major Problem Area:	Siloxanes eroding microturbine impellers and glassing of the heat recovery portion of the unit
System Size:	2 x 1.5 ft. diameter vessels, 225 lb. of media each (in series)
Installed Cost:	$22,000
Annual O&M:	$4,100
Annual Cost Savings:	$49,000 in avoided power purchases

Bergen County Utility Authority, Little Ferry, NJ –Generator Engine, OCR Catalyst Protection

In February of 2002, Bergen County started up a SAG™ system to protect their Caterpillar Generator Engines and OCR catalyst from fouling. Bergen County had not been able to stay in compliance with NJDEP Air Emission Standards by utilizing their digester gas due to siloxane contamination. Following is a brief summary of this installation:

Total Gas Flow:	200 to 800 SCFM (turn-up/turn-down capability included in design)
Siloxane Contaminants:	Siloxanes D4 and D5
The Major Problem Area:	Siloxanes fouling engines, SCR catalyst
System Size:	3 x 4 ft. diameter vessels, 3,600 lb. of media each (in series)
Installed Cost:	$500,000 including ancillary equipment
Annual O&M:	$35,000
Annual Cost Savings:	$350,000 in natural gas costs alone plus lower maintenance on the engines and SCR catalyst from running cleaner digester gas

Note: The Bergen County Utilities Authority was recognized for Innovative Air Pollution Control Technology for this project as a direct result of installing a SAG™ System. The press release follows:

> Fair Lawn, NJ, March 21, 2003 – The Consulting Engineers Council of New Jersey (CECNJ), has recognized environmental firm Malcolm Pirnie, Inc. with a 2003 Engineering Excellence Award. Pirnie received an Honor award for its installation of an innovative biogas cleaning system at the Bergen County Utility Authority's (BCUA) wastewater treatment plant in Little Ferry, NJ. The award was presented to Pirnie at an awards banquet in New Brunswick last evening. This project was also recognized as a finalist in the National American Council of Engineering Companies competition.

Ocean County Utility Authority, NJ –Generator Engine, SCR Catalyst Protection

In February of 2003, Ocean County started up a SAG™ system to protect their Waukesha Generator Engines. A SAG™ System was piloted on one engine and a determination was made to install a full scale system on all the gas. Following is a brief summary of this installation:

Total Gas Flow:	350 SCFM
Siloxane Contaminants:	Siloxanes D4, D5
The Major Problem Area:	Siloxanes fouling engines
System Size:	3 x 3 ft. diameter vessels, 2,400 lb. of media each (in series)
Installed Cost:	$212,000
Annual O&M:	$12,000
Annual Cost Savings:	$348,000 in natural gas costs and direct engine maintenance

Since the initial installation at Carson Utilities in Sacramento, CA, there have been 47 additional SAG™ Process installations in the United States. The most recent startup on digester gas was at the Santa Cruz WWTP in California.

SAG™ System Design Considerations

SAG™ technology is easy to apply and is the only technology proven to effectively remove siloxanes from digester gas. It is also the only proven technology to offer a process guarantee for low level removal of siloxanes. The initial step is digester gas analysis. Before a SAG™ siloxane removal system can be designed, it is necessary to know what is in the biogas. There are three primary analyses that provide the necessary information. These are the EPA TO-14 test for volatile organics, the ASTM Procedure D-5504 GC/SCD for sulfur species, and SIL-1 GC/MS analysis for the individual siloxane species (the SIL-1 test is a "modified Dow procedure.") All three tests are needed because all three groups of contaminants have an impact on the overall treatment strategy, process component sizing and SAG™ gradient configuration. The EPATO-14 test measures for 60 specific organics including chlorinated solvents and BTEX compounds. A sample of the gas to be analyzed is collected in a Tedlar bag or vacuum canister and submitted to the laboratory for analysis by GC/MS. The ASTM D-5504 measures for both organic and inorganic sulfur species including the mercaptans and hydrogen sulfide. The same gas sample submitted for the EPA TO-14 can be used for the ASTM D-5504.

The SIL-1 Field Test Kit developed and supplied by AFT uses the impinger method. This method involves the use of two midget impingers containing a specific volume of an analytical grade solvent, like methanol or hexane, usually 15 ml, operated in series. Through these impingers is bubbled a small slip stream of the biogas through a rotameter for a specified period of time. The siloxanes in the biogas are absorbed into the solvent. The impingers are packed in a specialized container containing frozen gel packs and shipped overnight to the laboratory for subsequent analysis by GC/MS. Each of the siloxane species present and its concentration is measured and reported in total μg (micrograms) in the impinger solvent. The results from each impinger are added to obtain the total weight of the siloxane species. By knowing the weight or mass of the siloxanes and the volume of gas that was passed through the impingers, the initial concentration of each siloxane in the biogas can be determined. Figure 3 (below) contains a diagram of the SIL-1 sample collection apparatus.

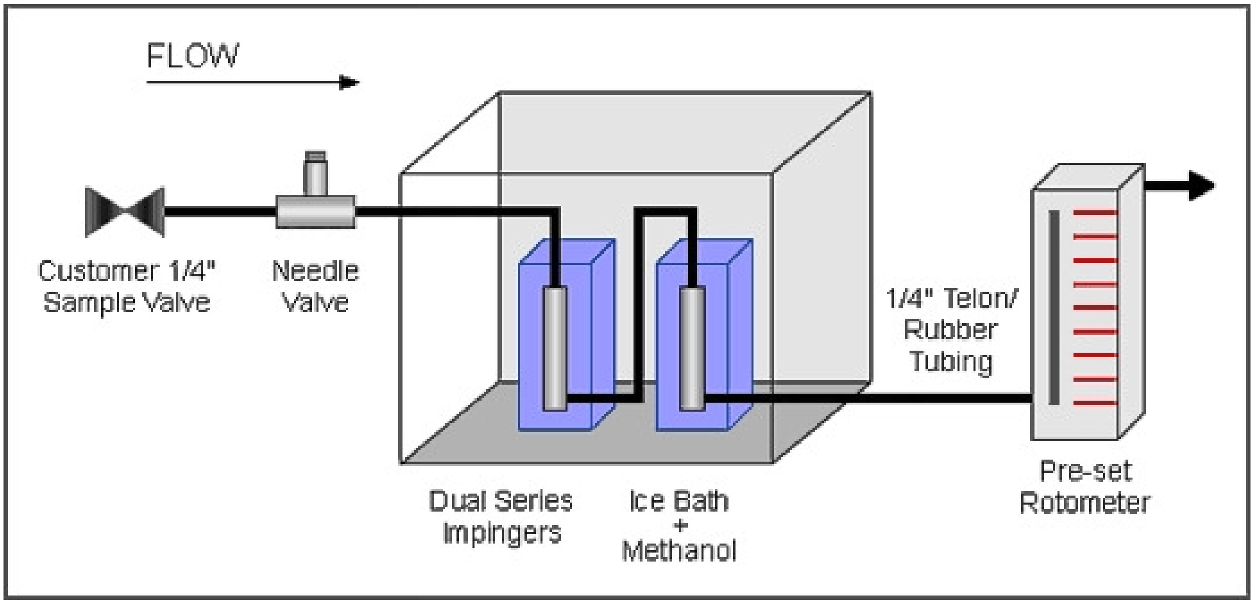

Figure 3 – SIL-1 siloxane sample collection apparatus

The SAG™ Process has proven to be the most effective siloxane removal method available. The SAG™ Process uses a novel form of polymorphous graphite developed by AFT to remove siloxanes from methane containing many types of organics. The SAG™ PMG™ media uses a novel 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 SAG™ technology consists of porous pelletized or granular media contained in a vessel sized by the gas flow, pressure, temperature, siloxanes and organic species. There are many types (more than 270) of SAG™ media 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 contaminant species (like chlorinated solvents and sulfur compounds) and can be incorporated into the same vessel(s). The SAG™ media loaded into the vessels is determined by 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 for reducing high levels of organic contaminants ahead of the SAG™ Process. Incorporation of chilling ahead of a SAG™ System requires intricate engineering to assure optimum performance. Chilling alters the orthobaric pressures of the digester gas constituents and affects how each downstream SAG™ gradient performs. For this reason, AFT has developed a fully integrated turnkey process, SAGPACK™, where chilling is to be utilized. Normally, a SAGPACK™ Module requires piloting on the gas stream to determine the process design and operating parameters. AFT can perform a "paper" analysis on the gas stream constituents to determine if the SAGPACK™ approach would be beneficial. It should be noted that chilling requires energy, which robs the yield of power generated from the gas. Nonetheless, chilling can be a viable option as one of the steps in reducing siloxanes in digester 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 or for most warranties. Research conducted in 1999 and 2000 on biogas liquefaction revealed that even at a temperature as low a 268 degrees below 0 °F., some siloxanes remained in the gas stream.

Summary

Effective utilization of digester gas from municipal and combined waste agricultural sources presents a major opportunity for WWTPs to lower operational costs by reducing or avoiding the purchase of natural gas, electricity or heat from outside sources. As energy costs rise, the focus of all digester operations will be to find ways to reduce these costs. AFT removes the guesswork and simplifies the process of how to utilize digester gas. AFT offers:

- Gas testing
- An analysis of current operations
- Recommended modifications in operations
- Small scale and full-scale piloting
- Siloxane removal system design and construction
- Installation and start-up assistance
- A process performance guarantee
- Maintenance services
- Ongoing assistance to assure optimum system performance

The benefits of removing siloxanes (and other silicon-containing contaminants) from digester gas are:

- Longer maintenance intervals for boilers and heat transfer equipment
- Longer "up" time for generator engines
- Longer life for emission control catalysts
- Lower abrasion of generator engine components:
  - Doubling of spark plug life
  - Extending engine oil life from 500 hours to 3000 hours
  - Doubling or even tripling engine heads, cylinder linings, pistons, impellers and heat recovery component life
  - Increasing engine run time up to 40,000 hours before maintenance is required
  - Lower CO and NO_x emissions.

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4) Ocean County Utilities, Joe Vollman "Reduced Maintenance Costs for Operation if IC Engines with SAGTM Technology Filtration on Digester Gas."

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7) Malcolm Pirnie, Press Release, March 21, 2003 "Bergen County Utilities Authority Treatment Plant Recognized for Innovative Air Pollution Control Technology."