

# Making Power Generation Make Sense by Removing Siloxanes from Digester Gas

*P.M. Tower and J.V. Wetzel, Applied Filter Technology, Inc., Snohomish, WA, USA*

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## **ABSTRACT**

The cost of utilizing biogas in boilers or converting biogas into electricity from municipal digesters can be adversely affected by contaminants. Among the contaminants found in biogas are silicon-containing chemicals like siloxanes. Damage from siloxanes can cost a 5 MGD Wastewater Treatment Plant with a generator engine \$60,000 per year or more.

Siloxanes are found in almost all toiletries and cosmetics and find their way into digester gas through wastewater. Details on the siloxane species will be covered, along with their damage potential. Equipment for the removal of siloxanes can pay for itself in a very short time. The technology for removal of siloxanes from biogas is described, along with the cost savings. The paper will present several case histories where digester gas was used, in California, and elsewhere, with and without treatment, for removal of siloxanes. Savings are detailed and on-line time increases are documented.

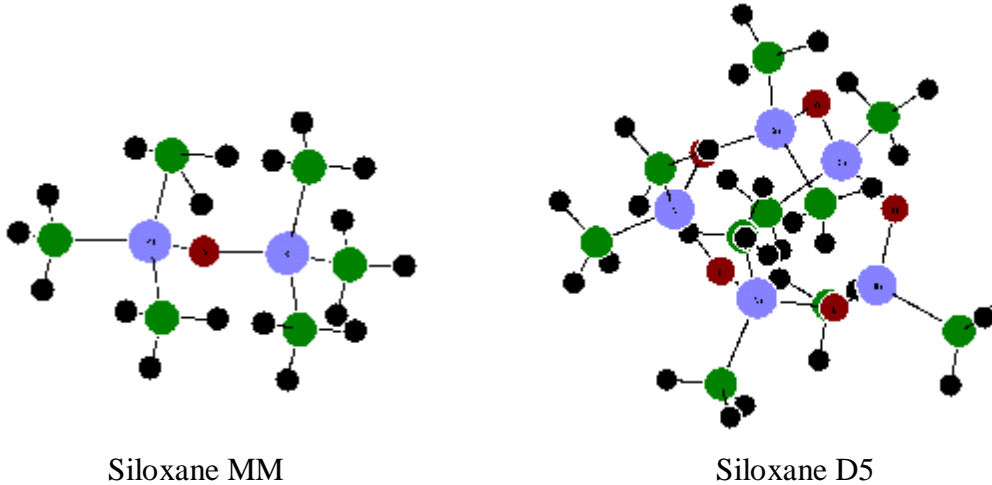
## **WHAT ARE SILOXANES?**

Siloxanes are volatile contaminants that are not broken down or “digested” by the sewage treatment process (in this case, anaerobic digesters). Volatile organic contaminants (VOCs) in digester gas contain mostly carbon, hydrogen, and oxygen, but can also contain nitrogen and halogens. Siloxanes contain carbon, hydrogen, oxygen, and also silicon. Siloxanes are from a broad chemical family of compounds known as organosilicons. They are sometimes called “silicones” in the ingredient list on product labels. Siloxanes are widely used in toiletries and cosmetics such as deodorants, hair sprays and gels, lipsticks and glosses, lotions, shaving products and others. Interestingly, they are also used in dry cleaning fluids as dispersants for non-aqueous detergents. Most siloxanes have the appearance of a clear, oily liquid.

Industrial uses of organosilicons are in the manufacture of some plastics and wire coatings. Most of the siloxanes that find their way into digester gas come from personal care products. As the demand for more personal care items increases, so does the use of siloxanes. The use of siloxanes is increasing worldwide. The use of siloxanes is expected to increase at a rate of 5% to 8% per year. We expect this to cause siloxane increases in digester biogas.

Siloxanes have 2, 3, 4, 5, or 6 silicon atoms in them. There are single-silicon atom molecules in digester gas, but they are not siloxanes. Two common organosilicons that are not siloxanes are tetramethylsilane and trimethylsilanol. The three primary siloxanes found in

digester gas. These are hexamethyldisiloxane, or MM, or L2, octamethylcyclotetrasiloxane, or D4, and decamethylcyclopentasiloxane, or D5. MM is what is called a linear molecule, whereas D4 and D5 are cyclical molecules. D4 and D5 are sometimes called “cyclomethicones.” Below are pictures of the MM and D5 structures.



Hexamethyldisiloxane, is sometimes called MM nor L2. Its molecular formula is  $\text{Si}_2(\text{CH}_3)_6\text{O}$ . MM is very difficult to remove from digester gas because of its high volatility. Decamethylcyclopentasiloxane, or D5, as it is sometimes called is very prevalent in digester gas. Its molecular formula is  $\text{Si}_5(\text{CH}_3)_{10}\text{O}_5$ . D5 is easier to remove from digester gas because of its lower volatility.

## DAMAGE FROM SILOXANES

When siloxanes are burned, they form silicon dioxide,  $\text{SiO}_2$ , the main ingredient in sand. Silicon dioxide accumulates on the heated surfaces in combustion equipment, especially in the cylinders, on the valves and on the heads of IC generator engines. An IC generator engine running on 400 SCFM of biogas containing just 1 ppmv of siloxane D5, for example, will generate approximately 59 kg or 130 lb. of silicon dioxide per year. Because this is a solid, and not a gas, some of this silicon dioxide will remain in the engine and cause considerable damage that increases the cost of operating the generation equipment. If there is also sodium, aluminum, magnesium, iron, or similar elements glass-like materials called silicates can form (Tower, 1,2,3,4). Silicates are extremely abrasive to generator engine moving parts.

Here are some examples of silicon dioxide deposits.



Silicon dioxide deposits on boiler tubes



Silicon dioxide deposits on piston crown.

Obviously, this boiler was not performing very well when the silicon dioxide built up this thick layer of deposits. Because there can be other minerals in digester gas, the silicon dioxide deposit can also be grayish, tan, or brown in color. To the right is a picture of a piston crown in an IC engine that suffered severe silicon dioxide and silicate damage. This engine has to be completely re-built at a cost of around \$90,000.

### **CASE HISTORY – SANTA CRUZ**

Santa Cruz, CA had a plant expansion in 2001 and added a cogeneration engine (Waukesha 12 cylinder) to generate approximately 0.82 MW of power. This is in addition to a smaller V-6 engine that is fired on natural gas and generates 0.5 MW.

Shortly after the cogeneration engine was placed into service, it required head and valve service. The engine was operated for about a year or so before it was decided to explore the cause of the engine damage. Siloxanes were detected in the digester gas at a concentration of between 1.5 and 3.0 ppmv. Plant personnel then began to determine what type of treatment could be used, and contacted AFT. AFT designed a SAG™ treatment system for the removal of siloxanes. This is a passive system consisting of two vessels operated in series, each vessel containing a special media selected for the Santa Cruz digester gas characteristics. Key decision factors were maintenance cost and downtime. The system was procured and installed in early of 2003.

The digester gas treatment system has been operational for almost 20,000 hours now, and there has been no hear or valve maintenance on the engine. Plant maintenance personnel expect the engine to go to 28,000 hours or more before maintenance is required. Additional savings have been realized in increased spark plug life, increased intervals between oil changes, and more energy produced due to less down time.

Significant savings have been realized since the installation of the treatment equipment:

Area	Before	After	Annual Savings
Lost Power Generation	3 – 6 Weeks per Year	1 – 3 Weeks total at 28,000 Hours	\$ 6,000
Head & Valve Maintenance	5,000 – 8,000 Hours	28,000 Hours	\$75,000
Spark Plugs	~ 500 Hours	1,200 – 1,500 Hours	\$ 2,500
Oil Changes	500 – 750 Hours	1,500 Hours	\$11,700
Total Savings	---	---	\$95,200

Above are the approximate savings that Santa Cruz has realized. The lost power generation time used to be 1 to 3 weeks every 5,000 to 8,000 hours. This is expected to go to 1 to 3 weeks every 28,000 hours (they are at 20,000 hours now) with no head or valve maintenance. A complete engine tear-down and re-build is not expected to be performed until 60,000 hours. Spark plug and oil change intervals have at least doubled. The total savings realized at Santa Cruz paid for the siloxane removal system in about one year.

## CASE HISTORY – STOCKTON

The City of Stockton, CA had been operating naturally aspirated Waukesha engines when maintenance problems began to occur in 2001. AFT was contacted to design a siloxane removal system, which was subsequently installed in September of 2003. This system consists of two 60 inch diameter dish top and bottom vessels piped in series. The media is changed out of one vessel on approximately an annual basis. Stockton later changed to “lean burn” engines, and have operated these for about a year and a half. Thus, the operating experience on each type of engine is much less than the operating experience at Santa Cruz. Nonetheless, some cost savings are readily apparent.

Area	Present	Goal	Annual Savings
Lost Power Generation	None	1 – 2 Weeks total at 30,000 Hours	\$ 14,000
Head & Valve Maintenance	None	30,000 Hours	\$112,500
Spark Plugs	~ 500 Hours	> 1,000 Hours	\$ 4,000
Oil Changes	500 – 600 Hours	> 1,000 Hours	\$ 26,300
Total Savings	---	---	\$156,800

The Stockton Silxane removal system is expected to pay for itself in one year and 2 months.

Below are pictures of the Santa Cruz and Stockton siloxane removal systems:



Santa Cruz Siloxane Removal System



Stockton Siloxane Removal System

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