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TREATMENT SOLUTIONS FOR LANDFILL GAS FUEL APPLICATIONS

White Paper October 2007

SILOXANES IN LANDFILL GAS INCREASE MAINTENANCE COSTS FOR COMBUSTION EQUIPMENT

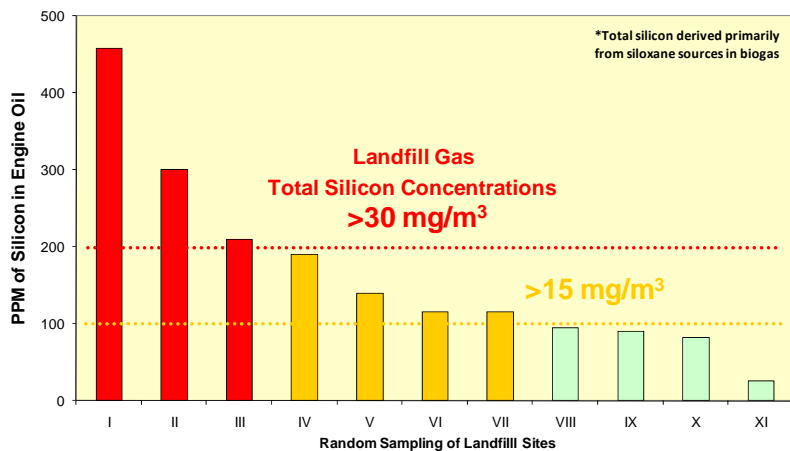
What are siloxanes?

Siloxanes are non-toxic silicon-bearing organic compounds that are added to many domestic products such as deodorants to improve their texture and feel. They are a recent addition to the mix of chemicals we put into our solid waste or pour down our drains. As their use becomes more widespread, their concentration is gradually building in our landfills and digesters.

Where are siloxanes?

Siloxanes can now be found in every landfill and digester in North America and Europe. Thirty years ago this would not have been the case. Newer landfills are tending to show higher concentrations of siloxanes, reflecting their expanding use in more and more domestic products. The siloxane problem can only worsen. Still, many older sites with lower siloxane levels can be tolerably managed with creative maintenance schemes and modified operating practices, but even these solutions come at a cost – for instance, one trick to cope with siloxanes is to reduce capacity. Xebec estimates that approximately one third of all landfills using internal combustion equipment to generate electricity from gas would have very good economic reasons to consider investing in a dedicated siloxane removal system. Another third could handle the problem acceptably well with adapted maintenance and operating methods. The middle third obviously falls in between, without a clear choice either way.

One Third of All Landfill Sites Have a Severe Siloxane* Problem



Why are Siloxanes a Problem?

Siloxanes are volatile compounds that evaporate and migrate out with the landfill and digester gases to be combusted either harmlessly in a flare, or harmfully inside internal combustion equipment. When methane and other hydrocarbons burn, all the combustion products are gases that exhaust easily from the system. Silicon-bearing organic compounds burn as well, but the combustion product of the silicon part is very fine crystalline silica, which is a solid. Silica in its granular form is better known as sand. The crystalline silica from burning siloxanes sticks to hot surfaces inside internal combustion equipment, coating them with a thick, hard, abrasive layer that also insulates these interior surfaces, allowing heat to build up where it should not. If the concentration of siloxanes in the landfill and digester gas is high enough, this accumulation of silica deposits can severely affect the maintenance intervals of the internal combustion equipment. There will be much more downtime and many more parts to replace —operators can be faced with full head and turbocharger change outs, or engine rebuilds after only 9000 hours of running time instead of 25,000; spark plugs and oil changes may last as little as 400 hours.



Silica build-up on heads and scrapped pistons of Caterpillar and Jenbacher engines

Where does siloxane damage occur?

Operators of landfill gas engines, turbines and boilers want their equipment running full time and at full capacity. They also must respect tough emission standards and the realities of maintaining modern equipment fuelled by landfill gas. Shortened maintenance intervals caused by acid formation and siloxane damage worsen the problem.

The challenges faced by operators of gas engines are numerous as many components are affected in many ways:

Spark plugs

- Heads
 - Valves
 - ⊞ Pistons
 - ⊞ Liners
 - ⊞ Rings
 - ⊞ Exhaust Manifolds
 - ⊞ Sensors
 - ⊞ Turbo Chargers
 - ⊞ Waste Gate Valves
 - ⊞ Heat Recovery Units
- Silica deposits on **spark plugs** cause pre-mature failure, fouling, and misfiring with change intervals as short as two weeks.
 - **Heads** suffer from silica deposits causing premature detonation and increasing compression ratio leading to poor emission levels.
 - **Valve guttering** happens when heavy deposits form on exhaust valves leading to pre-ignition and piston failure
 - Heavy deposits on the **pistons** will increase compression ratio and the piston rings do not expand during combustion due to silica deposits on the top ring which leads to high oil consumption.
 - **Liners** suffer from glazing as a glass coating forms
 - Piston **rings** stop scraping cylinder walls properly leading to high oil consumption
 - **Exhaust manifolds** coat internally and require cleaning
 - **Thermocouples & Oxygen sensors** can be fouled resulting in incorrect readings
 - **Turbo charger housings** can be damaged due to cutting from the silica
 - **Waste gate valves** will not function properly due to the heavy deposits
 - **Heat recovery units** become clogged leading to poor heat transfer

TECHNOLOGY CHOICES

What are the solutions?

- ⊖ Capacity Reduction
- ⊖ Refrigeration
- ⊖ Carbon Adsorption
- ⊖ Regenerative Adsorption

When siloxane concentrations are just too high, the better solution is to remove them altogether before they reach the internal combustion equipment. Several techniques have been tried with varying degrees of success. Very large activated carbon towers will adsorb siloxanes, and just about everything else, too, but they cannot be efficiently regenerated, so the large quantities of spent adsorbent must be changed frequently, and this waste material, now rendered a hazardous material, costs more to dispose of than it does to buy! Refrigeration condenses out about half the siloxane concentration, so it is helpful, but still it cannot meet the specifications of the equipment manufacturers. Xebec Adsorption has developed a regenerative landfill and digester gas purification system that can remove siloxanes to concentration levels below the original equipment manufacturers' specifications. Also, because these systems are regenerative, the size of the towers and the quantity of adsorbent is far less, the frequency of change out is reduced, and the spent material is non-hazardous and may be landfilled¹.

De-rate capacity 20%

Refrigeration removes 30-50% Of siloxanes

Spent carbon is expensive to dispose of

Regenerative adsorption removes >95% siloxanes

OEM engine modifications reduce maintenance intervals up to 40% over standard gas engines, except most LFG engines already come with modification packages.

Engine de-rating to 80% of rated capacity reduces siloxane damage, but at the cost of reduced revenue.

Refrigeration can partially reduce siloxanes by 30-50%.

¹ Subject to local applicable regulations — Xebec submits a certified TCLP analysis to the appropriate authority prior to disposal. The adsorption media is repeatedly regenerated, and hazardous compounds do not accumulate.

Carbon adsorption
removes siloxanes, but
large quantities of
hazardous spent carbon

When is siloxane removal needed?

- ⊖ Oil changes
after 400 hrs —
severe problem
- ⊖ Oil changes
after 800 hrs —
moderate problem
- ⊖ Changing plugs
after 400 hrs —
severe problem

How are siloxanes measured?

- ⊖ Ice bath methanol
impingement
- ⊖ Oil impingement
- ⊖ Gas bags
- ⊖ GCMS
- ⊖ Silicon in engine
oil

adsorbent have to be regularly replaced.

Regenerative adsorption removes over 95% of siloxanes.

Not all sites have a sufficient siloxane concentration to justify a dedicated treatment system. New engines have been modified to extend maintenance intervals in spite of the presence of siloxanes in the fuel. Nevertheless, at the worst sites, even with these improvements there are savings to be had with a fuel treatment system. The prime indicator as to whether fuel treatment is economically justified is the rate of accumulation of silicon in the engine oil. If silicon levels accumulate such that change is indicated after 500 hours operation, then it's time to think about it.

In about a third of cases the siloxanes can be managed with modified maintenance and capacity schedules, another third clearly needs active fuel treatment, and the middle third requires more detailed study of the economic impacts.

There is as yet no such thing as a dedicated siloxane detector. To find out how much siloxane is in the landfill gas, samples must first be collected and then sent to a laboratory for analysis. There are several direct sampling techniques which may be used; none of which can claim to be the standard and some of which are cumbersome and time-consuming. The easiest is the gas bag sample, and the most complex is the ice bath methanol impingement method. The analysis technique most often used to measure the concentration of siloxanes in the sample is called gas chromatography mass spectrometry (GCMS), which is a well-developed and accepted process used for organic chemical analysis in many different applications. All of this is to say that finding out how much siloxane is in the gas can be a complicated affair.

Another very good but indirect indicator of siloxane concentration is the amount of silicon that accumulates in the crankcase oil of reciprocating engines; this too requires taking samples and laboratory analysis. Considering that engine manufacturers have well-

established processes in place and often require this testing anyway, developing a link² between siloxane levels in the landfill gas and silicon levels in the oil may be a worthwhile alternative.

² Silicon loading in the engine oil can also occur from other sources such as the air intake — a site evaluation to set a baseline reference would be indicated.

CRITERIA FOR A LANDFILL GAS SILOXANE TREATMENT SOLUTION

- ⊖ **Effective: 95-99% silicon removal**

The criteria upon which a landfill fuel treatment system for siloxanes is evaluated must include effectiveness & reliability, right price, and ease of operation & maintenance.
- ⊖ **Reliable**

To be effective, any removal system must be capable of consistently removing 95-99% of the siloxanes present.
- ⊖ **Automated**

For some applications such as micro-turbines, this may approach 99.9% removal.
- ⊖ **Reasonable cost**

Reliability means no surprises — the equipment is ready on demand and with steady performance.

The ideal fuel treatment system is invisible, however the next best thing is an automated operation with predictable and manageable maintenance schedules, and as little gas sampling as possible.

The cost to purchase, operate and maintain a fuel treatment system must, at the end of the day, put money in your pocket. Beforehand it is important to know the cost of not treating a serious siloxane problem — additional maintenance costs for piston heads, sleeves, spark plugs, etc. plus lost revenue from unscheduled downtimes. For instance, the rate of gap growth on a spark plug operating with untreated landfill gas can be ten times greater compared to treated fuel — OEM spark plugs can cost over \$65 apiece.

REGENERATIVE ADSORPTION SYSTEMS

Basic adsorption process

- ⊖ Landfill gas feeds a tower filled with adsorbent
- ⊖ Siloxanes stick to the adsorbent
- ⊖ Heating releases the trapped siloxanes

gas (like siloxane) is physically removed from a bulk gas (like landfill gas) by the contaminant gas molecules selectively adhering to the surface of very porous materials called adsorbents. The adsorbent comes in granular form and is packed into a tower to get good contact between it and the gas being treated. As the landfill gas flows through this bed of adsorbent material, it gradually becomes loaded with siloxanes until it can no longer take on any more. At this point the loaded tower is switched offline using valves and then is heated to a high temperature, typically above 300°F. Under these conditions the adsorbent can no longer hold onto the siloxanes and they are released. Afterwards the bed is cooled down at which point the tower is fully regenerated and ready to be switched back online for the next cycle. Adsorbents are engineered materials and can in some cases be custom made to suit a specific application.

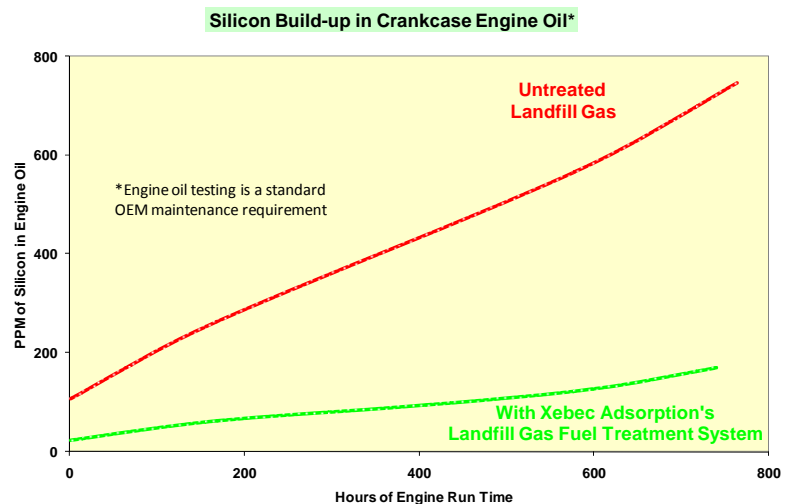
At low operating pressures, heat is the only option available for regeneration and the process is called Temperature Swing Adsorption (TSA). If the operating pressure is at 60 PSIG or above, there is the possibility of dropping the pressure, which will also cause the adsorbed gas to be released and allowing for regeneration. This technique is called Pressure Swing Adsorption (PSA). Both methods can be used for siloxane removal from landfill gas.

Adsorption is a process in which a contaminant

BENEFITS OF REGENERATIVE ADSORPTION

- ⊖ Silicon in engine oil is reduced
- ⊖ Maximum reduction in silicon damage
- ⊖ Lower maintenance costs
- ⊖ Increased operating revenues
- ⊖ Happier mechanic

The benefits of regenerative adsorption can be readily seen. Where silicon in the engine oil was monitored prior to installation of a landfill gas fuel treatment system, levels will be seen to be significantly lower. Accompanying the reduced silicon concentration will be a marked downwards trend in the frequency of oil changes and replacement of spark plugs. In the longer term, overhauls, repairs or replacement of heads, pistons, liners, rings, sensors, exhaust manifolds, turbochargers, etc. will fall back towards the OEM recommended intervals. Budgets for replacement parts will go down while revenues from increased time on-line will go up. Most noticeably, the mechanic will have less to complain about.



XEBEC'S LANDFILL GAS FUEL TREATMENT SYSTEM

- ⊖ Coalescing filter removes bulk water
- ⊖ TSA or PSA configurations
- ⊖ High or low pressure
- ⊖ Waste heat may be used for regeneration
- ⊖ Open or closed loop purge
- ⊖ Flared or condensed purge
- ⊖ Particulate filter protects combustion equipment

A practical landfill gas fuel treatment system will have site specific components and features to complete the equipment. The first element is an inlet coalescing filter to remove bulk water, and possibly oil, from the untreated landfill gas. This is followed by the adsorption unit which can be configured as TSA or PSA with either open or closed loop regeneration circuits depending upon the equipment at the landfill site.

In an open loop arrangement, the purged siloxanes are sent to a flare; this method is the simplest approach with the least added components, but is only feasible where an available flare is in continuous operation.

A closed loop arrangement returns the purge gas to the inlet of the coalescing filter with no loss of landfill gas. In this case the siloxanes in the purge partially dissolve in the condensate coming off the after cooler, and are then removed via a water separator and automatic drain valve. Because a closed loop design involves a recycled gas stream, the equipment is larger and more sophisticated than with an open loop design.

Where TSA is used, it is possible to use waste heat where sources are in place. Following the adsorption unit, a particulate filter is installed to protect downstream equipment.

BENEFITS OF XEBEC'S LANDFILL GAS FUEL TREATMENT

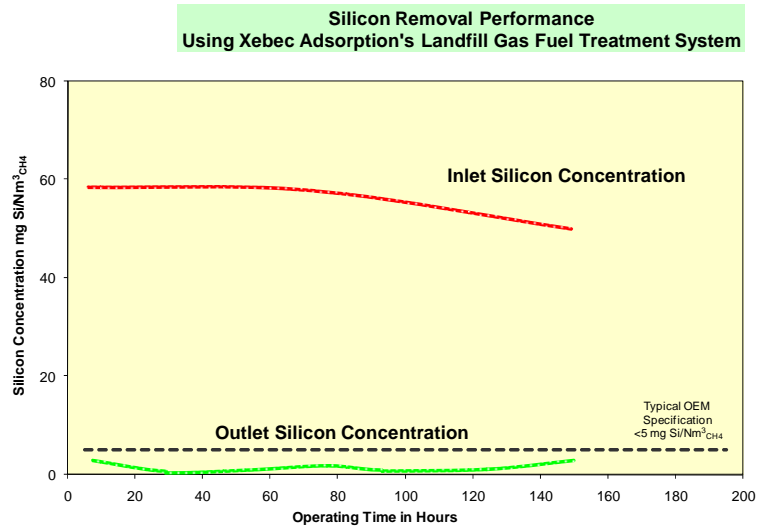
- ⊖ **Total silicon content meets engine OEM specifications**

OEMs use a variety of confusing units to measure the permitted amount of silicon/siloxanes in landfill gas fuel. For the sake of common comparison, Xebec converts everything to one standard unit. Our landfill gas fuel treatment systems exceed the OEM requirements for silicon/siloxane concentrations.
- ⊖ **Adjustable power input**

It is also possible to design the system with turndown capacity. With more frequent regeneration cycles, more energy is used but there is also lower total silicon in the treated landfill gas. The adsorption systems can be designed with the potential to increase capacity without having to immediately commit to higher operating costs.
- ⊖ **No hazardous waste**
- ⊖ **Reliable**
- ⊖ **Measurable performance**

Because the TSA systems are continuously regenerated at high temperature, there is no cumulative build-up of hazardous compounds in the adsorbent beyond a minimum threshold. The EPA's TCLP Method 1311 is the base standard used by most jurisdictions for leachable compounds from waste material. While conformance for a given jurisdiction must first be confirmed, spent adsorbent can in general be safely landfilled.
- ⊖ **40 years experience engineering & building adsorption equipment**
- ⊖ **Engineered designs tailored to application**

Xebec has been engineering, designing and building customized adsorption units for 40 years —we know how to construct reliable and robust equipment. Xebec has factory technicians and a team of design engineers to support their equipment.
- ⊖ **Direct support from OEM**



Xebec Adsorption designs, engineers and builds customized regenerative adsorption solutions for landfill gas fuel treatment applications, in particular silicon remediation systems for critical internal combustion equipment.

OTHER XEBEC ADSORPTION LANDFILL GAS PROGRAMS

Xebec Adsorption also provides engineered landfill gas filtration solutions.

Xebec Adsorption is also developing landfill gas treatment systems for H₂S, VOC, NH₃ and CO₂ removal to produce any quality of gas including pipeline and LNG.

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