Separation of siloxanes from biogenic gases using packed-bed adsorbers

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1 Summary of the problem

Operators of fermentation gas plants (landfill sites, sewage and biogas plants) are increasingly observing that maintenance and repair work to the engines of combined heat and power plants (CHP) needs to be carried out at much shorter time intervals than originally planned and expected.

The main reasons behind this are the impurities and trace contaminants in fermentation gas that cause massive problems in modern gas engines. In particular, organic silicon compounds (siloxanes) in the gas lead to increased wear and tear in the combustion chamber, which necessitates additional repairs with long downtimes and can, in the worst cases, cause the engine to be damaged beyond repair.

The plant operator strives for optimum efficiency of the CHP and maximum availability so that the cost-effectiveness of the gas utilisation system is not jeopardised.

Mounting cost pressure due to continually increasing operating costs incurred by maintenance and servicing work, downtimes and operational logistics, and not least by increasing insurance premiums for machinery breakdown and loss of production, is leading to the use of cutting-edge gas cleaning technologies. If the engine's exhaust gas needs to be cleaned with a catalytic converter, for example, in order to comply with the legal exhaust emission limits, it is obligatory in almost all cases for the fermentation gas to undergo a gas cleaning process. In particular, gas cleaning with activated carbon or in combination with further cleaning processes produces results that generate a sustainable decrease in operating costs.

2 Utilisation of fermentation gas

It is sensible to utilise the fermentation gas directly within the plant, usually for operation of the CHP or combustion in boilers. The electricity produced is directly utilised or fed into the national grid. The heat produced is used to heat the fermenter and the buildings. A recent development is to feed the gas from biogas plants into micro gas networks, in which case the CHP is operated using heat sinks.

3 Gas composition

3.1 Main components of sewage gas

In wastewater treatment, biogas is generated during anaerobic stabilisation of sewage sludge in digestion towers. The biogas (sewage gas), which is usually used for energy purposes during the sewage sludge fermentation process, produces up to 2.5 kWh/m³ of electricity and 3.3 kWh/m³ of heat which can be used for energy.

The following table shows the typical gas composition of different sewage plants:

	Main components			
[% v/v]	CH_4	CO_2	O_2	N_2
Average value	62.7	34.4	0.6	2.4
Number of samples	179	177	276	177
Minimum	45.1	11.8	0.0	0.1
Maximum	85.2	43.4	5.9	22.2

Source: Umweltanalytik RUK GmbH, Longuich, Germany

The effectiveness of the energy recovery depends on the composition. The physical properties of biogas are:

- Density: 1.2 kg/m^3
- Ignition temperature: 700 °C
- Ignition concentration: gas content 6-12 %
- Relative humidity: 100 %

3.2 Impurities in sewage gas

Sewage gas generally carries a contaminant load from the wastewater consisting of volatile organic silicon, sulphur and halogen compounds. These contaminant loads lead to serious wear and tear, high levels of maintenance and damage to gas engines or turbines (Figure 1). The gas therefore needs to be suitably treated before use (Figure 2).

Figure 1: Silicon oxide deposits on a gas engine piston.

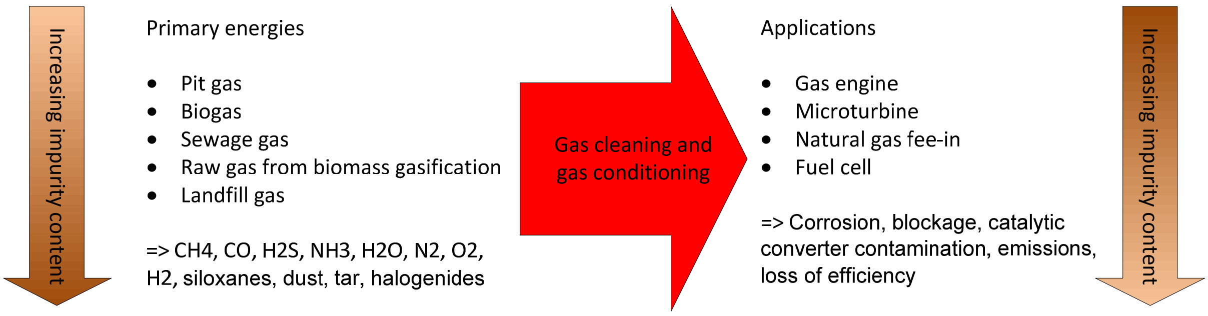


Figure 2: Impurities that affect gas engines.

The following table shows the main, typical impurities in sewage gas. Hydrogen sulphide and organic silicon compounds in particular cause massive and lasting damage to gas engines:

	Inorganic trace gases	BTEX		Hydrocarbons		
[mg/m³]	H_2S	Benzene	Toluene	C6 to C10	> C10	Total org. Si comp.
Average value	433.6	0.2	31.0	103.7	161.7	14.9
Number	172	126	122	111	110	308
Minimum	0.0	0.0	0.0	3.0	2.0	0.0
Maximum	4240.0	5.0	924.0	967.0	783.0	317.4

Source: Umweltanalytik RUK GmbH, Longuich, Germany

3.3 Organic silicon compounds

The main organic silicon compounds in evidence in sewage and landfill gas are the group known as the siloxanes with the general chemical formula H_3Si – (O-SiH_2) – O-SiH_3 and their decomposition products such as trimethylsilanol. The generally known product designation for the siloxane compounds is silicone.

Silicones and siloxanes are classed as largely non-hazardous with regard to their toxicity and environmental damage potential.

Over the last few years, the use of organosilicon substances has increased massively. This is due to their chemical and physical properties that make them suitable for a wide range of applications. Siloxanes are water-resistant and therefore suitable as water-repellent agents for textiles, paper, inks and coatings and as additives for impregnating construction materials. Siloxanes are extremely temperature-resistant, so long-chain compounds can be used as engine lubricants.

They also exhibit plastic-like behaviour, i.e. they can be processed and made to behave like liquids on the one hand, or like malleable or flexibly elastic material on the other. These properties lead to them being used as anti-foaming agents in washing and cleaning materials, glues, sealants, coatings and moulding materials.

Short-chain siloxanes are gentle on the skin and are therefore used instead of Vaseline in creams and cosmetics. Silicones have the greatest insulating properties of all synthetic materials and are largely temperature-independent. This makes them ideal for high-voltage current insulation.

The daily and widespread use of polysiloxanes leads to their presence in waste water and therefore in the waste cycle – in landfill sites, sewage plants and co-fermentation biogas plants. Here, the siloxanes (usually the cyclic siloxanes D4 & D5) are transformed into a gaseous state during the digestion process. Relevant concentrations of hexamethyldisiloxane and trimethylsilanol also form within landfills.

During the thermal utilisation of fermentation gas in gas engines, organosilicon compounds are oxidised into microcrystalline silicon dioxide (quartz). This acts as an abrasive, causing abrasion of cylinder bore surfaces and engines (see Fig. 1).

This problem is relatively new, triggered by the continually increasing commercial use of siloxanes and their associated introduction into the environment.

The last few years have seen a huge increase in the worldwide production of a wide range of different types of silicone. The industry reports annual growth of 7%.

3.4 Requirements for CHP engine manufacturers

The following table shows the stipulated parameters for gas quality, based on the example of a gas engine manufacturer. When these values are compared to the above-mentioned contaminant concentrations in the raw gas, the need for gas cleaning in order to ensure long-term prevention of damage to the engines is clear.

Parameter	Symbol	Limit value	Unit
Methane number	MZ	< 80	kWh/m^3_N
Calorific value	Hu,N	< 5	$mg/m^3_{N\ CH4}$
Chlorine content	Cl	< 100	$mg/m^3_{N\ CH4}$
Fluorine content	F	< 50	$mg/m^3_{N\ CH4}$
Total chlorine/fluorine	Σ(Cl,F)	< 100	$mg/m^3_{N\ CH4}$
Dust content	< 5 µm	< 10	$mg/m^3_{N\ CH4}$
Oil vapour		< 400	$mg/m^3_{N\ CH4}$
Silicon content	Si	< 5	$mg/m^3_{N\ CH4}$
Sulphur content	S	< 300	$mg/m^3_{N\ CH4}$
Hydrogen sulphide	H_2S	< 200	ppm
Ammonia content	NH_3	< 50	$mg/m^3_{N\ CH4}$
Relative humidity	φ	< 60	%

4 Gas cleaning as a measure to prevent engine damage

The prevention of damage to gas engines and lasting improvements in machine availability can only be addressed through the use of upstream gas cleaning systems.

Systems of this kind are currently being used for sewage gas, with ensuing technical and economic benefits. In Germany, Siloxa Engineering AG is one of the market leaders for gas cleaning systems.

In the sewage gas and biogas plant sector, a process technique for the separation of organic silicon compounds based on activated carbon adsorption combined with upstream gas drying has become a highly successful, established method.

For the use of gas cleaning systems to be worthwhile, it must be cost-effective. In other words, the operating costs for gas cleaning must be lower than the additional costs for maintenance, servicing, machinery breakdown or loss of production caused by the silicon.

4.1 Activated carbon adsorption as a proven process for gas cleaning

One of the properties of activated carbon is to adsorb organic compounds. With plants run according to the activated carbon adsorption principle, clean gas qualities of < 1 mg siloxanes/$m^3_{\text{sewage gas}}$ are achieved.

Adsorption in a packed bed with activated carbon replacement is a straightforward, very effective and safe process. With optimum conditioning of the gas and suitable plant design, the specific costs of activated carbon replacement can be optimised or significantly reduced.

When it reaches its maximum uptake capacity, the activated carbon is regenerated by the activated carbon manufacturer or a service provider. The consumption of operating resources and therefore the costs are largely determined by the gas quality and the quantitative and qualitative contaminant load.

The adsorption properties of activated carbon can be optimised by various physical parameters. The moisture in the gas significantly influences the uptake capacity. The higher the relative humidity, the lower the uptake capacity of the activated carbon. The technical process should therefore be configured to ensure the minimum amount of moisture throughout the adsorber. This requires the gas to be systematically dried prior to the activated carbon adsorption process.

4.2 Gas cleaning systems with activated carbon packed-bed adsorbers

In principle, the process technology consists of two treatment stages.

For the adsorption process, the sewage gas to be cleaned must have low relative gas humidity. To ensure this, the SILOXA gas cleaning system has at least one tube bundle heat exchanger in which the moisture-saturated gas is heated before it enters the activated carbon filters in order to achieve a relative gas humidity of ≤ 50 % (stage 1). In the second stage, the sewage gas is cleaned by activated carbon adsorption.

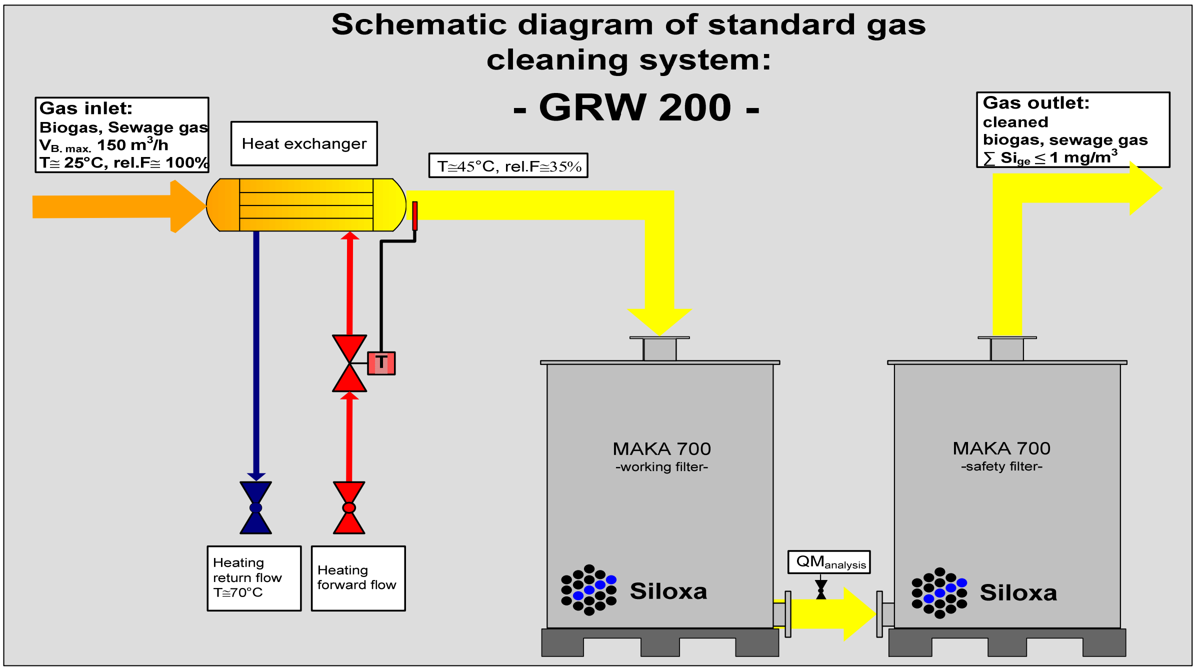


Figure 2: Schematic diagram of gas cleaning system.

The system features two activated carbon filters through which the gas is passed in succession (series connection). Gas cleaning is performed in the first activated carbon filter (working filter). The second filter is a safety filter (control filter) which only takes over separation of contaminants when the working filter's uptake capacity is exhausted and a filter breakthrough is not detected in time. The uptake status is checked by regular gas sample testing of the pure gas. Manual samples are taken downstream from the working filter.

The reason for the series connection is that no cost-effective technology exists for measuring siloxane concentrations online downstream from the activated carbon. At present, therefore, the technology only allows for periodic measurements. Since the intake concentrations into the filter can fluctuate significantly, it is not possible to specify fixed replacement intervals. It is also necessary to take into account the fact that, in the event of the uptake capacity being exhausted, siloxane concentrations are significantly higher in the outflow from the activated carbon filter than in the inflow to the filter due to the desorption effect. To rule out significant damage to the gas engine, a breakthrough of the siloxanes must be prevented. For the separation of siloxanes, therefore, SILOXA only uses series connection (working filter/control filter).

The activated carbon filters are expediently designed by Siloxa as replaceable filters (mobile and for low gas flow rates [approx. 200 m³/h]) for gas flow rates up to around 200 m³/h or as stationary filter systems (for high flow rates).

Figure 3: SILOXA MAKA 100 replaceable filter system.

To restore full cleaning performance, the whole (saturated) working filter is replaced with a replacement filter containing new activated carbon. The control filter, which has already used up some of its uptake capacity, can now be used as the working filter and the fresh new filter as the safety filter. This method of operation allows almost full capacity utilisation of the activated carbon and therefore plays a key role in making activated carbon gas cleaning highly cost-effective. The filters can be changed quickly in just a few easy steps with no long interruptions to operation.

Figure 4: SILOXA FAKA 3.000 K2E and TWIN FAKA K2E gas cleaning system.

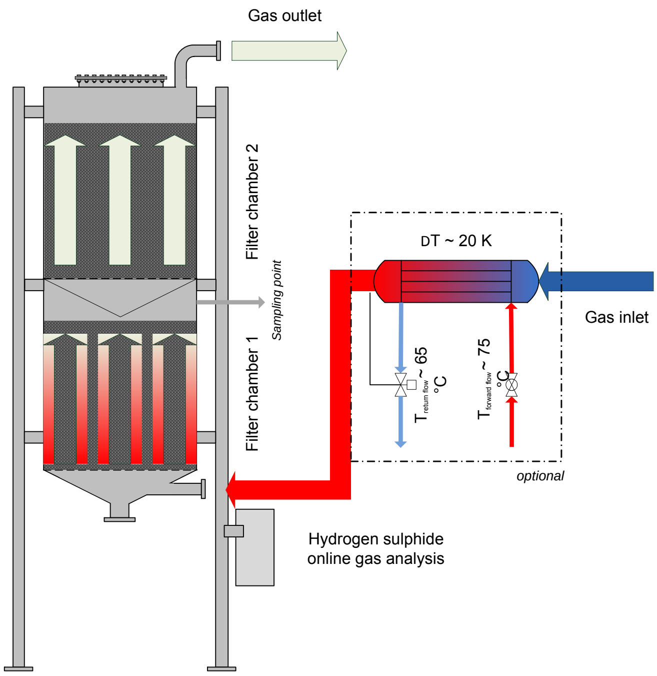
Alternative gas cleaning systems for flow rates > 200 m³/h - 1500 m³/h are designed as FAKA stationary filter systems (vertical activated carbon filters).

The activated carbon container is suspended in a three-legged support structure. For easy changing of the activated carbon, the bottom of the container is cone-shaped (for emptying) and a walk-on surface is built onto the top (for refilling).

The system provides access to the work platform (ladder or steps) and features an electric chain hoist with crane boom for the filling process with Big Bag packaging.

For the cleaning process, the landfill gas passes through the filter from the bottom to the top. In the filter, the activated carbon lies in loose form on a sieve plate. The FAKA is divided into two chambers. The first chamber corresponds to the working filter in the serial connected system. If a breakthrough of the siloxanes downstream from the first chamber is detected by periodic gas analyses, the activated carbon can be discharged by emptying it into a Big Bag. The carbon from the 2nd chamber is then automatically transferred to the 1st chamber via a valve between the two chambers. The control filter, which has already used up some of its uptake capacity, thus becomes the working filter – following the principle of series connection. The control filter (2nd chamber) is then filled with fresh carbon.

Siloxa activated carbon adsorber
TYPE FAKA K2 (twin-chamber)



The twin-chamber technology means the FAKA system does not require any complex piping. This makes this technology very cost-effective. For larger gas flow rates or high contaminant loads, twin FAKAs can be used, or customised filter systems with up to 80,000 l of activated carbon volume can be planned.

Figure 5: SILOXA sewage plant gas cleaning system, Moscow, 5,000 m³/h.

5 Gas cooling

One of the basic properties of gas is to absorb different quantities of water (vapour) depending on the temperature. The warmer a gas is, the more it expands and the more water it is able to absorb. A fermentation gas with a temperature of 40 °C can absorb approximately 50 g of water per cubic metre at a relative humidity of 100 % (moisture-saturated). At a gas temperature of 45 °C, it can absorb as much as 64 g/m³. If the gas is then cooled, the gas volume decreases and so, therefore, does its water absorption capacity. For instance, if the gas cools down to 10 °C, it can only absorb around 9 g/m³ of water. The remaining water has to condense because of the low absorption capacity.

This process is generally called gas drying, which is not correct in the technical sense, since the gas is still 100 percent moisture-saturated after cooling. Only when it becomes warmer does the relative humidity drop and the gas can be defined as dried. Before it reaches the activated carbon, the gas therefore still needs to be heated, even if there is an upstream gas cooling unit, in order to arrive at the necessary 50 % relative humidity.

A positive side-effect of gas cooling is that the reduction in the water (vapour) content decreases the gas volume significantly. The volume of water vapour in a saturated biogas at 40 °C is 7.3 %, but after cooling to 3 °C, it is only 0.7 %. This significantly increases the percentage of methane in the gas. Where the contaminant concentration of siloxanes and hydrocarbons > C5 is concerned, it can be observed that approximately 20-30 % of these compounds are also condensed out when the gas is cooled to 3-5 °C. This takes some of the burden off the activated carbon and leads to lower consumption. For higher flow rates and contaminant loads in particular, a gas cooling unit can further improve the cost-effectiveness of an activated carbon gas cleaning system.

6 Operating results

Taking the operating data of Heidelberger Versorgungs- u. Verkehrsbetriebe GmbH (HVV), Heidelberg, as an example, the cost-effectiveness of the gas cleaning systems is shown below.

HVV operates 6 sewage plant sites with gas engines with upstream gas cleaning systems from SILOXA Engineering AG.

Sewage plant	Gas engines	Commissioned	SILOXA gas cleaning system commissioned
AZV (association for sewage treatment) Heidelberg	2 x MDE, 294 kW, approx. 8,200 h/a	27.06.2000	15.10.2002
AZV Hollmuth	1 x Köhler & Ziegler, 75 kW, approx. 7,000 h/a	14.10.2002	15.07.2003
AZV Medesheimer Cent	1 x Köhler & Ziegler, 75 kW, approx. 7,750 h/a	06.11.2002	24.07.2003
Sinsheim sewage plant	1 x G.A.S., 120 kW, 3 x G.A.S., 50 kW, 1,000 to 6,500 h/a	3x in 1995 1x in 2000	18.08.2004
AZV Untere Hardt	1 x Köhler & Ziegler, 185 kW, approx. 7,000 h/a	09.01.2005	08.11.2006
AZV Schwarzbach	1 x Köhler & Ziegler, 90 kW, approx. 7,000 h/a	12.05.2005	17.08.2005

6.1 Analysis results

6.1.1 Oil analyses

The analysis of the engine oil of two modules provides an example of how the SILOXA gas cleaning system works. Using the gas cleaning system enabled the concentration to be significantly reduced.

Siloxane contamination in the engine oil	Module 1		Module 2	
	Before installing the gas cleaning system [mg/kg]	**After installing the gas cleaning system** [mg/kg]	**Before installing the gas cleaning system** [mg/kg]	**After installing the gas cleaning system** [mg/kg]
Number of samples	6	4	6	4
Average value	105	5	103	5
Minimum value	70	7	63	7
Maximum value	156	3	162	3

6.1.2 Gas analyses

The following table lists the analysis results for the raw gas and the results after filter 1 (working filter) by way of example. The results show siloxane values after removal to be less than 1 mg/m^3_N.

Total organic silicon compounds (amended)	**Raw gas** [mg/m^3_N]	**After filter 1** [mg/m^3_N]
AZV Schwarzbachtal	77.9	0.4 (after 1,055 op. hrs.)
AZV Untere Hardt	18.4	0.4 (commissioning)

6.2 Comparison of operating costs

The costs per gas engine are compared below. The table shows the annual costs, both before using the gas cleaning system and after installing the SILOXA gas cleaning system at the AZV Heidelberg sewage plant (2 x 294 kW, MDE). The operating data was recorded by the sewage plant personnel for internal benchmarking purposes.

Installation of the SILOXA gas cleaning system	**before** Costs [€/a]	**after** Costs [€/a]
Oil change and additional work	Every 500 h	Every 1,000 h
200 l, € 2/l	6,400	3,200
12 spark plugs, € 40/h	7,680	3,840
8 h, € 50/h	6,400	-
Overhaul of the cylinder heads	10,000	
Total I (2 x 294 kW, MDE)	**60,960**	**14,080**
Emergency maintenance (additional)		
40 h, € 50/h	2,000	-
Activated carbon (full service)		5,850
Depreciation (7 a)		5,086
Total II	**62,960**	**25,016**

The comparison of the operating costs impressively demonstrates the significant cost saving of € 37,933 per year (amounting to € 265,608 in 7 years) gained by using gas cleaning systems to remove organic silicon compounds from the sewage gas before using it for energy purposes. In the case of the sewage plant shown here as an example, the investment paid for itself within one year.

7 Summary

Gas conditioning systems for biogas as upstream systems for gas utilisation for energy purposes are the state of the art. They effectively protect against damage caused by the introduction of siloxanes, in particular, as well as other impurities (H_2S).

SILOXA is the market leader in the field of process engineering for the elimination of siloxanes from sewage gas and biogas. SILOXA technology is based on uniquely needs-oriented, modular systems. These can be integrated into the gas line on a turnkey basis and are supplied ready for connection with all piping and wiring. The modules are suitable for both interior and exterior installation. They ensure reliable plant management and are particularly cost-effective.

Operating results of installed systems impressively demonstrate the following general findings:

- Improved gas quality
- Prevention of engine damage
- Increased availability of gas engines
- Reduced need for servicing and emergency maintenance
- Significant savings on operating costs