
Approaches concerning siloxane removal from biogas — A review

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Soreanu, G., M. Béland, P. Falletta, K. Edmonson, L. Svoboda, M. Al-Jamal and P. Seto. 2011. **Approaches concerning siloxane removal from biogas — A review**. Canadian Biosystems Engineering/Le génie des biosystèmes au Canada. 53: 8.1–8.18. One of the major barriers to the use of biogas as an alternative renewable energy source is the presence of siloxanes. At combustion temperatures, siloxanes are converted to silicon dioxide (SiO₂), which forms deposits on the combustion surfaces (pistons and cylinders) of gas processing equipment, thus reducing engine life and increasing overall operational and maintenance costs.

This paper presents key multidisciplinary information with respect to siloxane removal, aimed at evaluating various treatment options and identifying future research needs. Current removal methods are typically based on the adsorption process, while others employ gas-liquid absorption and refrigeration/condensation. Otherwise these methods are appropriate for siloxane removal with regard to siloxane physical-chemical characteristics (for example, low solubility in water, high solubility in organic solvents, volatility, chemical resistance) their application in practice is cost-limited. Adsorption and absorption methods become inappropriate when applied to moisture-rich biogas, and are often used in combination with a pre-treatment stage. Development of more cost-effective technologies, such as membrane separation and biofiltration is in progress, and initial findings suggest that these methods could represent an attractive alternative. **Keywords:** biogas, siloxane, environmental engineering, technology, treatment.

Une des barrières principales à l'utilisation des biogaz comme source d'énergie renouvelable alternative est la présence des siloxanes. Aux températures de combustion, les siloxanes sont convertis en bioxyde de silicium (SiO₂) qui forme des dépôts sur les surfaces de combustion (pistons et cylindres) de l'équipement de valorisation du gaz, de ce fait réduisant la vie des moteurs et augmentant les coûts globaux opérationnels et d'entretien.

Cet article présente des informations-clés multidisciplinaires relatifs à l'enlèvement du siloxane des biogaz, visant à l'évaluation des méthodes de traitement et l'identification des besoins de recherche. Les méthodes courantes d'enlèvement sont typiquement basées sur le processus d'adsorption, alors que des autres utilisent l'absorption gazeuse liquide et la réfrigération/condensation. Ces méthodes sont efficaces pour l'enlèvement du siloxane, en tenant compte des caractéristiques chimico-physiques du siloxane (comme exemple, la solubilité faible dans l'eau, la solubilité élevée dans les solvants organiques, la volatilité et la résistance chimique), cependant leur application est coûteuse. Les méthodes d'adsorption et d'absorption ne sont pas appropriées pour le traitement du biogas humidifié et une étape de traitement préliminaire est nécessaire. Des technologies

alternatives telles que les méthodes de séparation membranaire et la biofiltration sont en cours de développement, pourraient être entables dans les applications au biogas. **Mots-clés:** biogas, siloxane, génie environnementale, technologie, traitement.

INTRODUCTION

Biogas generated during the anaerobic digestion of sludge and other organic materials such as in landfills is considered a renewable energy source. These biogases are methane-rich, based on a typical composition of 60–65% methane; the balance being mostly carbon dioxide. However, trace amounts of undesirable compounds, such as hydrogen sulphide (H₂S) and siloxanes may also be present, which hinder their use in some energy recovery equipment. Issues related to H₂S presence in biogas and the possibilities for its removal, including biological methods, were previously discussed (Syed et al. 2006).

While H₂S, is listed as one of the top five pollutants in Environment Canada's National Pollutant Release Inventory (NPRI 2002), the impact of siloxanes on human health and on the environment has not been fully determined. Siloxanes are relatively non-toxic compounds and are usually present as inert additives to pharmaceutical products, cosmetic and personal care products (i.e., creams, hair styling products, lipsticks and deodorants), cleaning agents (detergents, etc.), sealants, etc. (Latimer et al. 1998; James 2000; Graiver et al. 2003). Under environmental conditions, no greenhouse effects resulting from siloxanes or their accumulation in air, soil or water have been reported (European Commission 1999; Parker et al. 1999; Graiver et al. 2003); however, recent Environment Canada studies show that when released to the environment, such as in municipal waste water streams, they are persistent, and may harm fish and aquatic organisms (<http://www.ec.gc.ca/default.asp?lang=EN&n=714D9AAE-1&news=546F7166-9C61-4CA5-BB67-804EC3F2AOED>). Siloxane concentrations in biogas are found as high as 60 mg/m³ (Hagmann et al. 1999; Monteith et al. 2006); however, trace concentrations have been demonstrated to damage gas processing equipment because of their oxidation to fine, white particles of silica (SiO₂) during combustion. These particles agglomerate and can form crystalline abrasive

deposits up to a few millimetres thick on the surface of gas-processing equipment, thus reducing engine life and increasing overall operational and maintenance costs (Huppmann et al. 1996; Graening 2003; Dewil et al. 2006; Accettola et al. 2008). In addition, the siloxanes in biogas were found to be responsible for fouling post-combustion emissions control – catalytic systems (Wheless and Pierce 2004; Accettola et al. 2008). Table 1 presents maximum siloxane concentration limits stated by various manufacturers of gas processing equipment. Limits for (micro) turbines and fuel cells are considerably lower than for internal combustions engines. The necessity of siloxane removal from biogas to levels below these limits is a priority for advancing the energy recovery potential of biogas.

Current technologies for siloxane removal from biogas are mainly based on physical adsorption processes using a variety of sorbent materials (i.e., activated carbon, silica gel, zeolites, molecular sieves, etc.). Alternatively, gas-liquid absorption (i.e., Selexol) and refrigeration/condensation are also available (Schweigkofler and Niessner 2001; Wheless and Pierce 2004). In addition, acid degradation (i.e., hot concentrated sulphuric acid) (Huppmann et al. 1996; Schweigkofler and Niessner 2001), membrane separation (Ajhar and Melin 2006) and biological methods (Accettola et al. 2008; Popat and Deshusses 2008) have also been identified. Preliminary studies suggest that siloxanes can be removed by microorganisms (i.e., *P. fluorescens*, *P. Putida*) under both aerobic and anaerobic/anoxic conditions (Grümping et al. 1999; Wasserbauer and Zadák 1990; Accettola et al. 2008).

Technical issues concerning siloxanes in biogas have recently been identified (Huppmann et al. 1996; Wheless and Pierce 2004). Consequently, the removal of siloxanes from biogas is a relatively new requirement, and few studies have been carried out in this field thus far. Issues related to the presence of siloxanes in biogas, including their occurrence pathway, physical-chemical characteristics, possible reaction mechanisms and key information relevant to removal methods are presented and discussed. Supporting information about these aspects is available in a review specifically dedicated to siloxanes in anaerobic

digestion of waste activated sludge recently published by Dewil et al. (2006).

OCCURRENCE PATHWAY FOR SILOXANE GENERATION IN DIGESTER BIOGAS

Based on information gathered from the literature, the fate of siloxanes in a wastewater treatment plant (WWTP) and their occurrence in biogas can be summarized as illustrated in Fig. 1. For more information on this subject the reader is referred to Dewil et al. (2006). Municipal and industrial sources of siloxane in wastewater and sludges include both personal care products from household use as well as effluents from silicon polymer manufacturing facilities. Two main classes of widely used siloxanes entering wastewater treatment plants are distinguished as follows: high-molecular weight polydimethylsiloxane (PDMS) (Xu 1999; Traina et al. 2002) and low molecular weight methylsiloxanes (MW <450) (Parker et al. 1999; Xu 1999). The lower molecular weight compounds are known as “volatile methylsiloxanes” (VMS) due to their higher vapour pressures and Henry’s law constants (Kochetkov et al. 2001) as compared to PDMS that are characterised by very low vapour pressure and are considered non-volatile (Dewil et al. 2006). Cyclic and linear VMS are typically detected in biogas (next section).

In fact, approximately 85% of cyclic VMS production is used in PDMS synthesis, while the remaining 15% is directly used in consumer products (based on 1993 US statistic; Xu 1999). Approximately 10% of PDMS and 3.3% of cyclic VMS used in consumer products enter wastewater treatment plants (Xu 1999; Traina et al. 2002). The behaviour (pathway) of VMS during typical wastewater treatment is quite different than PDMS. While PDMS is mostly (>90%) adsorbed onto the surface of solid particles, approximately 50% of VMS are volatilized from the liquid stream (i.e., due surface volatilisation and air stripping) and the remainder is sorbed together with PDMS to solid particles and carried with the sludge to the digester (Traina et al. 2002; Dow Corning 2005; Parker et al. 1999; European Commission 1999; Xu 1999).

Table 1. Maximum recommended siloxane concentrations for various gas processing equipment.

Gas processing	Manufacturer	Siloxanes (mg/m ³)	Reference
Heating (boilers)	–	NA*	Hingerl (2001)
Natural gas grid (natural gas + biogas)	–	Dependent on final use of gas mixture	
Internal combustion (IC) engines	Jenbacher	10	Wheless and Pierce (2004)
	Deutz	5	
	Caterpillar	28	
	Waukesha	25	
Microturbines	Capstone	0.03	
	Ingersoll-Rand	0.06	
Turbines	Solar	0.1	
Fuel cells	–	100 ppbv	
Vehicle fuel	–	Limits not yet established	–

*NA, siloxane removal not necessary.

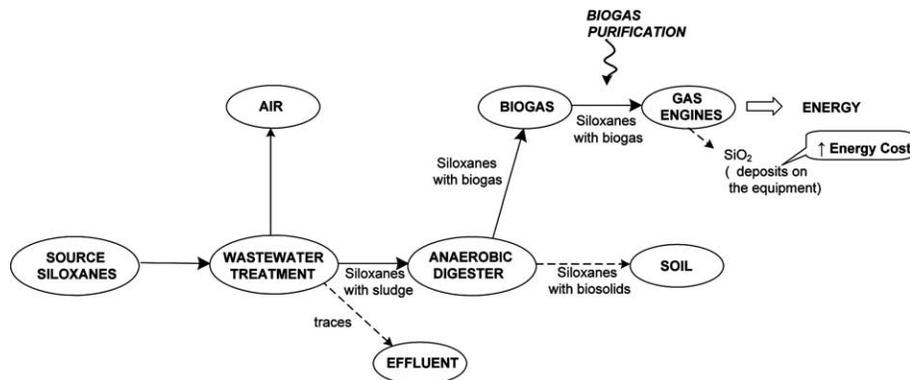


Fig. 1. Fate of siloxanes in a wastewater treatment plant (WWTP) and their occurrence in biogas.

According to Dewil et al. (2006) and Appels et al. (2008), the sludge floc extracellular polymeric substances (EPS) are the primary adsorbing sites for siloxanes. During the anaerobic digestion process, VMS are released into the biogas by volatilization from the sludge as well from the hydrolysis of PDMS to VMS, while the rest of VMS and non-hydrolysed PDMS (i.e., approx. 34% of total PDMS in WWTP influent) remain in the digested biosolids (Xu 1999; Parker et al. 1999; Traina et al. 2002; Accettola et al. 2008). An increase in the amount of siloxane discharged in the biosolids and/or released in the biogas has been noted when PDMS-based anti-foaming agents are added in the digester (Dewil et al. 2006). Depending on the method of biosolids disposal, siloxanes in the biosolids may further volatilize or be catalytically hydrolysed and/or degraded (Traina et al. 2002; Xu 1999; Dow Corning 2005; European Commission 1999, 2000). In the upper atmosphere, VMS are photochemically decomposed via a hydroxyl-radical mechanism to intermediate silanols and ultimately to amorphous silica (SiO_2), carbon dioxide and water (Dewil et al. 2006).

Table 2 presents typical VMS concentrations found in the main stages of wastewater treatment. Significant siloxane removal rates observed during the treatment process, as seen by comparing siloxane concentrations in plant influents and effluents, can be explained by the simultaneous volatilization and sorption processes (European Commission 1999; Parker et al. 1999; Traina et al. 2002). Anaerobic/anoxic and aerobic biodegradation of siloxanes and other silicon-oils was recently demonstrated; however, this process was not identified as a key mechanism in siloxane removal during the wastewater treatment process (Parker et al. 1999; Traina et al. 2002). In an anaerobic digester, volatilisation may be the dominant process, depending on the digester conditions (i.e., fermentation, temperature, feeding, foaming phenomenon, residence time). Anaerobic digesters typically operate under mesophilic conditions. These conditions ($35\text{--}38^\circ\text{C}$) favour siloxane desorption from solids, and their subsequent volatilisation. Furthermore, higher digester operating temperatures, feeding frequencies, and solids retention times, have all been shown to increase biogas production in anaerobic digesters (Urbanic et al.

Table 2. Reported VMS concentrations in WWTP.

Sampling point	Unit measure	Siloxanes*						Reference
		L2	L3	D3	D4	D5	D6	
Influent	$\mu\text{g/L}$	<0.14	<0.014	–	<3.7	<26	<3.8	Kaj et al. (2005)
Sludge	$\mu\text{g/kg dw}^{**}$	<0.5–3	<1–64	–	96–960	1100–89000	220–11000	
Sludge cake	$\mu\text{g/kg dw}$	–	–	–	<80–500	–	–	European Commission (1999)
Effluent	$\mu\text{g/L}$	<0.0005	<0.0005	–	<0.06	<0.04	<0.04	Kaj et al. (2005)
Digester biogas	mg/m^3	0.007–0.030	0.026–0.030	0.329–0.742	2.91–4.12	36.74–41.48	<0.073–0.979	Monteith et al. (2006)

*L2 = hexamethyldisiloxane; L3 = octamethyltrisiloxane; D3 = hexamethylcyclotrisiloxane; D4 = octamethylcyclotetrasiloxane; D5 = decamethylcyclopentasiloxane; D6 = dodecamethylcyclohexasiloxane.

**dw = dry weight.

2007) and thus the amount of siloxane entrained in the gas. The presence of foam is known to increase the solid-liquid contact area and favours oil desorption (i.e., siloxane), while the breaking of the gas bubbles due to their internal pressure favours the volatilisation (Parnian and Ayatollahi 2008). Grümping et al. (1999) demonstrated anaerobic biodegradation of siloxane (octamethylcyclotetrasiloxane) in anaerobic sludges; however, this phenomenon was observed in long-time batch culture experiments (100 d). Typical sludge residence (retention) times in anaerobic digesters are much shorter. Graiver et al. (2003) state that siloxane evaporation rates from soils can be 2–20 times faster than their biodegradation in soil, thus biodegradation may be incomplete. It follows that anaerobic digestion conditions favour the volatilisation of siloxanes, rather than their biodegradation.

SILOXANE CHARACTERISTICS

The generic term “siloxanes” refers to the class of organo-metallic compounds, characterized by “Si-O-Si” linkages. The most common siloxanes in biogas are VMS (volatile methylsiloxanes), which have two methyl groups attached to each silicon atom (sp³ – hybridisation). VMS identified in biogas are cyclic (denoted “D”) and linear (“L”) such as hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5) and dodecamethylcyclohexasiloxane (D6), as well as hexamethyldisiloxane (L2) and octamethyltrisiloxane (L3), respectively (Wheless and Pierce 2004; Monteith et al. 2006). Non-volatile siloxanes such as PDMS are not expected to be present in biogas (Dewil et al. 2006; Appels et al. 2008).

Chemical structure and chemical-physical characteristics for the above-mentioned siloxanes are presented in Table 3. VMS have relatively low molecular weights (up to 450) and are oily colourless liquids at ambient temperature, with the exception of D3, which is a solid. Cyclic siloxanes (D3, D4 and D5) have the melting point above 0°C. The higher vapour pressure values observed for L2, L3 and D3 suggests that these siloxanes tend to volatilise earlier during the wastewater treatment itself. In contrast, the lower vapour pressure of D6 suggests that D6 tends to remain in sludge (Dewil et al. 2007; Appels et al. 2008). These observations could explain the lower L2, L3, D3 and D6 concentration found in biogas, compared to D4 and D5 (Monteith et al. 2006). As can be seen in the Table 2, siloxanes D4 and D5 are the most dominant siloxane species present in biogas.

VMS are characterised by chemical and thermal stability, low viscosity and very low solubility in water (usually <1, mg/L) (Huppmann et al. 1996; Varaprath et al. 1996; Latimer et al. 1998; Kochetkov et al. 2001). These characteristics suggest that removal methods based on decomposition reactions may not be effective. The high dissociation energy of the silicon-oxygen bond is noted below (Lowry and Richardson 1987). It should be noted that siloxane has the property to form colloidal dispersions under agitated conditions, resulting in an increased

siloxane aqueous solubility (Varaprath et al. 1996; Kochetkov et al. 2001; Soreanu et al. 2009). This phenomenon should be considered as a possible removal mechanism where applicable.

Bond type	Si-O, C-H > C-O, C-C > Si-H, Si-C > Si-Si
Bond energies, kcal/mol	103, 100 > 84, 81 > 72, 69 > 45

(the bonds involved in siloxane molecule are represented in bold)

However, siloxanes are soluble in many organic solvents, such as toluene, acetone, methanol, heptane, hexane, methylisobutyl ketone, etc. (Huppmann et al. 1996; Parker et al. 1999; GE Silicones 2001b; Graening 2003), which suggests that physical removal methods, such as absorption, could be effective.

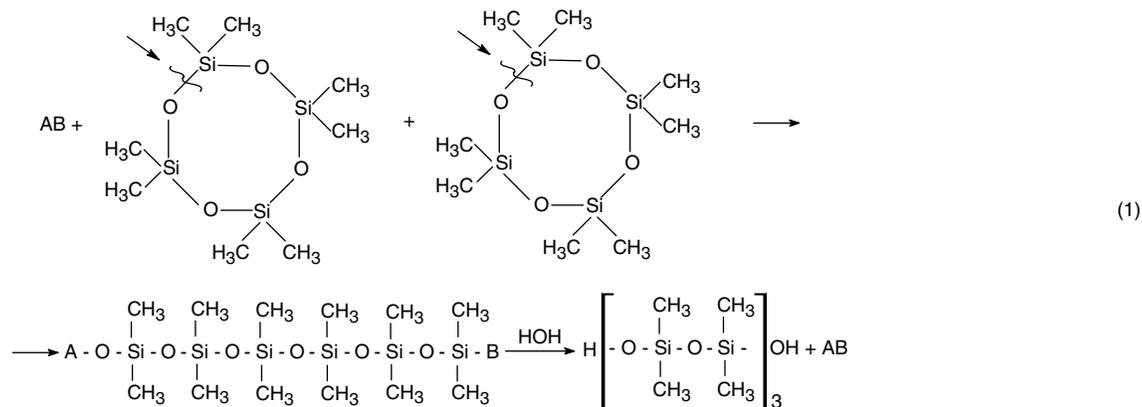
In addition, VMS are highly volatile from water, as indicated by a high Henry’s Law constant (>2.4). This characteristic suggests that under normal conditions, siloxane biodegradation may not be favoured. A relationship between the Henry constant and the molar volume of linear and cyclic dimethylsiloxanes (i.e., L2-L4, D4-D6) was determined by Kochetkov et al. (2001). These authors showed that the vapour pressure of siloxanes decreases with the molar volume, which in turn determines the partition of siloxanes at the air-water interface and thus the aqueous solubility. Yang et al. (2007) and Soreanu et al. (2009) also showed that the time to equilibrium of the hydrophobic compounds in a three phase system (gas-liquid-solid) increases with their molecular weight. Hamelink et al. (1996) reported that environmental co-solutes such as humic acid may further increase Henry’s law constant. VMS possess a high affinity for soil and are hydrophobic, as indicated by a high log octanol/water partition coefficients (>4) (European Commission 2000; Kochetkov et al. 2001). Therefore, physical adsorption could be also another effective removal method.

REACTIONS OF SILOXANES

Siloxane removal via physical processes (adsorption, absorption) is not subject to siloxane reaction. In contrast, in biological systems (i.e., anaerobic digesters, bioreactors for siloxane removal) siloxane molecules may undergo polymerization or alternatively may degrade depending on the conditions of their environment. These reactions typically occur under catalytic conditions (i.e., chemical, enzymatic) (Zeigler and Fearon 1990; Colas and Curtis 2004; Brandstadt 2005). Water and silanols may retard polymerisation (Zeigler and Fearon 1990; Jones et al. 2000). Hazardous polymerisation was reported for siloxane D3 (GE Silicones 2001b).

Polymerization of cyclic siloxanes

Cyclic siloxanes undergo ring-opening reactions, which occur via a radical-ionic mechanism (Eq. 1), which lead to the breakdown of Si-O bonds forming straight chain polysiloxanes (adapted from Zeigler and Fearon 1990).



where AB=initiator may be acidic (e.g., acid clays, H₂SO₄, CF₃SO₃H, HI₃, HF, HCl-FeCl₃,) or basic (e.g., GOH, GOR, GOSi, GR, GSR) where G =alkali metal, NH₄⁺ or PH₄⁺ (quaternary ammonium or phosphonium group); R =alkyl, polystyryl or poly(trimethylsilylvinyl).

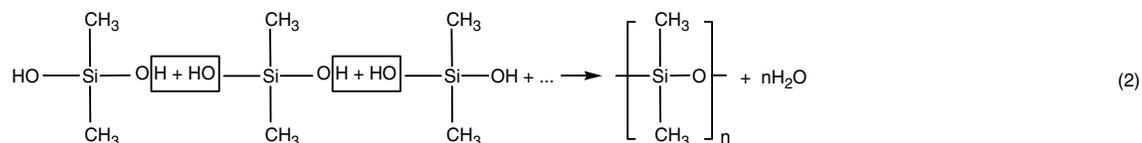
hydroxylation of a methyl group to a hydroxymethyl group and subsequent oxidation to a formyl group (Grümping et al. 1999; European Commission 1999; Sabourin et al. 1996; Prescott et al. 2003).

Formation of linear siloxanes by condensation of dimethylsilanediol

Dimethylsilanediol (DMSD) is a product of the degradation of cyclic siloxanes (Grümping et al. 1999; European Commission 1999). DMSD may form linear siloxanes via the elimination of a water molecule by the reaction of silanol groups as shown in the Eq. 2. (Rice University 2007)

METHODS FOR SILOXANE REMOVAL FROM BIOGAS

Potential methods for the removal of siloxane from biogas are presented in Table 4. Conventional methods are based on the adsorption of siloxane on the surface of adsorbent materials. Other existing methods for siloxane removal include gas-liquid absorption and separation by refrigeration and condensation. Recently, membrane separation and biological degradation have been considered.



Degradation of siloxanes by peroxidation

Appels et al. (2008) investigated the use of the oxidation techniques (Fenton oxidation, peroxidation with peroxy monosulphate and peroxidation with dimethyldioxirane) for removing siloxanes from waste activated sludge prior to digestion. In this reaction, siloxanes are converted to lower molecular weight siloxanes, silicones and silica. Moreover, the EPS of the sludge flocs are destroyed, enhancing the liberation and the volatilisation of the siloxanes. The most effective oxidant was found to be dimethyldioxirane, resulting in 85% of siloxane D4 removal, versus 50% D4 and D5 removal using the other reagents. Gas purification could also be used as a polishing step to further reduce the final siloxane concentrations.

Many technologies employ a combination of methods in order to increase system performance (i.e., refrigeration/condensation and activated carbon; refrigeration/condensation and gas-liquid absorption and activated carbon). Apart from physical methods, biological methods offer potential in the field of siloxane removal from biogas. Biotechnologies such as biofiltration are cost-effective for treating gases with trace contaminants, such as biogases. Some practical and technological considerations of these methods are presented below.

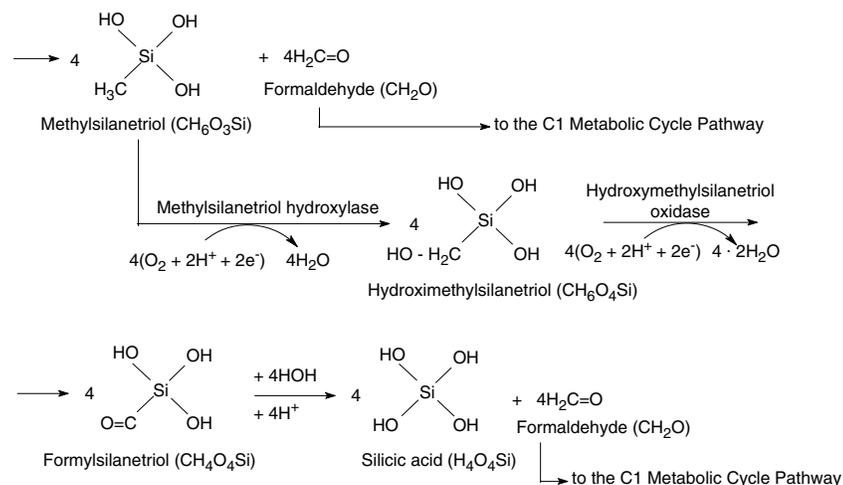
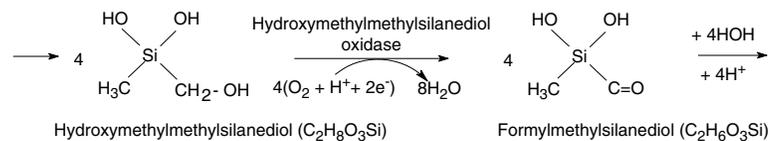
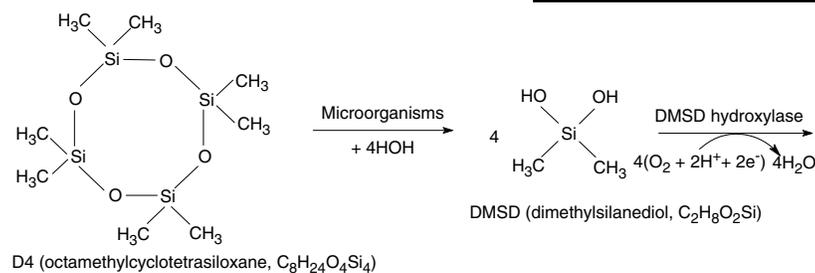
Biological degradation of siloxanes

Biodegradation of siloxanes (Eq. 3, adapted from Feng 2008) occurs with the formation of silicic acid, carbon dioxide and water as final products, via diols (i.e., DMSD), silanetriols and formaldehyde as the intermediate products. The degradation mechanism involves the

Gas-solid adsorption

Adsorption process occurs via physical attraction of siloxane molecule to an available site on the external and internal solid surface of an adsorption material. The accessibility of siloxane molecules to the internal adsorption surface depends on the pore size of the adsorbent.

For the purpose of biogas treatment, adsorbents are typically placed in columns, custom sized based on the sorption capacity of the adsorbent material and the siloxane concentration in the influent gas. The sorption



(3)

capacity of the adsorbent decreases as more and more of the sorption sites are occupied during the treatment process. As a result, after a defined period of operation called the “breakpoint time”, the siloxane concentration in the effluent biogas will increase. Once saturated, regeneration or replacement of the adsorbent is required. Recovered adsorption capacity after regeneration is usually 5–25% less than the initial capacity (Schweigkofler and Niessner 2001; Manocha et al. 2003).

Many types of adsorbents, silicon or carbon-based materials, are suitable for the removal of siloxanes from gas streams (Fig. 2). Physical properties of these types of adsorbents are presented in Table 5. The performance of the most common adsorbents for siloxane removal from biogas can be rated according to the scale below. In addition, Schweigkofler and Niessner (2001) showed that such adsorbents exhibit higher adsorption capacity for the cyclic siloxanes (i.e., D5) than for the linear siloxanes (i.e., L2). In the following section, their applications in biogas cleaning processes are discussed and commercial applications presented where applicable.

Siloxane adsorption

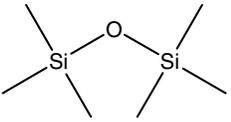
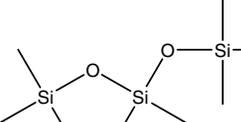
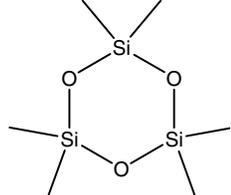
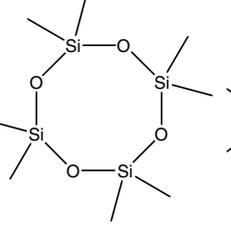
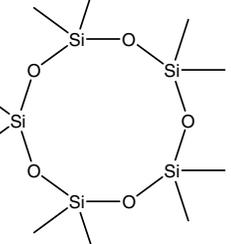
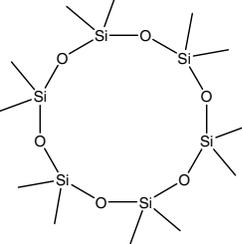
Activated carbon < Molecular sieves < Silica gel

Methane adsorption

Activated carbon > Molecular sieves > Silica gel

Adsorption on activated carbon Activated carbon is unlike other adsorbents due to its high surface area (600–1600 m^2/g) and porosity (Mycock et al. 1995). Activated carbons are versatile adsorbents, due to their non-uniform pore size distribution and shape (Manocha 2003). Activated carbon has non-polar characteristics, thus it preferentially adsorbs non-polar molecules and/or molecules with small degrees of ionisation (Mycock et al. 1995; Barton et al. 1999). As a result, activated carbon materials are suitable for adsorption of organic molecules such as siloxanes. However, activated carbon, used for the treatment of biogas, may also interact with methane, leading to a decrease in the adsorption capacity and methane content in the biogas itself. Methane adsorption on activated carbon is two times greater than on zeolite (Yang 2003). Alternatively, specially treated activated carbon can be manufactured, which does not remove methane from

Table 3. Chemical-physical characteristics of principal siloxanes present in biogas.

Characteristics	Siloxanes					
	Hexamethyl- disiloxane (L2)	Octamethyl- trisiloxane (L3)	Hexamethylcyclo- trisiloxane (D3)	Octamethylcyclo- tetrasiloxane (D4)	Decamethylcyclo- pentasiloxane (D5)	Dodecamethylcyclo- hexasiloxane (D6)
CAS No.	107 46 0	107 51 7	541 05 9	556 67 2	541 02 6	540 97 6
Structure*						
Formula	C ₆ H ₁₈ OSi ₂	C ₈ H ₂₄ O ₂ Si ₃	C ₆ H ₁₈ O ₃ Si ₃	C ₈ H ₂₄ O ₄ Si ₄	C ₁₀ H ₃₀ O ₅ Si ₅	C ₁₂ H ₃₆ O ₆ Si ₆
Physical state, appearance, odor	Liquid, clear colourless, odourless	Liquid, ^f clear, colourless, odourless	Solid, white, hydrocarbon odor	Liquid, ⁱ oily, clear, ⁱ colourless, odourless	Liquid, ^f clear, oily	Liquid, ^f clear, colourless, faint odor
Molecular weight	162.38	236.54	222.47	296.61	370.80	444.93
Boiling point, °C	101	153	135	175.5	210	^a 245
Melting point, °C	-59	-82	64	17.5	7.5	^a -3
Water solubility, mg/L at 23°C	^b 0.93	^b 0.034	^b 1.56	^b 0.056	^b 0.017	^b 0.005
Vapour density (air = 1)	^c 5.5	8.16	^h 8	>1	-	-
Viscosity, cP at 25°C	^a 0.86	^a 1.2	-	^a 2.6	-	-
Vapour pressure, mm Hg at 25°C	^a 42.2	^a 3.90	^g 3.53	^g 1.05	0.20	^a 0.049
Evaporation rate (butyl acetate = 1)	^a 3.8	^a 0.7	>1	^a 0.2	-	<1
Henry's Law Constant, dimensionless	^d 2.4±0.2, at 27°C	^d 121±12, at 27°C	-	^d 24±3, at 28°C	^d 12±2, at 26°C	^d 5.9±2.9, at 26°C
Log P _{ow} **	^e 4.2	^g 4.8	^g 4.47	^g 5.1	^g 5.2	^j 5.86
Reference	Acros Organics 2004a	Acros Organics 2004b	GE Silicones 2001b	Gelest Inc. 2003	James 2000	Dow Corning 1999
Other references	^a EPA 2004; ^b Varaprath et al. (1996); ^c GE Silicones 2001a; ^d Kochetkov et al. (2001); ^e European Commission 2000; ^f Kaj et al. (2005a); ^g ChemFinder Database; ^h Acros Organics 2005a; ⁱ Acros Organics 2005b; ^j Schweigkofler and Niessner (2001)					

*Chemdraw 9.0 Software.

**P_{ow} = octanol/water partition coefficient.

Table 4. Methods for siloxane removal from biogas.

Method	Scale	Siloxane removal efficiency, %	Estimated* operating cost (\$/m ³ h ⁻¹ treated gas)	Advantages	Disadvantages
Solid adsorption (activated carbon, zeolites, molecular sieves, silica gel etc.)	Full	^a 90–99	Medium	Simplicity High adsorption capacity High degree of regeneration possible (heating, solvents) Increased performance possible via multiple columns in parallel Can be used for biogas drying (except activated carbon) Low-medium costs Efficiency increase by the type of contacting phase (counter-current etc.)	Loss of adsorption material by regeneration process Minimum two units are necessary (i.e. one in use while second is undergoing regeneration) Risk of pressure drop Activated carbon not suitable for humid gases
Liquid absorption: (methanol, Selexol, etc.)	Full	^a 97– ^b 99	High	Simplicity Low reagent cost Non-toxic	High operational costs High solvent toxicity Environmental impact High energy required for regeneration (heating or distillation) Flammability of solvents Risk of corrosion Dangerous to handle and transport Difficult to regenerate High energy consumption
Degradation (sulfuric acid 97%)**	Laboratory	^c 95–99 (60°C) 56–70 (room temperature)	Medium	Simplicity Low reagent cost Non-toxic	Risk of low efficiency Loss of material by regeneration process Risk of fouling Risk of pressure drop
Refrigeration/ Condensation	Full	^b 15–50 (35–40°F) 95 (–20°F)	High	Simplicity Low reagent cost Non-toxic Can be used for biogas drying No media for disposal	Risk of fouling Risk of pressure drop Risk of membrane destruction (by chemical, pH, excess pressure) Risk of pressure drop
Biotrickling filtration	Laboratory	^d 10–20 ^e 10–43	Low	Simplicity Economical Ecological Low operational costs Can be regenerated	Risk of fouling Risk of pressure drop Risk of membrane destruction (by chemical, pH, excess pressure) Risk of pressure drop
Membrane	Laboratory	–	Medium	Simplicity Large surface area and small volume	Risk of fouling Risk of membrane destruction (by chemical, pH, excess pressure) Risk of pressure drop
Reference	^a Huppmann et al. (1996); ^b Wheless and Pierce (2004); ^c Schweigkofler and Niessner (2001); ^d Accettola et al. (2008); ^e Popat and Deshusses 2008				

*Scale semnification (\$/m³h⁻¹ treated gas): 1–8 (low); 8–20 (medium); >20 (high) (Jorio and Heitz 1999).

**Degradation with mineral acid is a common technique used in analytical sample preparation and will not be detailed in this paper.

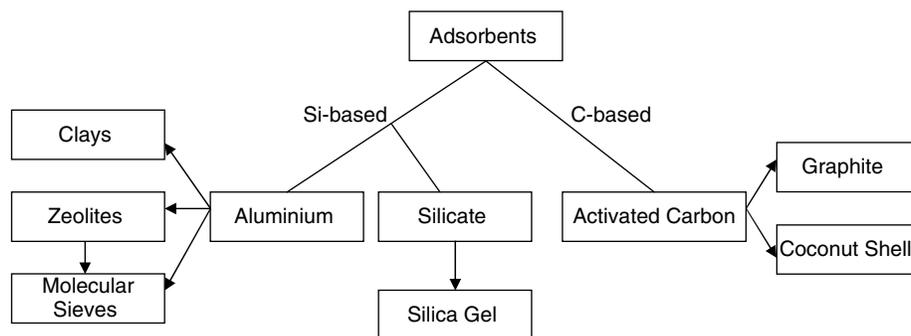


Fig. 2. Adsorbents for siloxane removal from biogas.

biogas, and thus is a possible adsorbent for biogas treatment. Activated carbon is found to be more effective for the adsorption of cyclic siloxanes over linear siloxanes (Wheless and Pierce 2004). Regeneration of exhausted adsorbent is carried out thermally (Miguel et al. 2002; Yang 2003). The desorption of siloxanes is often incomplete and therefore frequent replacing of the adsorbent is required (Dewil et al. 2006).

The performance of an activated carbon system depends on several factors, the most significant being the water content in the biogas. In a typical biogas treatment set-up, activated carbon systems are combined with other pre-treatment methods for water removal, such as refrigeration/condensation (Fig. 3), described later (Refrigeration/Condensation Section). The removal of water from biogas prior to an activated carbon unit significantly increases the activated carbon life and the system performance. According to Wheless and Pierce (2004), activated carbon can adsorb between 5,000 and 15,000 mg siloxanes/kg carbon, from compressed and dried digester gas (70–365 psig and 40°F dew point). These quantities correspond to an adsorption capacity of 0.5 to 1.5% siloxanes by weight.

Combined systems based on refrigeration/condensation and adsorption are currently in operation at Calabasas Landfill microturbines (Agoura, California). Biogas produced at flow rates between 150 and 180 ft³/min containing siloxane typically around 0.3 ppmv is compressed to 90 psig and chilled to 4.4°C in order to remove water, and to partially decrease its siloxane content (i.e., to 0.2 ppmv). The cooled gas is reheated to 15.5°C with compressed landfill biogas prior to the adsorption system. Two activated carbon vessels (i.e., graphite, coconut shell-based) are used to remove trace amounts of siloxanes remaining in the biogas after the refrigeration/condensation unit (Iacobini et al. 2004).

GEW RheinEnergy fuel cell plant (Cologne, Germany) uses a chilling/adsorption system to treat biogas produced at 110 m³/h. Very low siloxane concentration (<1 mg/m³) is detected in the outlet gas. The system uses a –30°C chilling gas temperature for this high removal performance (Accettola et al. 2008).

A commercially available process (SAGTM, patent pending) was developed by Applied Filter Technology, Snohomish, WA. The removal of siloxane takes place in two vessels (13.3 m³ capacity for each) equipped with a modified polymorphous graphite media with high affinity and selectivity for siloxane. According to Tower and Wetzel (2004), the system is able to treat biogas at a flow rate range between 1700 and 2800 m³/h at input siloxane concentration ranges between 0.58–1 mg D5/m³ and 4.52–13.0 mg D4/m³, respectively, over the course of few months. SAGTM adsorption systems are currently in operation at several sites in United States for purification of digester biogas (www.appliedfiltertechnology.com).

In an analytical application, Huppmann et al. (1996) reported that the desorption of cyclic siloxane (i.e., D4) adsorbed on activated carbon with hexane is less effective than for other sorbent materials (XAD resins) under the same conditions, but can be improved to 90% using ultrasonification. Schweigkofler and Niessner (2001) reported incomplete desorption of cyclic siloxane D5 (74–83% recovery) by thermal regeneration at 250°C, in comparison to efficient desorption (>95%) from silica gel under the same conditions. They also observed that thermal desorption of higher volatile linear siloxane L2 was possible with high efficiency (>95% recovery) for both silica gel and activated carbon.

The cost of siloxane removal using these types of systems is largely dependent on the inlet siloxane concentration in the biogas and the required frequency of recharging the packing bed. According to Wheless and Pierce (2004), operational costs are considered acceptable

Table 5. Physical properties of representative adsorbents (Mycock et al. 1995).

Adsorbent	Structure	Polarity	Internal Porosity, %	Surface area, m ² /g	Mean pore diameter, nm
Activated carbon	Amorphous	Non-Polar	55–75	600–1600	1.5–2.0
Molecular sieve	Crystalline	Polar	40–55	600–700	3.0–9.0
Silica gel	Amorphous	Polar	70	750	2.2

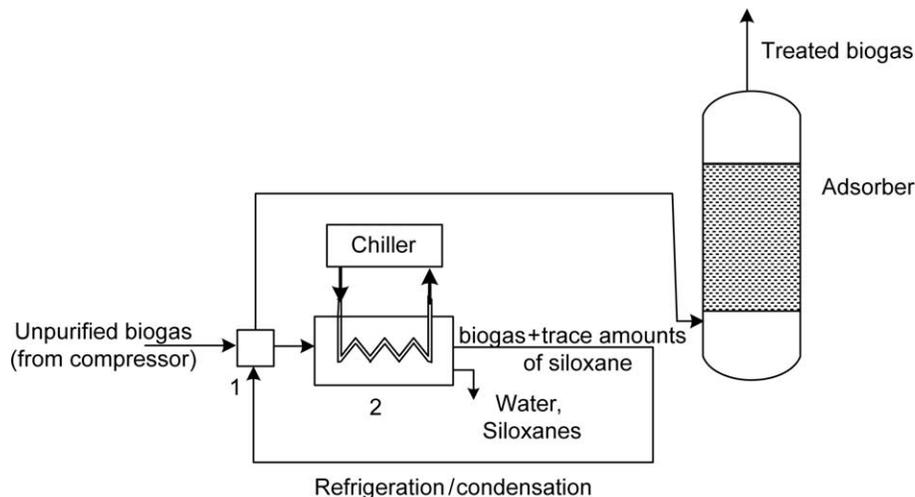


Fig. 3. Schematic diagram of biogas treatment for siloxane using refrigeration/condensation and adsorption. 1 = gas to gas heat exchanger; 2 = gas to liquid heat exchanger (adapted from Köhler and Ziegler Anlagentechnik GmbH 2010).

for very low inlet siloxane concentrations (up to 2 mg/m³); however at higher concentrations, the refrigeration/condensation and activated carbon process becomes costly. As an example, the system currently in operation at GEW RheinEnergy's fuel cell plant initial cost was \$107,000 with an estimated \$16,300/year in maintenance costs over a 10 year period (Accettola et al. 2008).

Adsorption on molecular sieves Molecular sieves are hydrous aluminosilicate minerals of the chemical formula Na₂O·Al₂O₃·nSiO₂·xH₂O, which are characterized by a three-dimensional crystalline regular porous structure and ionic exchange capacity (Hawley 1977). Molecular sieves preferentially adsorb molecules with high polarity and, thus, are comparable in water vapour adsorption (12–28% by weight) with silica gel (Ackley et al. 2003). Molecular sieves are capable of removing water molecules, siloxanes and other contaminants (CO₂, H₂S) from gases even at very low concentrations such as 1 ppm (1 mg/m³). Their adsorption capacity can be up to 2–3% siloxanes by weight (PpTek Ltd. 2004; Ackley et al. 2003).

The use of appropriate molecular sieve adsorbent materials could be an attractive option for biogas treatment because of their capability of performing selective removal of contaminants from gas streams, without splitting gas molecules. Siloxane molecules with specific geometry (e.g., siloxane D4-octahedral vs. siloxane D3-hexagonal) could be separated on molecular sieves having similar geometry and pore volume (i.e., octahedral, hexagonal, etc.). In addition, siloxane and methane molecules could be selectively separated on the basis of their molecular size. For example, siloxane molecules (i.e., D4) are considerably larger than methane molecules (i.e., 1 nm, vs. 0.381 nm, respectively) (Radhakrishnan and Gubbins 1997; Tartaglino et al. 2002). Methane molecules will pass through pores and will not be retained. Adsorption forces are strongest in pores having a size not more than twice the size of the contaminant molecule (Mycock et al. 1995).

PpTek Ltd. Advanced Purification Technology, UK, has developed a filter packed with molecular sieve granules for the removal of siloxanes, water and other corrosive contaminants from biogas. The filter is composed of a 700 kg packing bed with an adsorption capacity of more than 10 kg siloxanes (i.e., 14 g siloxanes/kg packing). Regeneration of the saturated packing bed is carried out by heating at elevated temperatures (i.e., greater than the boiling point of siloxanes), to remove both water and siloxanes. The packing bed can be regenerated 40–50 times before it is replaced. This system can treat siloxane-rich biogas (i.e., 50 mg/m³ siloxanes) with high removal efficiency (<1 mg/m³ siloxanes as L3, D4 or D5 in treated gas) (PpTek Ltd. 2004).

Another recently patented system (Donald et al. 2008) was designed for the treatment of biogas at a flow rate of 150 m³/h, maximum 45% RH and maximum 2 ppmv (approximately 12 mg/m³) input siloxane concentration (L2, L5, D3 and D6) for a 1 year period. The system consists of a coalescing prefilter (14 kg, 1194 mm height, 178 mm width, 178 mm depth) for the removal of aerosols/mists and two adsorption vessels (394 kg, 2692 mm height, 915 mm width, 915 mm depth) in series for siloxane removal. The coalescing prefilter is equipped with a borosilicate filter that has a retention capability of 99%. The first adsorption vessel is fully packed with activated carbon, while the second vessel is packed with 50% activated carbon, 25% silica gel and 25% 13X molecular sieve at the end. The prefilter reduces the oil mist content from 2 ppmv to 0.1 ppmv and the outlet siloxane concentration after the adsorption unit is <2 ppbv.

It should be noted that adsorbates adhere very strongly to molecular sieves making desorption difficult (Yang 2003). Regeneration is based on thermal desorption, however, due to the complexity of the process, regeneration of relatively inexpensive materials is rarely performed in practice. Instead, they are usually discarded and/or incinerated.

Adsorption on silica gel Silica gel is an amorphous substance having the molecular formula $(\text{SiO}_2) \cdot n\text{H}_2\text{O}$, commonly used as a desiccant due to its high affinity for water. In contrast to activated carbon, silica gel exhibits polar characteristics; thus, it preferentially retains polar molecules. Siloxane molecules will be retained on silica gel based on their partial polar character, due to $-\text{Si}-\text{O}-\text{Si}-$ bonds. Silica gel, therefore, can selectively retain organic substances. The adsorption force of silica gel is weaker than for zeolites/molecular sieves and thermal regeneration of spent silica gel is more easily achieved (Yang 2003). The interactions (H bridge) between siloxane molecule and silica gel is schematic represented in the Fig. 4.

The use of silica gel for siloxane and moisture removal from biogas was recently reported (Schweigkofler and Niessner 2001; Wheless and Pierce 2004). Schweigkofler and Niessner (2001), determined silica gel adsorption capacities of approximately 100 mg/g for siloxanes, which is about 10 times greater than activated carbon's adsorption capacity for siloxane. In addition, thermal regeneration of silica gel was found to be more cost-effective than activated carbon, thus in a real application, silica gel appears to have more potential than activated carbon for siloxane removal from biogas. However, Schweigkofler and Niessner (2001) report that relative humidity (i.e., $>20\%$ RH) in processed gas drastically affects the adsorption capacity of silica gel for siloxanes.

An adsorption unit packed with silica gel, designed for biogas drying at a sewage treatment plant, in Munich, Germany, was tested for siloxane removal in biogas (Schweigkofler and Niessner 2001). Similar to previously described activated carbon systems, the adsorber was tested with pressurised biogas (approx. 5 bar or 72 psig), in combination with a refrigeration condenser. The chilled biogas was passed through a silica gel adsorber, where siloxane removal took place. This system showed a removal efficiency of greater than 98%, for siloxanes D3, D4 and D5. After bed depressurization, the silica gel was regenerated via a stream of counter-current hot air.

Refrigeration/Condensation

At freezing temperatures and at reduced pressures, a portion of the compounds present in biogas condense and can be separated. This popular method is simple and can be used to remove both siloxanes and water from biogas. However, the high costs due to high energy consumption can preclude the use of this technology. The unit consists of a heat exchanger or cooling chamber where the compressed gas is circulated and chilled by a coil system filled with freezing agent which is pumped and recycled from a refrigerator. A schematic diagram of a refrigeration/condensation system for the separation of siloxanes from biogas can be seen in Fig. 3. Typically, the refrigeration/condensation process is used as a gas pre-treatment prior to the use of activated carbon (Fig. 3).

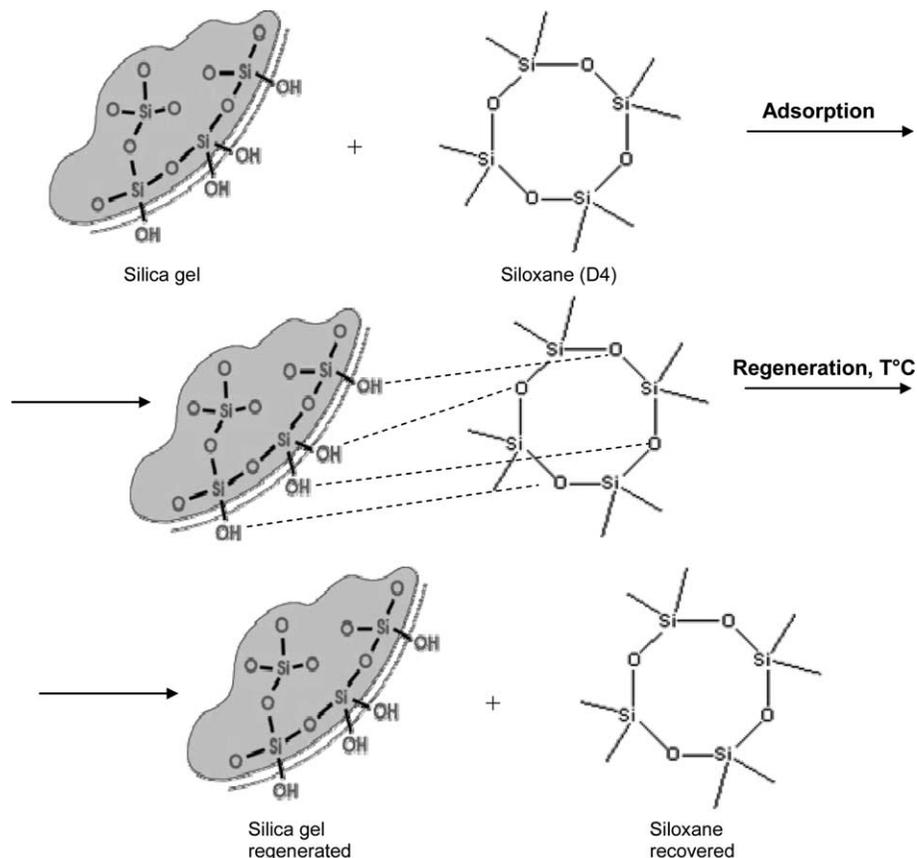


Fig. 4. Interaction between siloxane molecule and silica gel (adapted from <http://www.psaplants.com/silica-gel.html>).

It has been noted that refrigeration/condensation itself cannot normally achieve adequate siloxane removal. It is anticipated that the cooling unit used for retention of the siloxanes would be difficult to clean, however, no mention of this issue could be found.

Wheless and Pierce (2004) report that the performance of a refrigeration/condensation system can vary from low-moderate (15–50% siloxane removal) to high efficiency (95%), depending on the chilling temperatures employed (i.e., 1.6–4.4°C and –28.8°C, respectively). Schweigkofler and Niessner (2001) investigated several methods for siloxane removal from biogas and found that refrigeration demonstrated lower performance for siloxane removal than adsorption methods.

In practice, a satisfactory compromise between price and removal efficiency is difficult to achieve for treating siloxane-rich biogas. On the positive side, this technology is non-toxic and does not require disposal of its adsorption media as does the activated carbon method.

A refrigeration/condensation installation for siloxane removal from digester biogas was developed by Pioneer Air Systems and is in operation at the Los Angeles County Districts, USA. The installation is designed to remove 90% of siloxanes and consists of a several stage condenser that cools the biogas to approximately –23°C (www.pioneerair.com). Other refrigeration/condensation applications were previously discussed.

Membrane separation

In comparison with other separation methods, unique to membrane separation is the fact that the solid material (i.e., membrane) can be a very thin sheet, usually in the range of 0.2–2 µm, and the volume occupied by the membrane module is significantly lower than for other methods (Strathman et al. 1986; Meinema et al. 2005). Membranes can be polymeric or inorganic and are characterized by large surface areas for separation while occupying a small volume, whereas other separation materials are larger and can contribute to higher operational costs (Strathman et al. 1986). The permeability and selectivity of a membrane towards a certain molecule depend on both pore size and molecular interactions (Pandey and Chautan 2001; Meinema et al. 2005). The regeneration of membranes is usually achieved by purging off the contaminants with an inert gas or by using a solvent. Under adequate conditions, the membrane life can be 2–3 years (Strathman et al. 1986; Meinema et al. 2005).

Membrane systems currently in use for biogas treatment (IEA Bioenergy 1999) are either high pressure membrane systems which require pressurised gas to allow the gas to pass through membrane (e.g., 36 bar) or low/atmospheric pressure membrane systems in which molecules are separated by the diffusion of gas molecules through a selective microporous hydrophobic membrane and absorption in a specific absorbent (Fig. 5).

Membrane systems require pre-cleaning of the biogas prior to introduction to the membrane system, in order to protect the membrane against harmful compounds from

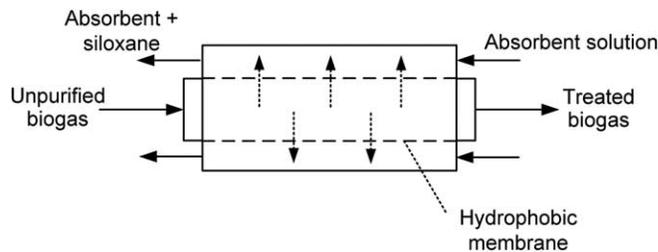


Fig. 5. Siloxane separation technique by gas-liquid absorption using membrane.

biogas such as hydrogen sulphide, oil vapours from compressors (i.e., for high-pressure membrane systems) or any particles in the biogas if present (IEA Bioenergy 1999). These compounds can damage the membrane by acidic conditions, mechanical destruction and fouling, respectively.

Recently, membrane separation has been considered for siloxane removal from biogas and to date only one preliminary report is available (Ajhar and Melin 2006). Ajhar and Melin (2006) have developed a PDMS (polydimethylsiloxane) membrane for selective siloxane removal from biogas. The simulated membrane selectivity for siloxane was 20 to 70 times more than for nitrogen. This membrane is also characterized by high water permeability, and is thus also suitable for water removal from biogas. This membrane can be also used for the removal of other harmful organic compounds such as BTEX (benzene, toluene, ethylbenzene and xylene) or halogenated hydrocarbons. Membrane separation was verified for siloxane D4 and further tests could be conducted for other principal siloxanes in biogas (i.e., linear and cyclic siloxanes).

In addition, fouling effects of siloxanes on membrane separators should be evaluated. The accumulation of siloxanes on the membrane surface may lead to pore blocking and membrane fouling, decreasing the membrane separation efficiency.

Membrane technologies are already in operation for CO₂ removal from biogas in The Netherlands and the USA (IEA Bioenergy 1999).

Gas-liquid absorption (scrubbing)

The treatment of biogas by gas-liquid absorption processes takes place via the transfer of contaminants from the gas phase into a liquid absorbent. This process can be achieved in a packed column (i.e., absorber or scrubber) via countercurrent contact between gas and absorbent solution (Fig. 6). The efficiency of the process depends on the packing surface area, the contact time and the solubility of contaminants in the absorbent solution. Commercialised packing materials (i.e., rasching ring, pall ring, berl saddle, tellerite) typically have dimensions between 10 and 80 mm and are constructed from plastic (i.e., polyethylene, polypropylene), porcelain, metal, stoneware, etc. These packing materials contain a void fraction between 63 and 95% and a surface area of 64 to 964 m²/m³pk (Mycock et al. 1995; Cooper and Alley 1986).

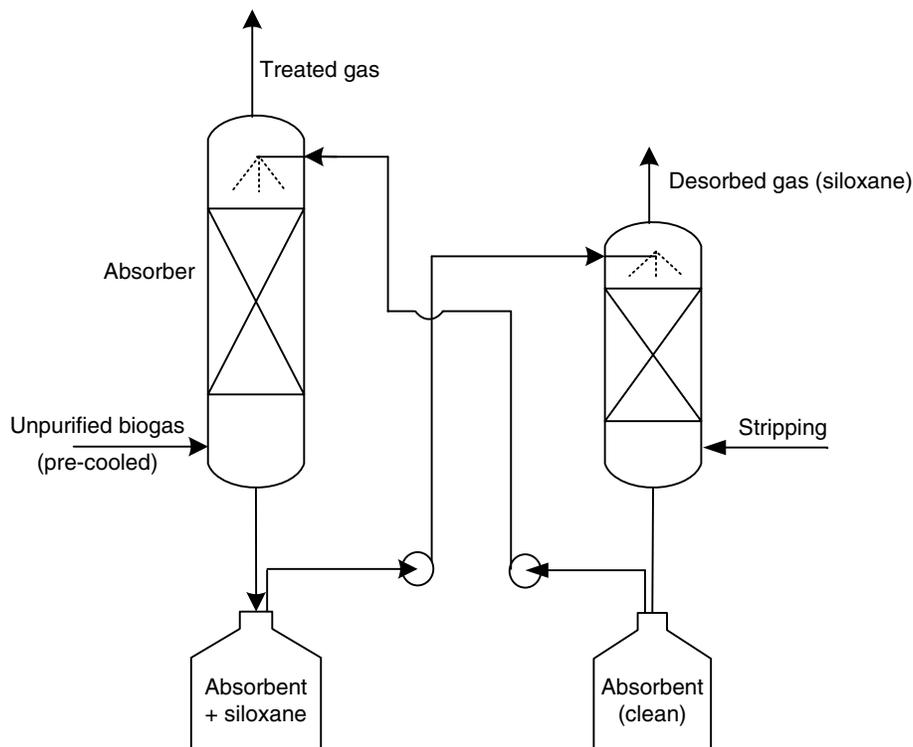


Fig. 6. Absorption system for siloxane removal from biogas with regeneration of waste absorbent solution (adapted from European Commission 2003).

Due to the chemical nature of siloxane, the most suitable absorbents for their removal from biogas are polar organic solvents. The use of solvents allows siloxane (and water) to be retained, while methane is not retained. The absorbent can be regenerated by heating, stripping or desorption (IEA Bioenergy 1999). The most popular solvent for application in biogas treatment is Selexol, a polyethylene glycol dimethyl ether, which can remove siloxanes as well as CO_2 and H_2S from biogases (Wheless and Pierce 2004; Maxwell 2004).

In practice, gas scrubbing systems often combine other pre- and post-treatment methods. Since the absorption process operates better at lower temperatures, gas is often cooled prior to the absorption stage. Activated carbon adsorption is also used as a polishing step after gas scrubbing.

The Köhler and Ziegler Anlagentechnik GmbH Company (Germany) has developed a gas scrubber with the ability to treat biogas for siloxane removal (Köhler and Ziegler Anlagentechnik GmbH 2010). Biogas is cooled prior to entering the scrubber. The absorbent may be either cold water or carbohydrite solution. In order to improve the mass transfer between the gas and liquid phases in the scrubber, the absorbent solution is sprayed as very fine particles on the packing filter counter-current to the flow of the siloxane-containing biogas. Siloxanes are retained in the absorbent solution and separated from the biogas. Activated carbon is recommended as a polishing step for optimal operation.

Siloxane removals up to 99% were reported for the Selexol unit. The remaining siloxane traces are removed in

an activated carbon unit (Wheless and Pierce 2004). According to Maxwell (2004), the Selexol unit can treat pressurized gases at 300 to 2000 psia feeding rates and at compositions up to 60% ($\text{H}_2\text{S} + \text{CO}_2$), v/v. This process takes place in a continuous counter-current solvent extraction tower where selective removal of contaminants takes place, based on their different solubility in Selexol solvent at different pressures. Regeneration of the solvent is carried out by evaporation or stripping with an inert gas. These systems are already in operation at Mountain Gate Landfill in Los Angeles at 1500 ft^3/min (Wheless and Pierce 2004). A full-scale application of the treatment of landfill biogas using an absorption process is also in practice in Dortmund-Huckarde, Germany (IEA Bioenergy 1999). Some patents related to the Selexol process application for H_2S and CO_2 removal are already available (Schubbert and Echt 2001).

Biological processes

The removal of gas phase contaminants by biological processes is a phenomenon that occurs at the liquid-biofilm interface and is dependent on the contaminant transfer from gas to liquid phase, dictated by the solubility of the contaminant in water. From this point of view, the application of biological processes for siloxane removal may be limited by the low solubility of siloxanes in water. On the other hand, some microorganisms are able to generate biosurfactants that increase the solubility of compounds, making biological processes possible (Accettola et al. 2008; Urum and Pekdemir 2004). Also, siloxane degradation rates may be improved using specific enzymes

i.e., silicase (Accettola et al. 2008; Brandstadt 2005; Müller et al. 2007).

Microorganisms such as *Pseudomonas* (*P. aeruginosa*, *P. fluorescens*, *P. Putida*), *Agrobacterium* (*A. radiobacter*), *Arthrobacter*, *Fusarium oxysporium* (a fungus) and indigenous microorganisms from sludge have been shown to degrade siloxane D4, dimethylsilanediol and other silicon organic compounds (Wasserbauer and Zadák 1990; Sabourin et al. 1996; Accettola et al. 2008). Some of these microorganisms have the potential for use in anaerobic siloxane removal, by carrying out anaerobic respiration using another electron acceptor (i.e., nitrate) instead of oxygen (Prescott et al. 2003; Candussio et al. 2005; Popat and Deshusses 2008).

Typical bioreactors used for gas treatment are bio-scrubbers (BS), biofilters (BF) and biotrickling filters (BTF). These systems have been described in Syed et al. (2006). In a biological system, the main siloxane removal mechanism is its biochemical transformation, other physical processes being only intermediary steps. According to Eq. 3, the main siloxane biodegradation products may be DMSD, silicic acid, water and carbon dioxide. These breakdown compounds are soluble in the aqueous phase contact solution (i.e., nutrient solution) and result in the liberation of the sorption sites of the packing media. Secondary reactions such as siloxane polymerization (Eq. 1) or diol condensation (Eq. 2) may also occur. It should be noted that the degradation product DMSD is non-volatile (Whelan et al. 2008), has long stability in aqueous solutions (Varaprath and Lehmann 1997) and is not expected to be present in the treated gas. DMSD can be further retained on adsorbents (i.e., styryl-divinylbenzene polymer, from which DMSD can be eluted with solvents (i.e., tetrahydrofuran), Varaprath et al. 2006).

To date, few studies have been carried out in the field of siloxane removal from biogas in bioreactors. This approach has been initiated and demonstrated at Profactor GmbH, Energy and Environmental Technologies, Austria. A laboratory-scale biotrickling filter was equipped with a 0.5 m height/0.07 m diameter packing bed composed of inert Pall Rings with 88% void volume and 350 m²/m³ specific surface (Accettola et al. 2008). The biotrickling filter was initially inoculated with an activated batch culture. A mineral medium was fed at the top of the bioreactor at a flow rate of 0.015 m³/h and co-current with air supplemented with siloxane D3. The biotrickling filter was tested at a constant loading rate (1.28 g m⁻³ h⁻¹), while biogas flow rate and siloxane concentrations were varied between 0.5 and 0.9 L/min and 77 and 46 mg D3/m³, respectively. Under these conditions, removal efficiencies up to 20% were obtained and the process performance increased with decreasing input siloxane concentration. The removal of trace compounds in such biosystems is always suspected to be physical, rather than biodegradation. In this study, no siloxane removal was observed in the absence of the biomass responsible for the biological process i.e., after the packing media was washed.

Popat and Deshusses (2008) investigated the D4 removal in aerobic and anaerobic (N₂) gas-phase BTF

(3.8 cm diameter, 390 mL packing volume), at a gas flow rate of 0.5 L/min and D4 concentration of 45 mg/m³. Cattle bone Porcelite (42% void volume, 3 mm piece diameter), having incorporated slow-release nutrients, was used as packing bed for the aerobic experiments, while lava rocks (58% void volume) were used for the anaerobic experiments. The BTF was initially inoculated with D4-degrading culture and activated sludge and continuously supplied with mineral solution at a rate of 0.185 m/h. Siloxane removal efficiencies of 10–43% were obtained, depending on the contact time and the mass transfer. According to the authors, the maximum possible D4 mass transfer rate in BTF is 30–100 mg m⁻³ h⁻¹. Comparable removal performances were observed under aerobic and anaerobic conditions. The analysis of CO₂ production confirmed that siloxane was biologically removed. For instance, the addition of a non-ionic surfactant (oleyl alcohol) in BTF enhanced the absorption capacity and the mass transfer rate of D4; however, no significant improvement of the biological performance was observed.

Other published studies present results of batch-culture experiments performed to determine the biodegradability of siloxanes or other silicon organic compounds, reaction mechanisms and biological degradation products (Wasserbauer and Zadák 1990; Sabourin et al. 1996; Lehmann et al. 1998; Stevens 1998; Grümping et al. 1999). Wasserbauer and Zadák (1990) reported the biodegradability of the silicones as a function of their molecular weight noting that higher molecular weight silicones (i.e., PDMS) are more biodegradable than low molecular weight silicones (i.e., Decamethyltetrasiloxane, Hexamethyldisiloxane, Octamethyltrisiloxane). Products of siloxane breakdown products were not identified in this study. Soreanu et al. (2009) investigated the siloxane partition in shaken flasks containing culture medium, solid media and D4 or D5 vapours in anaerobic gas-phase. Based on the silicon-mass balance, the dominant removal mechanism was abiotic (adsorption and absorption, including the formation of the colloidal siloxane), while the biological process accounted about 5–8% from the total removal efficiency (i.e., 44–82%). Only 3% D4 removal was obtained by Grümping et al. (1999) in anaerobic gas-phase non-acclimatised cultures after 3 months (DMSD identified as the main degradation product). In contrast, Popat and Deshusses (2008) observed complete D4 removal in aerobic acclimatised batch cultures after the same period of time (no siloxane removal in the control samples). According to these authors better performance can be expected when using bioreactors.

The uses of biological processes for biogas treatment must also take into consideration the presence of hydrogen sulphide in biogas. Biotrickling filters have already been demonstrated for the removal of hydrogen sulphide from biogas under anoxic conditions (Soreanu et al. 2008). Simultaneous removal of both hydrogen sulphide and siloxane by an anaerobic process could represent an attractive cost-effective alternative to more expensive conventional biogas treatment technologies.

CONCLUSION

Siloxanes have recently been identified as one of the most important barriers for using biogas as an alternative green energy source. These barriers include the economical impact due to the detrimental effects of siloxanes on gas engines, even at low concentrations. Siloxane removal from biogas can be achieved by a variety of methods. The success of each method is dependent on the careful consideration of both the characteristics of siloxane and the biogas itself, any chemical, physical and/or biological processes present, as well as the practical and technological aspects of the technology.

Existing technologies are mainly based on physical processes; however, these methods are expensive. A cost-benefit analysis is required when considering a combined activated carbon system with refrigeration/condensation for water removal from biogas. Despite its large surface area, activated carbon is less efficient in comparison to other sorbent materials such as molecular sieves or silica gel that are able to function as desiccants as well and can achieve water removal concurrently. Refrigeration/condensation systems can partially remove both siloxanes and water from biogas in a single unit, but are expensive to operate. Gas-liquid absorption requires pre-treatment of biogas in order to increase the system performance.

Future efforts should concentrate on the evaluation of existing methods, the analysis of possible improvements to these methods and in the development of new technologies. Membrane separation is not yet developed for siloxane removal from biogas, but may be a viable alternative to the existing technologies. Non-conventional biological methods have recently been considered for siloxane removal from biogas. Specific microorganisms can perform siloxane degradation under aerobic or anaerobic conditions. Siloxane removal from biogas by biological methods could represent a viable environmentally friendly alternative as the biodegradation of siloxanes regenerates the sorption sites on the adsorption media and even more so if it can be accomplished concurrently with the biological removal of hydrogen sulphide.

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List of abbreviations

- WWTP = wastewater treatment plant
 EPS = extracellular polymeric substances
 PDMS = polydimethylsiloxane
 DMDS = Dimethylsilanediol
 VMS = volatile methylsiloxanes
 L2 = Hexamethyldisiloxane
 L3 = Octamethyltrisiloxane
 D3 = Hexamethylcyclotrisiloxane
 D4 = Octamethylcyclotetrasiloxane
 D5 = Decamethylcyclopentasiloxane
 D6 = Dodecamethylcyclohexasiloxane.