# BIOGAS PRETREATMENT FOR COGENERATION

NEW JERSEY WATER ENVIRONMENT ASSOCIATION
SPRING CONFERENCE
ATLANTIC CITY

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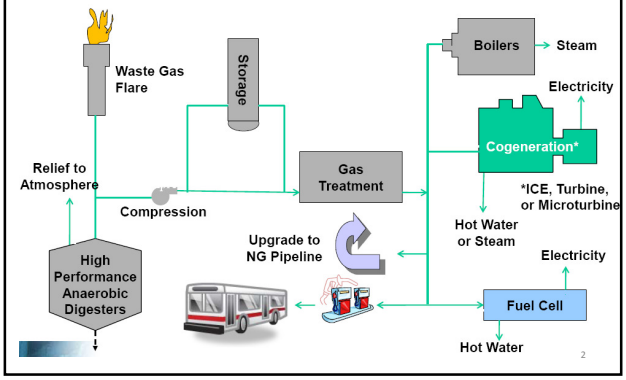
## Pretreatment Guided by End Use of Biogas

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## Why Biogas Should Be Treated?

- **Moisture:**
  - ❖corrosion, together with acid gases
- **Hydrogen Sulfide ($H_2S$):**
  - ❖ corrosion in mechanical moving parts of prime movers
  - ❖ breakdown of lubricants, leading to bearing, piston ring and seal failures
- **Siloxanes:**
  - ❖ scaling leading to failure of mechanical components
  - ❖ breakdown of lubricants, leading to bearing, piston ring and seal failures

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## Solid Deposits on Boiler tubes

(Ref. Applied Filter Technology)

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## Solid Deposits on Spark Plugs

**Deposits on spark plugs cause pre-mature failure, fouling, and misfiring**

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## Coated Piston Top

(Ref: Applied Filter Technology)

**This increases compression ratio and the piston rings do not expand during combustion due to the deposits on the top ring which leads to high oil consumption**

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## *Deposits on Cylinder Head*

**Cause premature detonation and increasing compression ratio leading to poor emission levels**

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## Solid Deposits on Turbine Blade

**(Ref: U.S. EPA)**

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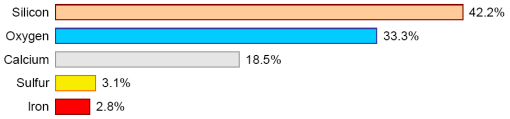
## Elemental Analysis of Silicate-Based Deposit




**ROOT CAUSE = SILOXANES**

**Combustion of Siloxanes yields Silicone Dioxide ($SiO_2$), the white solid powder shown in previous photographs**

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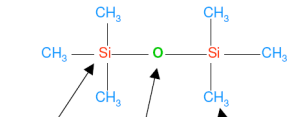
## What are Siloxanes?

**A family of man-made organic compounds that contain:**

- **Silicon (Si)**
- **Oxygen (O)**
- **methyl groups ($CH_3$-)**



LINEAR SILOXANE
Hexamethyldisiloxane

SIL(icon)+OX(ygen)+(meth)ANE = SILOXANE

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## Sources of siloxanes and silicones in wastewater

- Antiperspirants
- Skin Care Products
- Deodorants
- Shampoo
- Hair Conditioners
- Liquid Soaps
- Industrial Products

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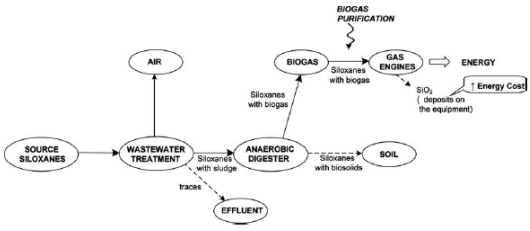
## Fate of Siloxanes in WWTP

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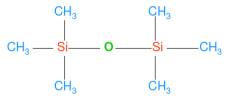
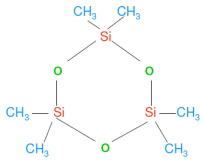
## Linear and Cyclic Siloxanes



LINEAR SILOXANE
(ex: Hexamethyldisiloxane)



CYCLIC SILOXANE
(ex: Hexamethylcyclotrisiloxane)

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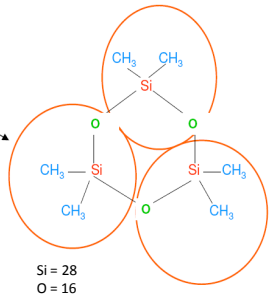
## Cyclic Siloxanes - Nomenclature

Dimethylsiloxane unit = called D unit



With 3 D units is called Hexamethylcyclotrisiloxane **D3**

With 4 D Units is called Octamethylcyclotetrasiloxane **D4**

With 5 D Units is called Decamethylcyclopentasiloxane **D5**

Si = 28
O = 16
$CH_3$ = 15
1 D unit = 74

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Organic silicon compounds (ppb) identified in the biogas of 50 WWTPs (Tower 2003).

| | Occurrence, number | Min. | Max. | Average |
|---|---|---|---|---|
| Butoxytrimethylsiloxane | 1 | --- | --- | 920 |
| Methoxytrimethylsilane | 1 | --- | --- | 227 |
| 1,1,3,3-Tetramethyldisiloxane | 1 | --- | --- | 85 |
| Pentamethyldisiloxane | 2 | 51 | 100 | 76 |
| Hexamethyldisiloxane, L2 | 10 | 46 | 2 260 | 847 |
| Octamethyltrisiloxane, L3 | 12 | 32 | 465 | 183 |
| Hexamethylcyclotrisiloxane, D3 | 5 | 285 | 8 700 | 2 155 |
| Octamethylcyclotetrasiloxane, D4 | 46 | 33 | 20 144 | 2 456 |
| Decamethylcyclopentasiloxane, D5 | 47 | 102 | 18 129 | 3 422 |
| Dodecamethylcyclohexasiloxane, D6 | 3 | 37 | 765 | 352 |
| Tetramethylsilane | 1 | --- | --- | 170 |
| Trimethylfluorosilane | 1 | --- | --- | 610 |
| Trimethylpropoxysilane | 1 | --- | --- | 5 200 |

**Greater than 90% probability that the digester gas stream will contain Siloxanes D4 or D5.**

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## Most Common Siloxanes found in Digester Biogas

- **Fall into two broad chemical compositions:**
  - Linear
  - Cyclical.
- **The two most common linear siloxanes are:**
  - Hexamethyldisiloxane (L2) aka (MM)
  - Octamethyltrisiloxane (L3) aka (MDM)
- **The two most common cyclical siloxanes are:**
  - Octamethylcyclotetrasiloxane (D4)
  - Decamethylcyclopentasiloxane (D5).

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## Combustion of Siloxane D5

$$C_{20}Si_5H_{30}O_5 + 20\,O_2 \rightarrow 5\,SiO_2 + 10\,CO_2 + 15\,H_2O$$

**INPUT DATA:**

**Engine: 1 MW**
**Biogas : 155 x $10^6$ SCF/year = 4.36 x $10^6$ $m^3$/year**
**Siloxane D5 = 1 ppmv = 15 mg/$m^3$**

**RESULTS:**

**Siloxane input:** 65.25 kg/year = 144 lbm/year = 176 moles/year

**$SiO_2$ produced**= 880 moles/year = 52.8 kg/year = **116 lbm/year**

**If 0.5% is deposited** = 2.64 kg/year = **5.8 lbm/year**

**If 0.1% is deposited** = 0.528 kg/year = **1.16 lbm/year**

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## Impact on Warrantees

Growing trend:

- Manufacturers of engines and turbines are qualifying their warrantees with stringent limits on siloxanes in the fuel supply.
- Whereas limits were between 5 to 35 mg/m3, now, we are seeing limits stipulated under 5 mg/m3.
- Additionally, some manufacturers have been decreasing the limits for silicon in the engine oil (i.e., 1 mg/L in the oil).

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## MANUFACTURER SILOXANE LIMITS

(Ref: Wheless & Pierce, 2004)

| Engine Manufacturer | Siloxane ($mg/m^3$) |
|---|---|
| ICE Caterpillar | 28 |
| ICE Waukesha | 25 |
| ICE Jenbacher | 10 |
| ICE Deutz | 5 |
| Solar Turbines | 0.1 |
| Ingersoll Rand Microturbines | 0.06 |
| Capstone Microturbines | 0.03 |

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## Engine Manufacturer Siloxane Limitations

(Ref: Schroedel et al., 2009)

| Manufacturer | Siloxane Concentration |
|---|---|
| Caterpillar Inc. | 0.60 µg Si/BTU |
| Dresser Waukesha | 25 µg/L (25 g/m3) |
| Solar Turbines | 10 mg Si/$Nm^3$ $CH_4$ |
| Capstone Turbine Corp. | < 5 ppbv |

Schroedel Jr., Peter V. Cavagnaro, and Jerald W. Peterson, "*Siloxanes The hidden threat to biogas systems*", WE&T, WEF, August 2009

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## Siloxanes Sampling Not Standardized

- At least 10 methods used worldwide.
- In the United States, collection methodologies are primarily :
  - ✓Impingers containing either methanol, mineral oil
  - ✓Sorbent tubes;
  - ✓Summa canister
  - ✓Tedlar bags.
- Need also to standardize reporting units

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## Comparison of Sampling Techniques

| Performance Criteria | Canister | Impinger | Sorbent Tube |
|---|---|---|---|
| Ease of sampling | Excellent | Poor | Fair |
| Representative sample | Fair/Poor | Excellent | Fair |
| D4/D5 Siloxane recovery | Fair | Excellent | Fair/Poor |

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## Siloxanes Thermo-Physical Properties

| Name | Molecular Weight (g/mole) | Vapor Pressure at 25°C (mm Hg) | Aqueous Solubility (mg/L) |
|---|---|---|---|
| **D3** | 222 | 9 – 14 | 1.56 |
| **D4** | 297 | 1 – 1.3 | 0.056 |
| **D5** | 371 | 0.15 – 0.4 | 0.017 |
| **D6** | 445 | 0.02 | 0.005 |
| | | | |
| **L2** | 162 | 31 | 0.93 |
| **L3** | 236 | 4 | 0.034 |
| **L4** | 310 | 0.55 | 0.007 |
| **L5** | 384 | 0.07 | 0.00007 |
| | | | |
| **Benzene** | 78 | 95 | 1,800 |

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## Siloxane Removal Systems

1. ADSORPTION
2. COOLING-ADSORPTION IN SERIES
3. DEEP CHILLING (about – 30°C)
4. ABSORPTION
5. PROMISING TECHNOLOGIES

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## ADSORPTION

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

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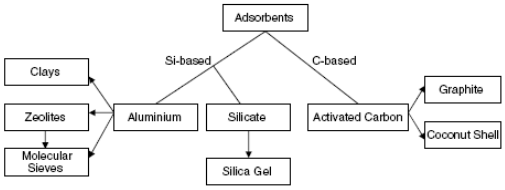
## Adsorbents for siloxanes removal from biogas

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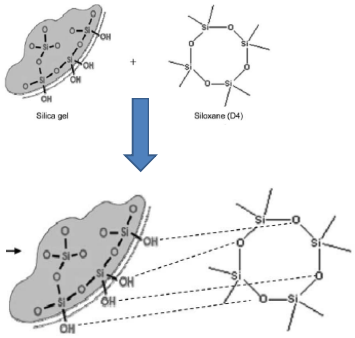
## Silica Gel: Adsorption of D4

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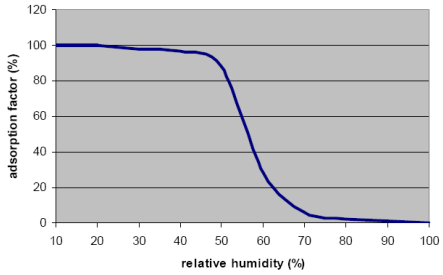
## Effect of Humidity on Adsorption Capacity

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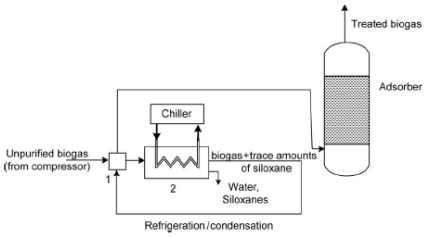
## Siloxanes removal using refrigeration/condensation and adsorption




- Cooling removes about 25 % of Siloxanes
- Deep chilling removes about 95 % of Siloxanes

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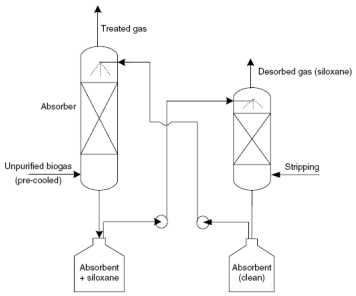
## Scrubbing (Gas-Liquid Absorption)




**Due to the chemical nature of siloxanes, the most suitable absorbents are polar organic solvents. Selexol, a polyethylene glycol dimethyl ether, can remove siloxanes as well as CO2 and H2S**

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## Technology Trend – Current R&D

**Membrane Based Separation**

**Biological**

**Peroxidation**

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## Brown Grease to BIOGAS

**Growing sustainability trend to increase biogas production through co-digestion**

**Impact on Siloxanes concentration?**

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## CONCLUSION

**Siloxanes are expensive components to remove, but its even more expensive if they are not removed.**

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QUESTIONS ?

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