The Threat to Sustainable Energy – Siloxanes

Composition, Removal, and Fate

By

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Presentation Outline

- Introduction
- Digester Gas Conditioning
- Siloxanes
  - Compounds
  - Issues
- Siloxane Removal Systems
- Baltimore Case History
- Mass Balance
- Summary

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Introduction

- Sustainable Energy Sources
  - Digester Gas
  - Landfill Gas
- Digester Gas Use in Wastewater Treatment Plants
- Observed Build Up of Material
  - Identified as Silicon Dioxide
  - From Burning of Siloxanes
- Problems
  - Excessive Maintenance
  - Equipment Failure

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Digester Gas Conditioning

- Historically Simple
  - Moisture
    - Sediment and Drip Traps
    - Foam and Moisture Separators
  - Hydrogen Sulfide
    - Iron Sponge
    - Resins
- Purpose
  - Corrosion Prevention
  - Gas Heating Value
  - Protection of Piping

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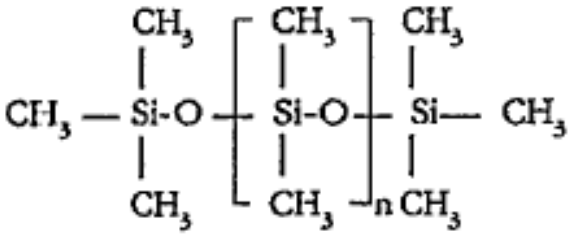
Siloxanes

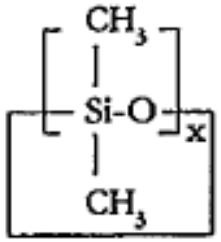
- Literature First Addressed in Early 1990s
- Silicone Research Program - Silicones Environmental, Health, and Safety Council of North America (SEHSC)
  - Initiated in 1994
  - www.sehsc.com
- Silicon
  - Second Most Abundant Compound on Earth
  - Naturally Occurring in Inorganic Materials
  - Sand, quartz, flint, granite, clay, mica

Organosiloxanes

- Bond with Carbon Methyl Group
- Volatile Methylsiloxanes (VMS)
- Formal USEPA Ruling
  - 1994
  - Exempted from Regulation as VOCs
- Commonly Present in Wastewater



typically, n = 0-4



typically, x = 4 -6

(Dow, 1997a)

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Organosiloxanes

Acronym	Siloxane Compound	MW	Si-Atoms	%Si	Boiling Point
D3	**Hexamethylcyclotrisiloxanes**	**222.43**	**3**	**37.76**	**134 C**
D4	**Octamethylcyclotetrasiloxanes**	**296.61**	**4**	**37.76**	**175C**
D5	**Decamethylcyclopentasiloxanes**	**370.77**	**5**	**37.76**	**210 C**
D6	**Dodecamethylcyclohexasiloxanes**	**444.98**	**6**	**37.89**	**245 C**
M_2 (MM)	**Hexamethyldisiloxanes**	**162.36**	**2**	**34.49**	**100 C**
MDM	**Octamethyltrisiloxanes**	**236.53**	**3**	**35.51**	**152 C**
MD_2	**Decamethyltetrasiloxanes**	**310.69**	**4**	**36.05**	**195 C**

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Silicon-Containing Organics

- Butoxytrimethylsiloxane
- Methoxytrimethylsilane
- 1, 1, 3, 3-Tetramethylsiloxane
- Pentamethyldisiloxane
- Hexamethyldisiloxane (MM)
- Octamethyltrisiloxane (MDM)
- Hexamethylcyclotrisiloxane (D3)
- Octamethylcyclotetrasiloxane (D4)
- Decamethylcyclopentasiloxane (D5)
- Dodecamethylcyclohexasiloxane (D6)
- Tetramethylsilane
- Trimethylfluorosilane
- Trimethylpropoxysilane

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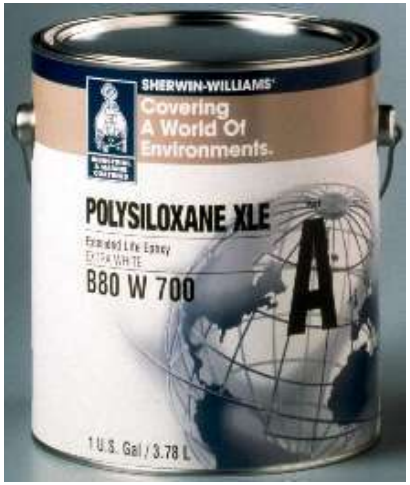
Sources of VMS

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



Photos from Environment Canada, S.Bacus, et. al.

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Gas Sampling and Analysis

- Multiple Analysis Methods Available
- Caution When Comparing Data
  - Reporting Units
  - Test Procedure
  - Sampling Procedure
- Consider Establishing Program
  - Establish Baseline
  - Anticipate Increased Maintenance
  - Track Changes Over Time
  - Develop Data for Future System

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Silicon Dioxide

- Inert White Powder (may be colored with byproducts)
- Formed when VMS Burned
- Base Material for Glass, Sandpaper, Grinding Tools
- Initial Observations Assumed from Dirt
- Earliest Problems Observed in Landfill Gas Combustion
- Most Studies within the Last Decade
- Identified VMS as Source of Silicon Dioxide Deposits

Problems Created by Silicon Dioxide – Engines

- Deposits
  - Pistons
  - Intake and Exhaust Valves
  - Cylinder Walls
  - Engine Heads
  - Turbochargers
- Excessive Maintenance
  - Grinding of Valves and Heads
  - More Frequent Top End Overhauls

From AFT

From J. Peterson

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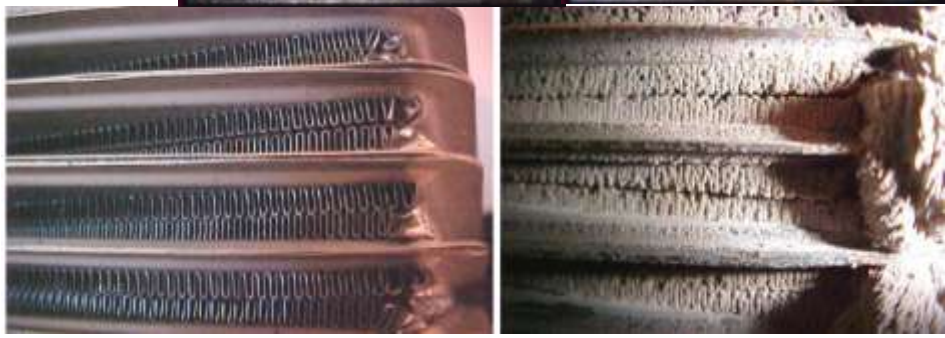
Problems Created by Silicon Dioxide

- Turbine Deposits
  - Powder and Hard Enamel
  - Complete Tear Down and Cleaning
  - Water Washing for Powder
- Microturbine Deposits
  - Reduction in Output
  - Recuperator Fouling
  - Very Low Siloxane Levels Recommended
- Boilers
  - Coating Interior
  - Plugging of Fin Type



From SCS Energy

From ProFactor,
F.Accettola

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Engine Manufacturer Siloxane Limitations

Manufacturer	Level of Silicon
Caterpillar	**0.60 ug Si/Btu**
Waukesha	**25 ug/l**
Solar	**10 mgSi/nm^3 CH4**
Capstone	**<5 ppbv**

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Siloxane Removal Systems

- Passive
  - Adsorptive Media (physical)
  - Absorptive Media (chemical)
  - Media Removed and Replaced
- Active
  - Thermally or Chemically Regenerated
  - Supercooling
    - Sub-zero Temperature Dew Points
    - Condensate Returned to Treatment Plant

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Case Study

Back River Wastewater Treatment Plant

Location	**Baltimore County**
Site Area	**466 acres**
Service Area	**140 square miles**
Design Capacity	**180 MGD**
Hydraulic Capacity	**449 MGD**
Population Served	**994,000**
Buildings	**33**
Building Area	**468,000 sf**

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Back River Wastewater Treatment Plant

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Back River Wastewater Treatment Plant

City of Baltimore Energy Office

- Completed Multiple Projects with Johnson Controls, Inc.
  - Performance Contracts
  - City Buildings
- Identified Back River WWTP as Major Energy User
- Selected Johnson Controls/AECOM Team for Project
  - Past Experience at Back River
  - Past Experience Working Together
- Project Costs Paid through Operating Savings

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Energy Conservation Measures

- Digester Gas Utilization
- Digester Recirculation Pump Improvement
- HVAC Improvements
- Direct Digital Control/Ventilation Optimization
- Lighting Improvements
- Water Conservation

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Back River Digester Gas Production

Digester Gas to Boilers (to heat digesters & bldg)	511 KCFD
Digester Gas to Plant	163 KCFD
Digester Gas to Flares	1,044 KCFD
Total Used	1,718 KCFD

2004 Data

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Siloxane Concentrations

	5/4/2004	5/7/2004	12/1/2005	1/11/2006
Name	ug/m3	ug/m3	ug/m3	ug/m3
Hexamethylcyclotrisiloxane (D3)	ND	ND	ND	ND
Octamethylcyclotetrasiloxane (D4)	4,000	940	2,530	5,460
Decamethylcyclopentasiloxane (D5)	124,000	59,520	124,000	258,000
Dodecamethylcyclohexasiloxane (D6)	ND	ND	ND	ND
Hexamethyldisiloxane (L2)	NR	ND	ND	ND
Octamethyltrisiloxane (L3)	ND	ND	ND	ND
	128,000	60,460	126,530	263,460

Siloxane Removal System - Supercooling

- Proven Technology
- Separate Building
- -10° to -20°F Dew Point
- 750 cfm each
- Filtered
- Condensate Returned to the Treatment Plant

Gas Conditioning Skid Performance

	4/30/2008	4/30/2008
Name	µg	µg
	inlet	outlet
Hexamethylcyclotrisiloxane (D3)	---	---
Octamethylcyclotetrasiloxane (D4)	72	ND
Decamethylcyclopentasiloxane (D5)	2,300	ND
Dodecamethylcyclohexasiloxane (D6)	ND	ND
Hexamethyldisiloxane (L2)	ND	ND
Octamethyltrisiloxane (L3)	ND	ND
	2,372	ND

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Siloxane Mass Balance

- Condensate Returned to the Plant
- Address Potential of Build Up
- Literature Research Completed

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Siloxane Literature Research

- Influent Concentrations Highly Variable
- Influent Concentrations Impacted by Industry
- D4 and D5 Most Common in Wastewater
- Hydrophobic and Adsorbs onto Solids
- Activated Sludge Plants Remove Most Siloxanes
- Not Biologically Inhibitory
- Do Not Degrade in Conventional Treatment Processes
- Some May Volatilize
- Siloxanes Will be Present in Digester Gas

Siloxane Mass Balance Criteria

- Set Influent Concentration at 250 µg/l
- Set Effluent Concentration at 3 µg/l
- 48% Removed in Primary Sedimentation
- 10% Volatilized in Aeration
- 10% in Digester Gas
- 25% to Dryer will Volatilize and be Recycled
- Recycled in Proportion to the Solids Capture

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Mass Balance – Without Gas Conditioning

Influent @ 250 µg /l	ppd	%	
At 1 MGD Siloxane to WWTP	2.08750	100.000%	
Volatilized in Aeration or at Weirs	0.20875	10.000%	
Plant Effluent	0.08330	3.990%	~ 10 µg /l
Digester Gas	0.17955	8.601%	~ 57,000 µg /l
Wastewater Solids	1.61590	77.409%	~ 290,000 µg /l

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Mass Balance – Existing Conditions

Influent @ 250 µg/l	ppd	%	
At 1 MGD Siloxane to WWTP	2.08750	100.000%	
Volatilized in Aeration or at Weirs	0.20875	10.000%	
Plant Effluent	0.00002	0.001%	~ 3 µg/l
Digester Gas	0.25329	12.134%	~ 77,000 µg/l
Wastewater Solids	1.62543	77.865%	~ 300,000 µg/l

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Mass Balance – With Gas Conditioning

Influent @ 250 µg/l	ppd	%	
At 1 MGD Siloxane to WWTP	2.08750		
WWTP Influent with Recycle	3.4565	100%	
Volatilized in Aeration or at weirs	0.34557	9.998%	
Plant Effluent	0.00003	0.001%	~ 3 µg/l
Digester Gas	0.00292	0.084%	~ 89,000 µg/m3
Wastewater Solids	3.10794	89.917%	~ 560,000 µg/kg

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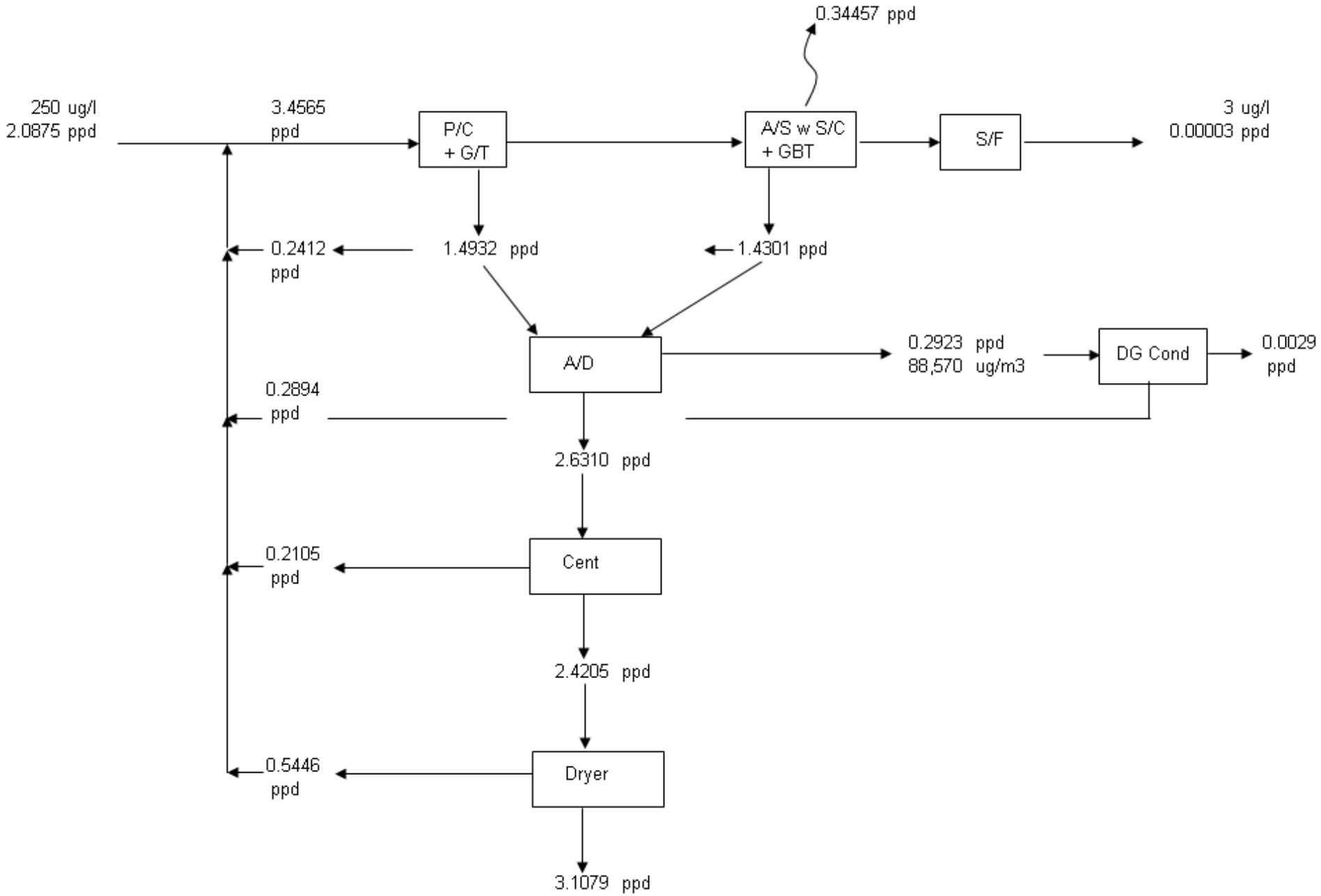
0.34457 ppd
250 ug/l
2.0875 ppd
3.4565
ppd
P/C
+ G/T
A/S w S/C
+ GBT
S/F
3 ug/l
0.00003 ppd
0.2412
ppd
1.4932 ppd
1.4301 ppd
A/D
0.2923 ppd
88,570 ug/m3
DG Cond
0.0029
ppd
0.2894
ppd
2.6310 ppd
0.2105
ppd
Cent
2.4205 ppd
0.5446
ppd
Dryer
3.1079 ppd


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Summary

- Landfill and Digester Gas are Sustainable Energy Sources
- Siloxanes are Ubiquitous in the Environment
- Increasing Concentrations Likely with Increasing Use
- Siloxanes Threaten These Sustainable Energy Sources
- Limited Technologies Available for Siloxane Removal
- Ultimate Fate of Siloxanes Must Be Considered

Conclusions and Recommendations

- Siloxanes Need to Be Considered
  - Do Initial Analysis to Establish Baseline
  - Do Routine Analysis to Establish Trend
- Consider Impact of Siloxanes
  - Design
  - Construction
  - Operations and Maintenance

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