REDUCING BIOGAS POWER GENERATION COSTS BY REMOVAL OF SILOXANES

P. M. Tower and J.V. Wetzel, Applied Filter Technology, Inc., Snohomish, Washington, USA

ABSTRACT

The cost of utilizing digester biogas (DBG) to fire boilers or to power electricity generator engines or microturbine-driven generators is adversely affected by biogas volatile contaminants (VCs). Among the VC contaminants found in DBG are volatile inorganic contaminants (VICs) like ammonia and hydrogen sulfide, and volatile organic contaminants (VOCs) that range from those containing one (1) carbon atom to as many as thirty (30) carbon atoms. These VOCs are made up of primarily carbon, hydrogen, and oxygen but can also contain sulfur (like methyl mercaptan), halogens such as bromine, chlorine and fluorine (like methylene chloride and chlorodifluoromethane), and organosilicons (such as trimethylsilanol and siloxanes).

While sulfur and halogen-containing VCs are harmful because they produce noxious emissions, corrosive acids upon combustion (and can foul some emission catalysts), the damage caused by organosilicons like siloxanes is far worse. Some of the problems encountered with all three types of VCs in biogas are discussed with their commensurate impact on operating costs at the Mangere Wastewater Treatment Plant (WWTP) in New Zealand. The focus of this paper is primarily on the removal of the organosilicons (mainly the siloxanes) and secondarily on the removal of hydrogen sulfide (H_2S).

KEYWORDS

Biogas, Power Generation, Cost Reduction, Siloxane Removal, Hydrogen Sulfide Removal, Mangere

1 INTRODUCTION

Prior to Applied Filter Technology's (AFT's) involvement, recent upgrades to the Mangere Wastewater Treatment Plant had been undertaken that included both infrastructure and processes. Infrastructure-related upgrades over the previous several years include adding digesters (now numbering 7 -- with more planned) and piping for conveyance of waste activated sludge and biogas. Process-related changes include the addition of Treated Waste Activated Sludge (TWAS) to the digesters instead of Primary Activated Sludge. Other changes include replacing the older digester gas mixing system with a jet mixing system. In addition, a complete upgrade was made of the cogeneration system starting at the compressor room and including the LP dryer, new blowers, pipelines, and new biogas generator engines. Picture 1 below shows the gas collection piping for Digester No. 6.

Soon after startup, premature engine wear was discovered in the new biogas fuelled generator engines. Hydrogen sulfide (H_2S) and siloxanes in the biogas had been previously identified as possible causes of generator engine damage. Deposits taken from the engine cylinders were analyzed and determined to contain calcium (46%), sulfur (36%), and silicon (16%). In October of 2002, Watercare Services, Ltd. commissioned Meritec Ltd. (now known as Maunsell Ltd.) to identify, evaluate, and select the preferred methods for treating the biogas to meet generator engine specifications. The overall aim of this project was to provide the Mangere WTP with the most economical means of reducing the H_2S and Siloxane content of the biogas to meet generator engine specifications and to compare the additional costs of this treatment to the potential benefits in cost reduction for operating these engines.

In December, 2002, Meritec Ltd. contacted AFT to determine the feasibility, capital cost, and operating and maintenance (O&M) costs for a siloxane removal system based on the SAG™ Process. SAG™ is an acronym for "segmented activity gradient" which refers to the process for sequential removal of contaminants like siloxanes from biogases. In addition, AFT was consulted on the H_2S removal system. A Catalytic Iron Sponge (CIS™) was proposed because it was determined to be the most cost effective for H_2S removal. Meritec provided analytical information on the Digester Biogas, from which AFT developed the design of the siloxane removal system.

Photograph 1: Digester No. 6 Gas Collection Piping

Removal of the H_2S is necessary not only from a power generation equipment protection standpoint, but also to protect the media in the SAG™ System that removes the siloxanes. Under certain circumstances, the H_2S will deposit elemental sulfur in the pores of the SAG™ media, reducing its ability to remove siloxanes and shortening its replacement interval. Since it had been determined that the H_2S removal system would not be operational at the time the SAG™ System had to be started up, this was an important detail that had to be addressed in the equipment design.

ABOUT SILOXANES

Siloxanes are organosilicon molecules that also contain mostly carbon, hydrogen, and oxygen, but can also contain nitrogen and halogens. Their primary use for the consumer market is in toiletries and cosmetics of all types, including deodorants, hair sprays and gels, lipsticks and glosses, lotions, shaving products and others. A little research in the home will turn up products with “dimethicone,” “dimethiconol,” dimethicone polyol,” “dimethicone copolyol,” “dimethicone/vinyl dimethicone crosspolymer,” “phenyl methicone,” “phenyl trimethicone,” “cyclomethicone,” “cyclopentasiloxane,” “cyclohexasiloxane,” “stearoxytrimethylsilane” “caprylyl trimethicone SV,” and “disodium dimethicone copolyol sulfosuccinate” in the ingredient list. These are products in a broad group of hundreds of chemicals known as silicones, which are all forms of organosilicons or siloxanes. To further emphasize the problem, use of siloxanes is increasing worldwide as new uses for these materials are discovered and commercialized. Commensurate siloxane increases in biogas are expected.

Siloxanes and organosilicons are a problem in biogas because they form silicon dioxide, SiO_2, upon combustion. SiO_2 is a white powdery substance that accumulates on the heated surfaces in combustion equipment, especially in the cylinders of IC generator engines. An IC generator engine burning 220 Nm^3/H (400 SCFM) biogas containing just 1 ppmv of siloxane D5, for example, will generate approximately 59 kg (130 lb.) of SiO_2 per year if operated continuously. Not all of this SiO_2 will remain in the engine; however, what does remain can cause considerable damage and add greatly to the cost of operating the generation equipment. The presence of sodium, aluminum, magnesium, iron, and other elements leads to silicate formation (Tower, 2002, 2003, 2004). Silicates are glass-like materials that are extremely abrasive to generator engine internals. Photograph 2 below shows the SiO_2 and silicate deposits on a piston taken from one of the generator engines. Additional information on the common siloxanes found in biogas appears in Appendix D.

Photograph 2: SiO_2 and silicate Deposits on piston crown and rings

2 BIOGAS TREATMENT SYSTEM DESIGN CONSIDERATIONS

2.1 OVERVIEW

The combination of gases, water vapor, and VCs (VICs and VOCs) comprise what is called the biogas matrix. Simply defined, the biogas matrix is made up of molecules of gases, water vapor, and contaminants. In this gas matrix are the “permanent gases” which are predominantly methane, carbon dioxide, nitrogen, oxygen, and trace amounts of 2-carbon atom to 5-carbon atom alkanes and alkenes. VCs usually comprise a tiny fraction of the biogas matrix. Even so, they can produce a lot of damage. For this reason, it is critically important to determine the complete biogas molecular matrix in order to properly design gas conditioning and contaminant removal equipment.

Since it is necessary to reduce the moisture level in the biogas, the volume percent or mole percent of the permanent gases and water vapor must be measured. This information is critical to the design of the gas conditioning equipment preceding the siloxane removal system. Once the permanent gases and moisture level of the biogas have been determined, the enthalpy of the gas can be calculated and used in the design basis. For the power generation equipment, a moisture level not greater than 80% relative humidity (RH) is required (generator engine manufacturer specification). However, the SAG™ media can be fouled by water vapor at RH levels exceeding 45%. Thus, this requirement overrides that of the power generation equipment. For this reason, the gas conditioning equipment design is based on reducing the RH of the biogas to 45% or lower.

Other considerations for the gas conditioning equipment design are the gas temperature and pressure. In order to deliver the gas at suitable pressure to the generator engines, resistance in the H_2S removal equipment, siloxane removal equipment, piping, and other process components must be taken into consideration. For low pressure systems, the biogas is usually compressed by blowers to about 60 kPag (about 9 psig) or a little less. The heat of compression is rejected by aftercoolers built into the gas conditioning skid.

Digester biogas containing high levels of H_2S are corrosive to gas collection system piping and are especially corrosive to compressors or blowers. Because the digester biogas at the Mangere WTP contains a fairly high level of H_2S, location of the H_2S removal equipment is ahead of the blowers. After the gas is dried and compressed, the temperature is controlled to about 40 degrees C. (104 degrees F.) maximum. Since the SAG™ System media operates best at temperatures of 25 degrees C. (77 degrees F.) or lower, the siloxane removal system design has to accommodate this higher temperature and still perform adequately. Temperature losses in the gas pipeline further reduce the conditioned and treated biogas temperature to around 22 degrees C. (about 72 degrees F.) at the engines. A process flow diagram of the biogas treatment system is in Appendix E.

2.2 BIOGAS SAMPLING AND TESTING

There are four basic types of biogas composition data required for the design of a siloxane removal system. These are: 1) the permanent gas volume per cent; 2) the complete VOC profile, including the individual species and their concentrations; 3) the inorganic and organic sulfur contaminants and their concentrations; and 4) the individual siloxanes and their concentrations. Although not required for the design of the siloxane removal or hydrogen sulfide removal equipment, testing for total chlorine, total fluorine, and ammonia are also performed by Watercare Services due to the potential contribution to the engines' O&M costs and NO_x exhaust emissions.

While there are several tests available to determine the biogas composition in each of these 4 areas, the preferred methods are those which provide the most data. Since most biogas treatment system designs are based on just one or two analyses, it is critical to gather as much information as possible. Most wastewater treatment facilities utilizing anaerobic digestion do not have extensive biogas data over a long period of time, so VIC and VOC averages, composition changes, ranges from low to high values, and trends cannot be taken into consideration for treatment equipment design. From the perspective of good plant management practices (GPMP), a complete biogas analysis should be performed not less often than once per year. A robust design for biogas treatment equipment can and should be based on data that are not less than one year old and an additional set of data that is not less than 3 months old.

2.2.1 SAMPLING TECHNIQUES FOR VOLATILE CONTAMINANTS (VCs) AND PERMANENT GASES

Sampling of the biogas for "permanent gases," VICs, and VOCs can be done by several methods. The most common of these are: absorption tubes employing an adsorbent like charcoal or specialized resins; 1 liter and 6 liter metal canisters; and gas impermeable bags, such as those constructed of Tedlar®. Sampling for VOCs by absorption tubes is accomplished by drawing a specified volume of the gas through a charcoal tube. The charcoal in the tube absorbs or adsorbs the VOCs. Analysis of the absorbed or adsorbed VOCs is accomplished by stripping the absorbent media in the tube with a solvent like carbon disulfide or hexane. The solvent containing the stripped VOCs is analyzed by gas chromatography or gas chromatography coupled with mass spectrometry to determine and quantify the VOCs. By knowing the gas volume drawn through the charcoal tube and the concentration found in the solvent, the concentration of each VOC in the biogas can be calculated. Our experience with the charcoal tube sampling method reveals that it has several drawbacks. The first of these is poor reproducibility of results. Second, not all of the VOC species in the biogas are absorbed onto the charcoal, as they are displaced during the sampling period by more strongly adsorbed VOC species and water. For this reason, the identified and quantified desorbed species may not be representative of the actual biogas matrix. Third, even though there are three distinct charcoal tube analysis methods for the range of VOCs found in biogas (Pendergrass, 2003, 3 citings), the combination of their results covers just a fraction of what is possible with, for example, the Modified EPA 18 Method. . Fourth, when the charcoal tubes are stripped, the adsorbed species may not fully desorb, skewing the accuracy of the test results. There is also variability between tubes used for analyzing VOCs ("Determination of Tetrahydrofuran…," ca. 1998, "Determination of Pyridine…," ca. 1998). These phenomena are believed by AFT to be the reason for lack of reproducibility of test results with charcoal tubes, and, as such, they are considered to be best used as a semi-qualitative and semi-quantitative method. Charcoal tubes cannot be used to sample for the permanent gases.

Gas sampling canisters (such as Summa or Silco) offer several advantages over the other methods for VC analysis. First, a larger volume of gas can be taken at the time of sampling. Second, they are reusable. Third, they have a longer "hold" time between sampling and analysis than either of the other methods. The larger volume of gas (1 or 6 liters) permits a representative sample of the gas to be taken, with extra gas available for re-checks of spurious results. These canisters are easy to use and require no pumps to collect a sample from low-pressure gas sources as they arrive evacuated and under a vacuum. While these canisters are re-usable, they must be very carefully cleaned before re-use. One drawback is the greater cost to use these and also the higher shipping fees due to their weight.

Analysis of the biogas from a canister is accomplished through direct injection into a gas chromatograph or gas chromatograph coupled with a mass spectrometer.

Our preferred method of gas sampling is the 1-liter Tedlar bag. One or two 1-liter Tedlar bags provides enough sample to complete the permanent gases, sulfur species, and VOC analyses. These are light, easy to use, and are disposable. One drawback is the relatively short hold time before analysis of the sulfurous species. On rare occasions, Tedlar bags can leak, thus, the practice of using two bags in order to have a backup is employed. Unlike the evacuated metal canisters, a pump must be used if the gas source pressure is too low.

The permanent gases analysis can be accomplished only through the capture of a physical biogas sample, such as is obtained by the canister or Tedlar bag method.

2.2.2 SAMPLING TECHNIQUES FOR SILOXANES

While the same methods of sampling for the permanent gases, sulfur species, and VOCs may be used for siloxanes, the most reliable and most widely accepted sampling method is by chilled methanol impingement. This sampling method was developed by Dow Corning ("Organosilicon Compounds in Biogas…," 1999) and improved and expanded by Air Toxics (Saeed, et al., 2002). The procedure involves passing the biogas stream through two each (connected in series) midget impingers equipped with 20 ml capacity glass vials, each containing nominally 15 ml of high purity methanol ("Siloxanes in Air…" December 2001). The siloxanes present in the biogas dissolve in the methanol, and are later analyzed by direct injection into a GC/MS. Biogas flow is controlled to nominally 112 ml per minute via a needle valve and rotameter, which are part of the sampling train. After 180 minutes, the sampling is stopped, the vials are removed from the impingers, capped, and kept chilled at 4 degrees C. (40 degrees F.) until analyzed (Tower, 2002).

2.2.3 TEST METHODS FOR VCs AND PERMANENT GASES

TESTING FOR SULFUR-BEARING VCs

After a representative and adequate size of the biogas has been obtained by either a Tedlar bag or metal canister, the analytical tests are performed as soon as practical to avoid any biogas matrix deterioration. The first test that is run is for the sulfur species. In the United States, we use the ASTM D5504 method, which detects 20 different sulfurous compounds; including hydrogen sulfide (see Appendix A). This test is accomplished by direct injection of the biogas into a gas chromatograph equipped with an SCD (sulfur chemiluminescence detector). Results from this test are reported in either ug/m^3 or ppbv. The detection limit of this method for most sulfur species is in the low ppbv range, with some species able to be detected at lower than 1 ppbv. One drawback of the ASTM D5504 method is loss of the lower concentration organic sulfur species detection limit if any dilutions of the gas are necessary to bring very high H_2S levels into the instrument calibration range. Watercare's Laboratory Services Air Quality Group analyzes specifically for H_2S, methyl mercaptan (CH_3SH), dimethyl sulfide (C_2H_6S), and dimethyl disulfide ($C_2H_6S_2$) by gas chromatography.

TESTING FOR PERMANENT GASES

From the same Tedlar bag, the permanent gases, or expanded ASTM D1945 (see Appendix B) test is conducted. The permanent gases test is run by direct injection into a gas chromatograph and includes methane, carbon dioxide, nitrogen, and oxygen. The ASTM D1945 test includes hydrogen and gases containing 2 through 5 carbon atoms, as well as the heating value of the gas (BTU per cubic foot) and its total specific gravity.

TESTING FOR VOCs

With the ASTM D5504 and ASTM D1945, the EPA TO-14A test is also run. This test results in the detection and concentration, usually to the ppbv range, of 62 VOCs (see Appendix C). Since the inception of testing at the Mangere Plant, AFT has developed an expanded VOC test that detects (down to 100 ppbv) and quantifies over 250 different organic contaminants (P. Tower, 2003). This test, based on the modified EPA Method 18, includes the method TO-14A and semi-volatiles ("Method 8270C…," 1996). The necessity for a more expanded test is due to the presence of organic contaminants called "biogenics," like d-limonene, alpha pinene, and d-carene, which not included in other test methods.

TESTING FOR SILOXANES

The best method of analyzing the methanol from the impingers for siloxanes is by gas chromatography coupled with mass spectrometry (GC/MS). With this technique, not only is the total mass of siloxanes determined, but also the individual species and their masses. By knowing the volume of gas passed through the sampling train and the mass of siloxanes measured, their concentrations can be calculated. Unfortunately, the test method does not yet have the same level of detection as the ASTM D5504 or the EPA TO-14A. The lowest molecular weight siloxane routinely encountered, Hexamethyldisiloxane, or "MM" has a reportable detection limit 45 ppbv. The highest molecular weight siloxane, Dodecamethylcyclohexasiloxane, or "D6" has a reportable detection limit of 16 ppbv (Saeed, et al., 2002).

THE MANGERE TESTING PROTOCOL

Testing was begun in April of 2003 by the Laboratory Services Air Quality Group, a division of Watercare Services Ltd. The scope of their testing included the permanent gases, total chlorine (HCl & Cl_2), Total fluoride (HF & F_2), ammonia (NH_3), total sulfur, siloxanes, and moisture content. For the total chlorine, total fluoride, ammonia, and moisture content, Laboratory Services employed USEPA Method 26—Determination of Hydrogen Halides and Halogen Emissions from Stationary Sources, and USEPA CTM027—Determination of Ammonia Emissions from Stationary Sources. Discussion of these methods is beyond the scope of AFT's involvement in this project.

2.3 BIOGAS SAMPLING TEST RESULTS AND DATA INTERPRETATION

Results from the Laboratory Services Air Quality Group are listed below:

Permanent Gases: Methane 60 to 61%; Carbon Dioxide 37%, Nitrogen 1.7 to 2.6%, Oxygen 0.3 to 0.4%

Total Chlorine: HCl < 0.32 mg/m^3; $Cl_2 < 0.62$ mg/m^3

Total Fluoride: HF < 0.015 mg/m^3; F_2 0.036 mg/m^3

Moisture: 2.5%

Total Sulfur: H_2S 200 to 800 ppmv (other species are negligible)

Siloxanes: "Octamsil" (D4) 0.58 mg/m^3 (50 ppbv); "Decamsil" (D5) 4.52 mg/m^3 (313 ppbv)

VOCs (results in ug/m3):

Tetrachloroethene	667
1,3,5-Trimethyl Benzene	2845
1,2,4-Trimethyl Benzene	6222
O+M+P Xylenes	4622
Ethylbenzene	1822
n-Propylbenzene	267
Isopropylbenzene	444
Toluene	5734
sec-Butylbenzene	267
p-Isopropyltoluene	400
Heptane	1600
Hexane	1111
Trichloroethene	711
Benzene	622
cis-1,2 Dichloroethene	1333

It is these data, together with the biogas flow range, temperature and pressure that form the basis for the siloxane removal system design.

3 THE MANGERE WTP BIOGAS TREATMENT SYSTEM DESIGN

3.1 HYDROGEN SULFIDE REMOVAL SYSTEM

The hydrogen sulfide removal system consists of two vessels operating in parallel mode, each containing approximately 18 m^3 of iron sponge. To establish the minimum recommended contact time of 60 seconds required for H_2S removal, the linear velocity of the gas passing through the vessels is recommended to be in the 0.55 to 5.5 m/second (1 to 10 ft. per minute) range. Although it is not required to meet the engine manufacturer's specifications for the biogas, a properly operated iron sponge system can reduce the hydrogen sulfide level by 95% or more. The specification for the engines is 300 ppmv H_2S or less. The siloxane removal system, however, requires the hydrogen sulfide to be below 50 ppmv and preferably below 20 ppmv.

There are two separate modes of operating an iron sponge system—anaerobically and aerobically. An aerobically operated iron sponge system will have about three times the capacity for H_2S as an anaerobically operated system. Aerobic operation is accomplished by adjusting the oxygen content of the incoming biogas to approximately 1% by volume to promote catalytic function. This is usually done by introducing 5% by volume air into the biogas stream ahead of the iron sponge system. In addition, the pH of the iron sponge bed is kept at 8 or above, and preferably above 9 by the introduction of sodium carbonate solution, usually between 3% and 10% strength. The byproduct of catalytic or aerobic iron operation under alkaline conditions is the production of elemental sulfur (see equations 1, 2 and 3 below).

$$F_e2O_3 \cdot H_2O + 3H_2S \longrightarrow Fe_2S_3 + 4H_2O \quad (1)$$

$$2Fe_2S3 + 3O_2 + 2H_2O \longrightarrow 2Fe_2O_3 \cdot H_2O + 6S \quad (2)$$

$$4FeS + 3O_2 + 2H_2O \longrightarrow 2Fe_2O_3 \cdot H_2O + 4S \quad (3)$$

The byproduct of anaerobic iron sponge operation under acidic conditions is the production of iron disulfide, or FeS_2. FeS_2 consumes the iron that would be available for catalytic operation and slowly "kills" the media (see equations 4 and 5 below).

$$Fe_2O_3 \cdot H2O + 3H_2S \longrightarrow 2FeS + 4H_2O \quad (4)$$

$$FeS + S \longrightarrow FeS_2 \quad (5)$$

In addition to having a lower capacity for H_2S, anaerobically operated iron sponge can become pyrophoric and must be allowed to stabilize (oxidize) in air before it can be disposed. Usually, anaerobically spent iron sponge is removed from the vessels and spread onto the ground in a layer about 7 to 10 centimeters deep and allowed to pick up oxygen for several days. The formation of ferrous sulfide, FeS is undesirable in an iron sponge operation because at a temperature of 38 degrees C. FeS begins oxidizing to ferrous sulfate, $FeSO_4$. See Equation 6 below:

$$FeS + 2O_2 \longrightarrow FeSO_4 \qquad (6)$$

The upper temperature limit for operating a catalytic iron sponge system is 48 degrees C. (120 degrees F.). Above this temperature, equation 6 will proceed and severely shorten the life of the iron sponge media. It is also important to note that the reaction described in Equation (2) above is exothermic. The iron sponge media will increase in temperature 6.3 degrees C. (11.4 degrees F.) for every 1,000 ppmv of H_2S in the biogas. After use, the spent iron sponge may be disposed as a "non-hazardous" material. Because it contains high levels of sulfur, it is sometimes used as a soil amendment for fruit and vegetable crops.

For the present and future planned biogas flows, media life calculations were performed for both anaerobic and aerobic operations. The design flows are 1700 Nm^3H, the present average, 2800 Nm^3H, the next planned increase, and 3800 Nm^3H, an expected high flow after the installation of new wastewater treatment equipment. The details of the calculation are contained in Appendix F.

3.2 SILOXANE REMOVAL SYSTEM

Siloxane removal from the biogas is accomplished after the moisture and hydrogen sulfide have been reduced. Because there are several types of siloxanes, AFT proposed the use of its SAG™ Process for the best performance. The SAG™ Process utilizes media similar to activated carbon (graphite carbon based) but with modified pore structures to perform better on removal of the individual siloxane species. The media for siloxane D5 removal is called "DD;" for siloxane D4 removal, "DM," and for lower molecular weight siloxanes, "MD." By layering these media in the vessels in the order (from the gas inlet) of largest DD, DM, then MD, additional removal benefits of up to 50% may be realized over a homogeneous media bed. The SAG™ Process is patent pending. First, it should be noted that although only siloxanes D4 and D5 were detected during the biogas analyses, SAG™ Media for lower molecular weight siloxanes was also included to provide extra insurance against fouling. It is likely that other organosilicon species may be present in biogas or will be present in the biogas as global siloxane usage increases. AFT is working on a test method that will expand the range of siloxanes and organosilicons able to be detected and quantified.

When designing a siloxane removal system, the target life of the media is 60 days or greater. Because of the various flows and planned H_2S levels shortly after startup, the media life for the SAG™ siloxane removal system varies from a low of 50 days to a high of 180 days. The best equipment size to handle this flow range, given the required performance and media required, is two vessels, each containing approximately 13.3 m3 of media, or a total of just over 6,352 kg. Once SAG™ media is spent, it is usually disposed as a "non-hazardous" material in a landfill. Refer to Appendix F to view the various flows and estimated media lives for the siloxane removal system. Please note that the originally designed siloxane removal equipment is not large enough to handle the planned 3800 Nm3H flow, and additional equipment will have to be installed. For this reason, this flow was not detailed on the calculation grid for the siloxane removal system in Appendix F.

4 THE ECONOMIC BENEFIT OF H_2S AND SILOXANE REMOVAL

The savings in operation and maintenance costs on IC generator engines can be profound. Sometimes, the savings in just one maintenance item, like spark plugs, can be enough to economically justify installing a siloxane removal system. For IC generator engines, the typical payback period is usually between 6 months and 18 months. Below are some of the estimated cost savings that made this project economically feasible:

Figure 1: Anticipated Operating and Maintenance Cost Savings

Area of Cost Savings	Annual Cost at 1700 Nm3H	Net Present Value (NPV)
Natural Gas Burned	$142,510	$1,384,000
Engine Cylinder Damage	$400,000	$3,884,000
Spark Plugs	$155,000	$1,505,000
Oil	$54,000	$524,000

NPV of projects is based on 6% discount factor and 15 year project life. NPV factor is 9.712.

Photograph 3: Siloxane Removal Equipment during installation

The siloxane removal system was started up in late September of 2003, without the hydrogen sulfide removal equipment being operational. As was suspected, the SAG™ media began to remove the H_2S to below 100 ppmv. The impact of this phenomenon on siloxane removal was not readily quantifiable as samples are taken and analyzed every 2 weeks. Accordingly, after approximately two weeks of operation, the H_2S began to break through the SAG™ media. At this time the H_2S removal equipment (which is positioned ahead of the siloxane removal equipment) was ready to be brought on-line. Rough calculations indicated that the SAG™ media had picked up approximately 5% by weight of elemental sulfur by the time the H_2S was breaking through the SAG™ media above 200 ppmv. The impact of the H_2S on the SAG™ media was close to what was predicted and did appear to shorten the SAG™ media life.

5 SUMMARY

The purpose of this paper is to introduce the reader to the process whereby a robust biogas treatment system is designed and constructed for the removal of hydrogen sulfide and siloxanes. We studied the gas conditioning equipment which compresses, chills and removes water from the biogas before it enters the catalytic iron sponge process and is reheated to control its ability to condense water before it enters the siloxane removal equipment. The entire treatment train from the gas source at the digesters to the intake at the IC generators engines must be viewed as a process. All of the individual parts of this process must function in harmony for the desired biogas treatment to occur, including the up-front activity of obtaining a representative biogas analysis. Thoroughly analyzing the biogas and interpreting the results correctly must occur before any design work can begin. Periodic raw biogas analyses are also essential as well as the treated biogas analyses to determine changes in the gas composition and contaminant levels. This is "must have" information for troubleshooting.

At the Mangere WTP, the estimated savings afforded by the biogas treatment system are substantial. It is unfortunate that at this writing there are not more operational or cost comparison data. The biogas treatment system operation at the Mangere WTP should be reviewed after one full year of operation to determine how closely the actual savings compare to the estimated savings.

ACKNOWLEDGEMENTS

Photographs 1 and 2, and Figure 1 are courtesy of Maunsell, Ltd.

The authors wish to thank Mr. Warwick Cutfield, and Mr. Trevor Collins of Maunsell, Ltd. for their input and dedication to details on the overall biogas treatment process, and Dr. You-Sing Yong of Watercare Services Ltd. for providing analytical results on the biogas. AFT's involvement in this project would not have happened nor would it have achieved its level of success without the untiring efforts and brilliance afforded by the gracious personnel of Maunsell Ltd. and WaterCare Services Ltd.

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13. “Determination of Tetrahydrofuran in Air - Charcoal Tube Method / Gas Chromatography, MTA/MA-049/A01,” Instituto Nacional de Seguridad e Higiene en el Trabajo, Centro Nacional de Verificación de Maquinaria, Baracaldo (Vizcaya) Spain, (undated, ca. 1998), p. 7.

14. “Determination of Pyridine in Air - Charcoal Tube Method / Gas Chromatography, MTA/MA-038/A02,” Instituto Nacional de Seguridad e Higiene en el Trabajo, Centro Nacional de Verificación de Maquinaria, Baracaldo (Vizcaya) Spain, (undated, ca. 1998), p. 8.

APPENDIX A

ASTM METHOD D5504 SULFUR SPECIES

Hydrogen Sulfide

Carbonyl Sulfide

Methyl Mercaptan

Ethyl Mercaptan

Dimethyl Sulfide

Carbon Disulfide

Isopropyl Mercaptan

tert-Butyl Mercaptan

n-Propyl Mercaptan

Ethyl Methyl Sulfide

Thiophene

Isobutyl Mercaptan

Diethyl Sulfide

Butyl Mercaptan

Dimethyl Disulfide

3-Methylthiophene

Tetrahydrothiophene

2-Ethylthiophene

2,5-Dimethylthiophene

Diethyl Disulfide

APPENDIX B

ASTM METHOD D1945 GAS CONSTITUENTS

BY % VOLUME

Oxygen/Argon

Nitrogen

Carbon Monoxide

Methane

Carbon Dioxide

Hydrogen

Ethane

Ethene

Propane

Isobutane

n-Butane

Neopentane

Isopentane

n-Pentane

n-Hexane

n-Heptane

C6+

OTHER

Heat of Combustion (BTU/Cu.F.)

Total Specific Gravity

APPENDIX C

EPA METHOD TO-14A VOC SPECIES

Freon 12

Freon 114

Chloromethane

Vinyl Chloride

Bromomethane

Chloroethane

Freon 11

1,1,-Dichloroethene

Freon 113

Methylene Chloride

1,1,-Dichloroethane

Cis-1,2-Dichloroethane

Chloroform

1,1,1-Trichloroethane

Carbon Tetrachloride

Benzene

1,2-Dichloroethane

Trichloroethene

1,2-Dichloropropane

Cis-1,3-Dichloropropane

Toluene

trans-1,3-Dichloropropene

1,1,2-Trichloroethane

Tetrachloroethene

Ethylene Dibromide

Chlorobenzene

Ethylbenzene

m,p-Xylene

o-xylene

Styrene

1,1,2,2-Tetrachloroethane

1,3,5-Trimethylbenzene

1,2,4-Trimethylbenzene

1,3-Dichlorobenzene

1,4-Dichlorobenzene

Chlorotoluene

1,2-Dichlorobenzene

1,2,4-Trichlorobenzene

Hexachlorobutadiene

Propylene

1,3-Butadiene

Acetone

Carbon Disulfide

2-Propanol

trans-1,2-Dichloroethene

Vinyl Acetate

2-Butanone (Methyl Ethyl Ketone)

Hexane

Tetrahydrofuran

Cyclohexane

1,4-Dioxane

Bromodichloromethane

4-Methyl-2-Pentanone (MIBK)

2-Hexanone

Dibromochloromethane

Bromoform

4-Ethyltoluene

Ethanol

Methyl tert-Butyl Ether

Heptane

Acrylonitrile

TPH or NMOC (Hexane/Heptane)

APPENDIX D

AFT METHOD SIL-1 SILOXANE SPECIES

Pentamethyldisiloxane (PMDS)

Hexamethyldisiloxane (MM)

Octamethyltrisiloxane (MDM)

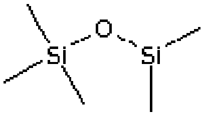
Octamethylcyclotetrasiloxane (D4)

Decamethylcyclopentasiloxane (D5)

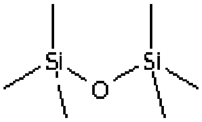
Dodecamethylcyclohexasiloxane (D6)

Molecular Structures: (at the end of each branch is a methyl group, CH_3)

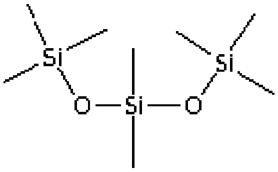
PMDS



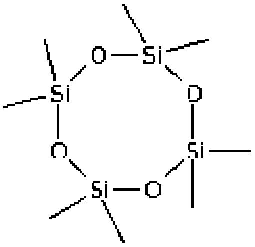
MM



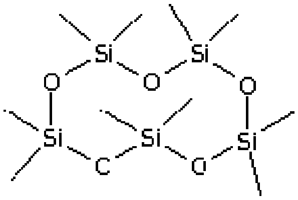
MDM



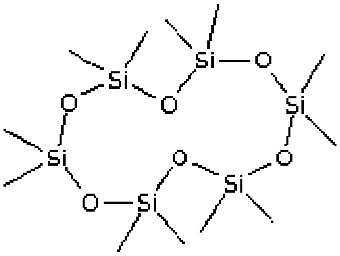
D4



D5

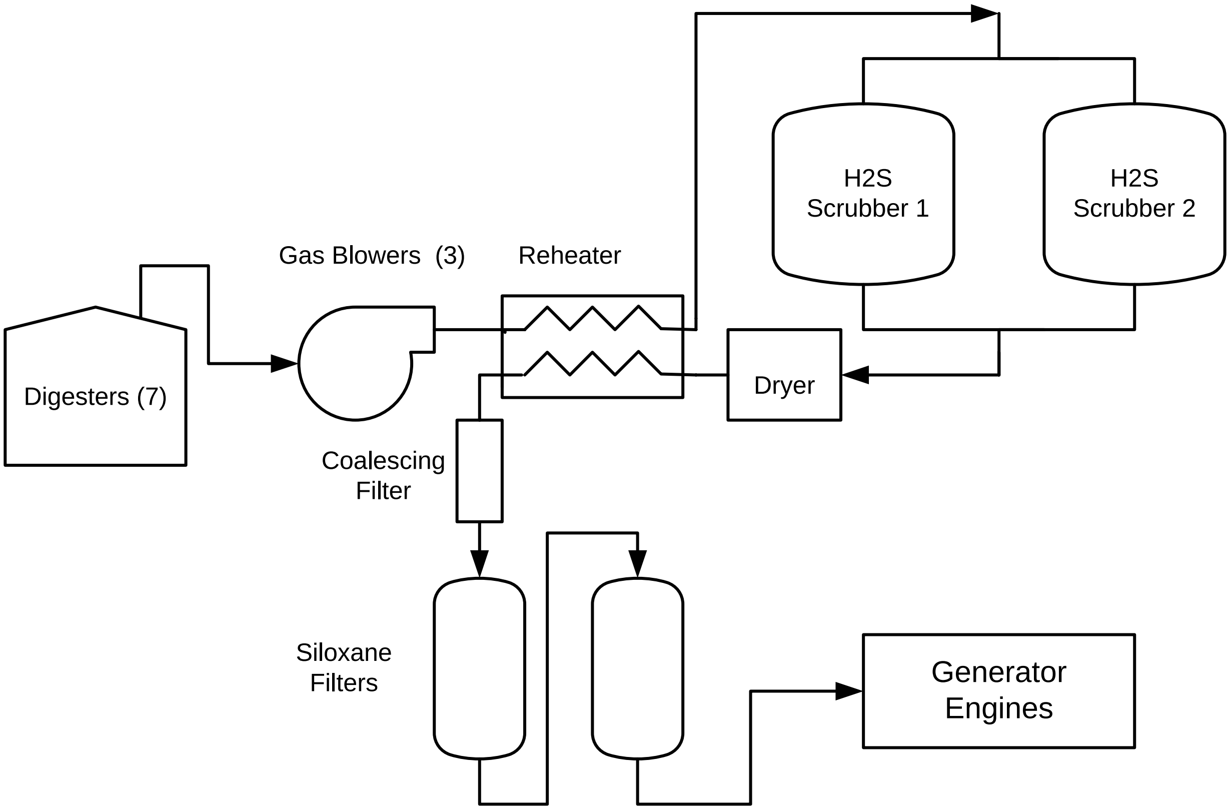


D6



APPENDIX E

MANGERE BIOGAS TREATMENT SYSTEM PROCESS FLOW DIAGRAM



APPENDIX F

MANGERE BIOGAS TREATMENT SYSTEM DESIGN CALCULATIONS

HYDROGEN SULFIDE REMOVAL SYSTEM (PARALLEL FLOW)

Hydrogen Sulfide Removal System Performance Estimates (Calculations performed at 781 ppmv)								Estimated CIS Media Life, Days		Contact Time, Seconds
Flow, Nm3H	Vessel Flow Scheme	Vessel Diameter, m	Media Depth m, nominal	CIS Media m^3, nominal	Velocity m/second	Resistance kPa, initial	kg CIS media			
								Anaerobic	Aerobic	
1700	Full, 1 on, 1 off	3.0	2.55	36	0.043	1.4	30,100	45	91	59
2800	2 on, 1/2 each	3.0	2.55	36	0.036	1.2	30,100	55	110	71
3800	2 on, 1/2 each	3.0	2.55	36	0.039	1.6	30,100	40	81	66

CIS = Catalytic Iron Sponge

SILOXANE REMOVAL SYSTEM (SERIES FLOW)

Siloxane Removal System Performance Estimates (Calculations performed at concentrations shown)										Estimated SAG Media Life, Days	
Flow, Nm^{3}H	ppmv H2S in biogas	Siloxanes in biogas, mg/m^3		Vessel Diameter, m	Media Depth, m,	SAG Media m^3, nominal	Velocity m/second	Resistance kPa, initial	kg SAG media		
		D4	D5							Siloxane D5	Siloxane D4
1700	800	4.52	0.58	2.13 (7 ft.)	1.86 (6 ft.)	13.3	0.085	1.5	6,352	> 90	90
1700	200	4.52	0.58	2.13 (7 ft.)	1.86 (6 ft.)	13.3	0.085	1.5	6,352	>180	180
2800	800	4.52	0.58	2.13 (7 ft.)	1.86 (6 ft.)	13.3	0.14	3.0	6,352	> 60	60
2800	200	4.52	0.58	2.13 (7 ft.)	1.86 (6 ft.)	13.3	0.14	3.0	6,352	> 140	140
2800	800	13.0	1.0	2.13 (7 ft.)	1.86 (6 ft.)	13.3	0.14	3.0	6,352	> 50	50