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FINAL PROJECT REPORT

REMOVAL OF SILOXANE AND H2S FROM BIOGAS USING MICROWAVE ENERGY

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PREFACE

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Removal of Siloxane and H2S from Biogas using Microwave Technology is the final report for the PIER project (grant number PNG-07-003) conducted by Sacramento Municipal Utility District. The information from this project contributes to Energy Research and Development Division's Renewable Energy Technologies Program.

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ABSTRACT

Siloxanes, hydrogen sulfide, and other biogas contaminants damage combustion equipment and interfere with post-combustion emission systems for nitrogen oxides, sulfur oxides, and hydrocarbon removal. A new biogas cleaning system removed hydrogen sulfide and siloxanes from biogas using media regenerated in microwave reactors. The biogas cleaning system had three steps: contaminant collection, media regeneration, and contaminant destruction. The goal of this project was conducting a field demonstration of the microwave regeneration of media saturated with hydrogen sulfide, siloxanes, and other biogas contaminants and of the microwave-induced destruction of these desorbed compounds. The field test was completed in October 2009 at Carson Energy Facility in Elk Grove, CA using a side stream of biogas produced from the Sacramento Regional Waste Water Treatment Plant.

An adsorber vessel was placed in the biogas supply stream. A carbon media mixed with other media such as molecular sieves, silica gels, or impregnated carbons was used to capture the contaminants. Rapid desorption of contaminants occurred when carbon media saturated with contaminants was placed in a microwave field. A microwave reactor removed water, hydrocarbons (including siloxanes), and hydrogen sulfide from the media. The regenerated media was recycled back to the adsorber. The contaminant gas from the regeneration step was chilled to condense water and hydrocarbons. The remaining contaminant gas flowed through a microwave carbon reactor where air was added so that hydrogen sulfide was converted to elemental sulfur and water. The sulfur was filtered out for disposal. The remaining contaminant gas flowed through a catalyst bed within a second microwave reactor where rapid oxidation of remaining hydrocarbons occurred. Siloxane was oxidized to silicon dioxide and removed. Water vapor, carbon dioxide, and the inert sweep gas flowed through the final carbon adsorber and were vented from the system. There was no flare needed to burn waste gas.

Keywords: Biogas, Upgrading, Microwave Regeneration, Media, Emission Control, Siloxane, H_2S, Activated Carbon, Impurity Destruction

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EXECUTIVE SUMMARY

Introduction

The U.S. Environmental Protection Agency (EPA) estimates a potential of 5,500-MW from biogas generated from landfills, wastewater treatment digesters, and animal waste digesters in the United States. Because of this potential, development of biogas resources in California is an important component of improving statewide distributed generation and reducing emissions of greenhouse gases such as methane. Siloxanes and hydrogen sulfide (H_2S) are the most troublesome biogas contaminants. During combustion, siloxanes are converted into silicates (SiO_2) which damage turbine blades, form harmful scales that increase engine wear, and foul post-combustion catalysts. The H_2S and halogenated compounds in the gas form corrosive acids that poison catalytic emission control systems otherwise suitable to reduce nitrogen oxides (NOx) on a natural gas-fired engine. Commercially available media adsorbents will adsorb H_2S, siloxanes, organic halides, and long chain hydrocarbons in biogas but are expensive and difficult to regenerate. Current media regeneration methods are complicated, expensive and can involve additional waste streams or flares.

Project Purpose

The overall goal of this project was to conduct a field demonstration of the microwave regeneration of media saturated with H_2S, siloxanes, and other biogas contaminants and of the microwave-induced destruction of these desorbed compounds. The objectives for meeting this goal were:

- Demonstrating that the microwave technology was technically ready for commercial applications to upgrade biogas generated from landfills, wastewater treatment facilities, and dairy farms.
- Showing that the quality of upgraded biogas was comparable to natural gas and could significantly reduce natural gas use in California.
- Identifying significant technical and environmental issues and barriers to commercializing microwave upgrading technology and to market acceptance for replacing natural gas with upgraded biogas.
- Investigating potential solutions for eliminating identified barriers to commercial applications of microwave biogas upgrading technology and ton market acceptance.
- Assessing the technical and economic feasibility of installing microwave systems for upgrading biogas.
- Identifying any new environmental and safety issues for the commercial applications of microwave technology for upgrading biogas.

Project Results

A two-part laboratory test was conducted to find a proper adsorption media and to obtain data required to modify equipment for field testing prior to starting a microwave technology field test at the Carson Energy Facility in Elk Grove, CA. The first part of the lab tests involved conducting several regeneration cycles of the granular activated carbon (GAC) currently used

and other media saturated with biogas at the Carson Energy Facility, and then selecting a media. The second part was conducting a series of laboratory experiments to investigate the microwave-induced destruction of H_2S and microwave regeneration of the selected HOX (a silica-based adsorbent used to remove the moisture and siloxanes in a gas stream) and GAC mix media saturated with siloxanes.

Four cycles of adsorption at Carson Energy and microwave regeneration at the CHA Corporation laboratory were completed using two batches of 50-lbs of CTC-70 GAC, which is an adsorption media. Microwave regeneration of CTC-70 GAC saturated with biogas was not as effective as expected based on previous field testing with solvent and oil vapors. The project team decided to investigate other adsorption media for biogas applications.

Three adsorption media, CTC-70 GAC, CTC-80 GAC, and HOX were tested using D5 siloxane in the one-inch quartz tube at the CHA lab. The initial D5 response times from the 50 gram bed with 5.0-liters/minute air flow rate were 80 and 150 minutes for fresh CTC-70 and CTC-80 GAC, respectively. After four cycles of regeneration, the initial D5 response times were 30 and 60 minutes for CTC-70 and CTC-80 GAC, respectively. The initial response time for the fresh HOX was much longer than both CTC-70 and CTC-80 GAC. However, HOX did not absorb microwave energy. The project team tested an equal volume of HOX and CTC-80 mix (a 50-50 mix). After four cycles of D5 adsorption and microwave regeneration, the D5 initial response time and adsorption capacity remained at 400 minutes and 35 grams of D5 per 100-grams of media, respectively. Consequently, the project team decided to use the 50-50 media mix consisting of equal volumes of HOX and CTC-80 GAC.

The H_2S was dissociated into hydrogen and elemental sulfur in a GAC bed using microwave energy. Its dissociation efficiency increased as the microwave power increased and reached an equilibrium of 85% at a microwave input power of 600 watts. Introducing oxygen to the reactor broke the equilibrium. The H_2S destruction efficiency increased as the ratio of the oxygen flow rate to the H_2S flow rate increased, reached a maximum of 99% at equal flow rates of H_2S and oxygen, and then decreased with further increases in the oxygen flow rate.

Using lab testing results, the project team modified the existing 100-pounds/hour (lb/hr) mobile microwave unit and constructed a microwave oxidizer. The oxidizer unit consisted of a microwave GAC reactor that destroyed H_2S and a catalytic oxidizer that oxidized hydrocarbons, including siloxanes. The outlet of the oxidizer had a GAC guard bed that captured any remaining hydrocarbons emissions after the microwave oxidizer and before venting to atmosphere.

The field testing consisted of three parts: testing the consistency of microwave regeneration, determining the effect of the regeneration rate on the microwave regeneration efficiency, and evaluating the operational reliability from the six-hour regeneration test. The project team also investigated the possibility of destroying H_2S and siloxanes in the GAC microwave reactor to eliminate the oxidation step and return non-condensable hydrocarbons to biogas.

Based on the field testing results, the project team revised the proposed commercial microwave biogas upgrading process. They evaluated two commercial applications: (1) a 100-lb/hr mobile

microwave system to provide onsite media regeneration service for existing biogas adsorption systems, and (2) installing an integrated adsorption and microwave regeneration system. Capital and operations and maintenance (O&M) costs for these two cases were estimated for the economic feasibility study.

Four cycles of adsorption and microwave regeneration were completed at the Carson Energy facility using two 75-pound batches of HOX and CTC-80 mix. Except during the second cycle, both batch CTC numbers were equal or greater than the fresh media CTC number of 40, indicating that the microwave regeneration rate of 35-lb/hr with a 6-kilowatt (kW) microwave reactor restored the media adsorption capacity. The average amount of liquid recovered was 5% of virgin media weight. More than 70 percent of the recovered liquid was hydrocarbon.

The CTC number of regenerated media increased from 36 at 40-lb/hr, reached 45 at 60-lb/hr, and then decreased to 43 at 80-lb/hr. The optimum throughput was 60-80 lb/hr for two microwave regenerators or 30-40 lb/hr for each 6-kW microwave regenerator.

The six-hour microwave regeneration test was conducted using one 6-kW microwave regenerator at 50-lb/hr and two GAC reactors of the oxidizer unit packed with CTC-70 GAC. The CTC number of regenerated media from the six-hr regeneration test was 38, which was 95 percent of the fresh media. The analysis of gas samples taken from the regenerator outlet and GAC reactor outlet indicated that 99 percent of both H_2S and siloxanes were destroyed in the GAC reactor by microwaves with about one second gas residence time. Therefore, the microwave oxidizer can be replaced by a microwave GAC reactor and the outlet gas from the GAC reactor can be recycled to the treated biogas, which will utilize the heating value of non-condensable hydrocarbon gases. The biogas can replace nitrogen sweep gas to avoid the addition of nitrogen to the treated biogas stream.

The analysis of gas samples from the oxidizer outlet and guard bed outlet showed that 97 percent of siloxanes entered into the microwave oxidizer were oxidized by microwaves and air. Half of the remaining siloxanes were captured by the GAC guard bed and resulted in the overall removal of 99 percent of siloxanes desorbed from saturated media. The siloxane analysis of adsorber outlet gas samples taken at 12, 24, and 48 hours of adsorption times indicated that the initial breakthrough time of regenerated media remained close to 24 hours, confirming that the microwave regeneration restored the fresh media adsorption capacity.

Major problems associated with operating the mobile microwave regeneration system were plugging media at the top of the microwave regenerator, plugging of vapor take-off with carbon fines, and over-heating of the microwave oxidizer unit. Introducing 0.5 standard cubic feet per minute (scfm) nitrogen flow into the top hopper prevented the media plugging problem. A separate refrigeration system needed to be built to supply cooling water to the oxidizer microwave generators. A better filtering system needed to be installed to prevent the vapor take-off plugging problem. The mobile microwave regeneration system should be automated to reduce labor requirements.

Although the siloxane removal capacity of regenerated media was confirmed, the siloxane removal efficiency of the media in the test adsorber could not be validated due to the limitations

of the test system and the highly variable lab reporting of low siloxane concentrations in the biogas samples.

The estimated capital costs were $392,000 and $273,300 for the 100-lb/hr mobile microwave regeneration unit and the 50-lb/hr integrated microwave system, respectively. The O&M costs were estimated at $0.64/lb and $0.36/lb for the mobile unit and integrated system, respectively.

The major conclusions from this study included:

- The biogas quality goals of 0.1 to 0.03 milligrams/meter^3 for siloxanes was not met for two reasons: limitations of the test adsorber and variations of siloxane reporting for different laboratories. The initially proposed adsorber system was designed to operate at lower pressures and flow rates. However, the blower and pressure regulator could not achieve the necessary pressure drop and flow. A new test adsorber was constructed to operate at plant pressure. The new test adsorber was smaller with higher flow rates to allow batches of media to be rapidly saturated with siloxane to evaluate multiple regeneration cycles. The flow rate of biogas in the test adsorber could not replicate a commercial adsorber and was too high to achieve the stated goal. The laboratory reporting of siloxane at low concentration had been an unresolved issue. Three different laboratories were used during this project to try to achieve consistent siloxane removal results. Results from one lab in one test run indicated the goal was met. Results from other labs in the same and different test runs indicated the goal was not met. Some siloxane species at the adsorber outlet were reported at higher levels than in the inlet of the adsorber. The high cost and length of turnaround time to analyze samples precluded further investigation.
- The H_2S in the biogas after treatment by the 50-50 media was measured at 20.3 parts per million (ppm) with an inlet concentration of 23.5 ppm. The 50-50 media was a poor adsorber of H_2S. However, when a second regenerable media of metal impregnated carbon was used after the 50-50 mix, the H_2S levels were reduced to below 10 ppm.
- The media consisting of 50 percent CTC-80 GAC and 50 percent HOX removed siloxanes and H_2S from biogas much better than GAC alone. The initial breakthrough time of D5 siloxane was 10 times longer for this media than CTC-70 GAC.
- The siloxane initial breakthrough time for media in the test adsorber was estimated to be 24 hours during the field testing at Carson Energy. Regenerated media demonstrated consistent siloxane removal capacity after four cycles of adsorption and microwave regeneration. However, consistent siloxane removal efficiency could not be validated due to system design and significant variations in lab reports at low siloxane concentrations.
- Microwave regeneration of the 50 percent CTC-80 GAC and 50 percent HOX media restored the fresh media adsorption capacity. CTC numbers of regenerated media ranged from 38 to 50 for eight cycles of the adsorption and microwave regeneration, which were very close to the fresh media CTC number of 40.
- Microwave regeneration of GAC saturated with biogas did not restore the adsorption capacity of fresh GAC. The initial breakthrough time of D5 siloxane was much longer for HOX than both CTC-70 and CTC-80 GACs. The D5 initial breakthrough time

remained constant at about 400 minutes for the CTC-80 GAC and HOX mix for four cycles.

- H_2S was converted into hydrogen and elemental sulfur in a carbon bed by microwaves. The conversion efficiency increased with microwave power, reached 85 percent at 600 watts, and decreased with additional microwave power input. Adding oxygen into the microwave reactor significantly increased the H_2S destruction efficiency.
- With one second gas residence time and 6-kW microwave power, siloxanes and H_2S desorbed from media were completely destroyed by microwaves. Consequently, the microwave oxidizer can be replaced by the GAC reactor to destroy siloxanes and H_2S in the desorbed gas and to recycle cleaned desorbed gas to the biogas stream.
- More than 93 percent of non-condensable hydrocarbon gases were oxidized in the microwave catalytic oxidizer and exhaust gas from the final GAC guard bed contained only one percent of non-condensable hydrocarbons.
- Liquid recovered during microwave regeneration was about 5-10 percent of media and 70 percent of recovered liquid was hydrocarbons.
- The CTC number of regenerated media varied from 36 to 45 as the regeneration rate varied from 40 to 80-lb/hr. The regeneration rate range from 60 to 100-lb/hr produced CTC numbers close to the fresh media CTC number of 40.
- The estimated cost of regenerated media was one third lower than fresh media, indicating that the microwave regeneration was a better choice than conventional thermal regeneration.

The project teams recommendations included:

- Conducting further testing of adsorption and microwave regeneration using various ratios of HOX and GAC to determine an optimum media and retention time for siloxane removal and destruction.
- Investigating the direct destruction of siloxanes and H_2S in the GAC bed by microwaves using simulated biogas and a pilot-scale reactor in the laboratory first and then test the process with real biogas at Carson Energy or at a landfill site.
- Performing laboratory and field testing to find and demonstrate a practical and economic method for removing significant H_2S from biogas.
- Performing a detailed economic feasibility study for using microwave methods for upgrading biogas specifically for dairy farms, landfills or wastewater treatment facilities.
- Conducting a pilot study on an existing thermal regeneration siloxane removal system to replace the contaminant flare with a microwave oxidation system.

Project Benefits

The undeveloped potential generation capacity at California landfills, wastewater digesters, and food digesters is estimated at 600 megawatts, which represents about 85 million feet^3/day of methane. Additional biogas can be utilized to produce electricity and thermal energy to reduce

natural gas use in California using this microwave biogas upgrading technology. The use of a microwave system to clean biogas can also reduce criteria air pollutants by eliminating the need for a flare or enabling catalysts to be used on conventional biogas combustion systems. Greenhouse gases generated in the manufacture, transport and disposal of single use media will be significantly reduced by recycling regenerated media. Commercialization by the CHA Corporation will also bring additional green jobs for manufacturing and installation to California.

CHAPTER 1: Introduction

1.1 Background and Overview

The US EPA estimates a potential of 5,500 Megawatts from biogas generated from landfills, wastewater treatment digesters, and animal waste digesters in the United States[1]. Development of Biogas resources in California is an important component of improving statewide distributed generation and reducing emissions of greenhouse gases such as methane. An economic biogas pretreatment is needed in light of tightening emission regulations and costly equipment maintenance due to biogas contaminants.

Siloxanes and hydrogen sulfide (H_2S) are the most troublesome biogas contaminants. During combustion, siloxanes are converted into silicates (SiO_2) which damage turbine blades, form harmful scales that increase engine wear, and foul post combustion catalysts. The H_2S and halogenated compounds in the gas form corrosive acids including sulfuric acid (H_2SO_4) and hydrochloric acid (HCl). Even small quantities of sulfur dioxide (SO_2) in engine exhaust will poison catalytic emission control systems otherwise suitable to reduce NOx on a natural gas fired engine. Commercially available media will adsorb H_2S, siloxanes, organic halides, and long chain hydrocarbons in biogas but are expensive and difficult to regenerate. Lower cost media, such as carbon, is buried or burned when spent thereby releasing contaminants back to the environment. Current media regeneration methods are complicated, expensive, and can involve additional waste streams or flares.

The Sacramento Waste Water Treatment Plant (SWWTP) produces biogas in digesters. The biogas is a mixture of methane, carbon dioxide, and water with sulfur and siloxane impurities. The sulfur is removed with an iron sponge and the gas is chilled to about 40 °F dew point to remove water. This treated biogas is piped to the Carson Energy facility for power generation.

The California Energy Commission (CEC) awarded a PIER grant to SMUD to demonstrate a biogas treatment system combining media adsorption and microwave treatment that can 1) remove siloxanes and H_2S from biogas to prevent combustion related damage and allow post combustion technologies on engines, turbines and boilers to meet 2007 CARB emission standards and 2) regenerate and reuse spent media at a cost less than existing single use media disposal and replacement methods.

Applied Filter Technology (AFT) and the CHA Corporation (CHA) joined with the SMUD to develop and demonstrate the most economic and environmentally friendly technology by combining CHA microwave technology with the AFT media and biogas treatment systems. AFT installed the biogas conditioning system that is currently being operated at the Carson Energy facility with single use media. AFT supplied two different granular activated carbons

[1] Sloe, Jon, Biogas, A Growing Niche for Distributed Generation, E-Source, DE-21, May 2003.

(CTC-70 and CTC-80) and silica-based HOX adsorbent for siloxane adsorption studies of the project.

CHA has first conducted a series of laboratory trials regenerating media having siloxanes and H_2S in microwave reactors. The results of these trials were used to design the field demonstration system. A portable microwave regeneration system using existing microwave equipment was assembled by CHA and was transported to the Carson Energy facility for the field testing. CHA started the field testing in April and completed it in October 2009.

1.2 Project Objectives

Project Goal: The goal of this project is to demonstrate that use of molecular sieve media and carbon adsorbent to remove H_2S, siloxanes, and other biogas contaminants from biogas combined with the microwave-induced regeneration of media and destruction of these contaminants is effective, economical, and can be implemented at landfills and digesters in California.

Because existing microwave equipment is being modified to build the demonstration unit at a low cost to the CEC and SMUD, the scope of this demonstration is limited to cleaning a slipstream of the available biogas at the SMUD Carson Energy facility for a limited duration. Assuming the size of the first media bed is about 100 lbs and that ten cycles of media are regenerated in the demonstration, about 64,000 scf of biogas will be treated by this demonstration system. All of this treated biogas will be used in the SMUD power plant and will replace about 40,000 scf of natural gas.

1. Biogas quality goals:

   Maximum Siloxane concentration of 0.1 to 0.03 mg/m^3

   Maximum H_2S concentration of 10 ppm

2. Determine the best (economic and efficacy) combination of media to meet biogas quality goals.
3. Remove 99 percent of the siloxanes, H_2S, and VOCs from the biogas with the best combination of media.
4. Remove 95 percent of the siloxanes, H_2S, and VOCs from the media with microwave regeneration.
5. Determine the optimum flow rate of media, sweep gas, and microwave power level to achieve 95 percent removal rate of siloxanes, H_2S, and VOCs from the media.
6. Achieve 85 percent of adsorption capacity of new media after five cycles of regeneration with media used to treat the biogas.
7. Achieve 95 percent oxidation efficiency for siloxanes, H_2S, and VOCs for the microwave-SiC oxidation reactor.

8. Achieve SO_2 removal efficiency greater than 95 percent in the microwave reduction reactor.

9. Achieve removal rates of 95 percent for SiO_2 and elemental sulfur in the particle filters.

10. Determine if the operational reliability of the microwave regeneration process can meet a 70 percent availability factor.

11. Document any mechanical and operational issues experienced during field testing of the microwave regeneration, oxidation, and carbon-SO_2 reactors that need to be addressed in the design of a full scale, automated system.

12. Identify any environmental and safety issues associated with commercial operation of microwave reactors for treatment of biogas.

13. Demonstrate that the microwave regeneration process can treat and recycle media at about $.40 per pound.

14. Demonstrate the capital cost and operational cost to install and operate an automated, full scale system at a landfill or digester site with power production would be about $.01 per kWh produced.

15. Clean about 64,000 scf of biogas that will replace about 40,000 scf of natural gas at the SMUD Carson Energy plant.

16. Determine the capital cost and operational cost to install and operate an automated, full scale system at an existing landfill or digester site to supplement existing media treatment. Express cost in terms of $/scfm gas treated and $/pound of contaminant removed.

17. Determine the capital cost and operational cost to install and operate a regional microwave treatment system to regenerate and service media at several new and existing landfill or digester sites. Express cost in terms of $/scfm gas treated, $/pound of contaminant removed and $/pound media treated and replaced.

CHAPTER 2:
Project Approach

2.1 Site Preparation

2.1.1 Existing Biogas System

The Carson Energy power plant is located next to the SRWWTP in Elk Grove, CA. Solids from primary waste treatment are placed in large digesters to produce biogas. The raw biogas is passed through iron oxide on media (iron sponge) to reduce H_2S from about 100 ppm to less than 30 ppm. The biogas is then compressed and water is removed. The compressed biogas is transported in an underground pipe about ½-mile to the Carson Energy plant. Figure 1 shows one digester. Figure 2 shows the iron sponge system with gas storage tanks and the biogas flares in the background. Figure 3 shows the biogas compressors.

Figure 1: SRWWTP Digester

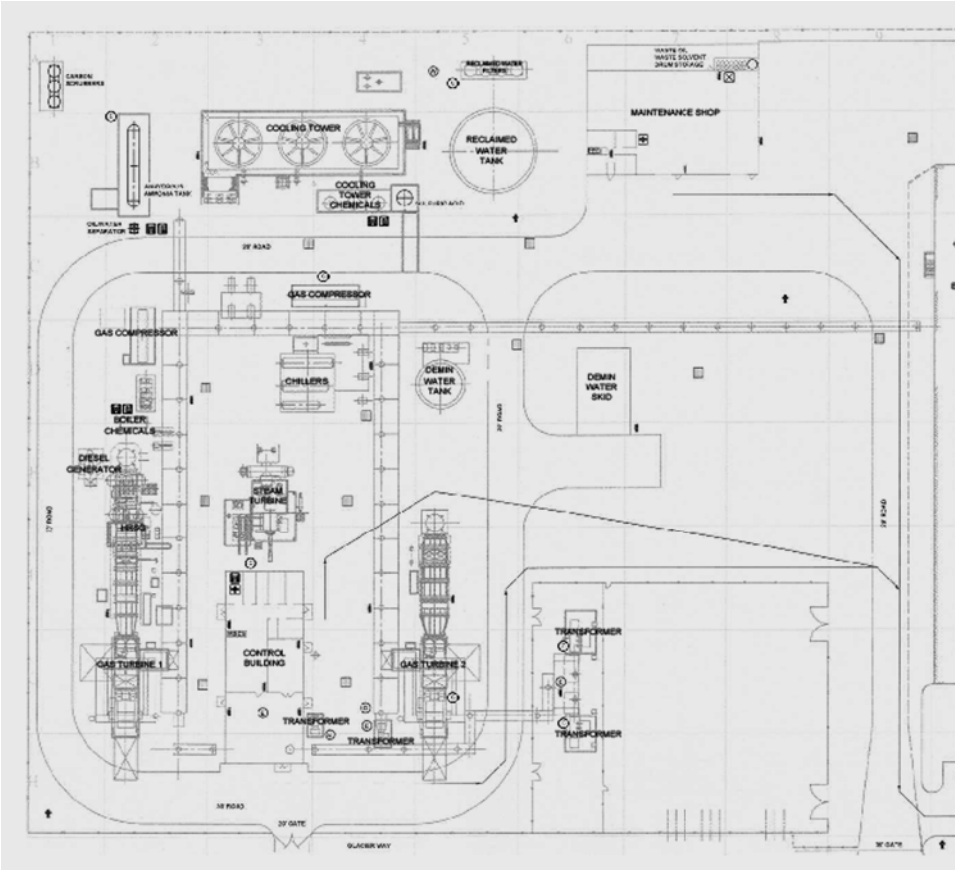
Figure 2: SRWWTP Iron Sponge H_2S Treatment

Figure 3: SRWWTP Biogas Compressors

Carson Energy is a SMUD owned power plant with a 42-MW gas turbine. The biogas is combusted in a duct burner after the gas turbine to power a second steam turbine and provide process steam to the adjacent Glacier Valley Ice Company. Steam is also routed back to the digesters to increase biogas production.

Figure 4 is a site plan of Carson Energy. The biogas from the SRWWTP enters the site in the upper left hand corner. The adsorber system for this demonstration is located in this area. The microwave treatment system site is located next to the gas compressor on the left.

Figure 4: Carson Energy Site Plan



Three large tanks containing 9,000 pounds each of Granular Activated Carbon (GAC), with two in operation in lead-lag configuration, are used to remove siloxane from the biogas. Each tank has three layers of carbon media segmented by pore size with the largest pore size in the gas stream first (SAG system). The SAG system removes siloxanes and remaining H2S to protect the NOx catalyst on the exhaust of the turbine and duct burner. The carbon is single use and one tank is changed out approximately every two months.

Figure 5 illustrates the existing biogas system with one of the three existing SAG media tanks in the background. There is a steam trace heating system located right before the SAG media tanks to warm the biogas and prevent water condensation in the tanks. The slipstream

modification will be installed upstream of the steam trace system and existing SAG media tanks.

Figure 5: Existing Biogas Pipeline System

2.1.2 Siting the Adsorber System (Task 5)

Slipstream inlet and outlet pipes were installed in the biogas pipeline upstream of the SAG tanks. Originally, two adsorbers were proposed as a multi-stage adsorption system to remove siloxanes and H_2S from the biogas. Because the pressure of the biogas supply line exceeds the pressure limitations of the selected adsorbers, another vessel designed for higher pressure was needed.

A local metal fabricator constructed a pressure vessel that would meet the specifications for the project. The new fabricated adsorber was made to ASTM specifications, about 16 inches in diameter and 24 inches tall and would hold about 2.8 cubic feet of carbon (about 85 lbs). The adsorber has a flange top with 16 bolts. The adsorber was connected to the inlet pipe of the slipstream and the inlet of the blower with hose. The flow was directed top down. Tests with carbon in the adsorber showed a low pressure drop across the blower with no overload condition. This adsorber was used to saturate the selected adsorbent with biogas for laboratory microwave regeneration tests. After several trials with the adsorber, it was determined that the system would saturate 50 lbs of media in about 24 hours.

Figure 6: Fabricated Adsorber Connected to the Blower

During the adsorption trials to determine media performance, flow rates were estimated. A flow meter was subsequently installed in the return leg of the slipstream prior to the onsite demonstration trials.

Figure 7: Flow Meter on Biogas Slipstream

2.1.3 Siting the Microwave Demonstration System

The microwave demonstration equipment was delivered to the Carson Energy site in April 2009. The primary requirements for siting were a hard surface, proximity to the adsorber system, 440-volt power and access to a water supply and drain (for cooling). Additionally, the location could not interfere with plant operations. The equipment was sited next to an unused gas compressor and the power panel for the compressor used as the source of temporary electric power. Hoses were used to provide cooling water from a nearby spigot. This location was about 150 feet from the adsorber system.

Figure 8 shows the portable microwave regeneration unit connected to the mobile microwave oxidizer in place at the Carson Energy site. Liquid nitrogen Dewars and miscellaneous gas cylinders were rented from Air Gas and used in conducting the field tests.

Figure 8: Portable Microwave System Installed at Carson Energy

2.2 Laboratory Testing, Media Selection and Equipment Sizing (Task 2)

The laboratory microwave research for this project consisted of two parts: (1) Conduct several cycles regenerating about 50 pounds of media saturated with biogas at the Carson Energy facility using a prototype microwave regeneration unit equipped with the microwave catalytic oxidizer, and (2) Conduct experiments investigating the possibility of generating SiO_2 from siloxanes during microwave regeneration of media saturated with siloxanes and also investigating the reaction of SO_2 with carbon in a microwave reactor. In addition, the microwave-induced decomposition of H_2S in carbon in a microwave reactor was investigated.

The overall goal of the first part of laboratory investigation was to prove that the microwave regeneration of media saturated with biogas impurities restores the media adsorption capacity close to the original adsorption capacity and that microwave catalytic oxidation destroys greater than 95 percent of volatile organic compounds (VOCs), siloxanes, and H_2S desorbed from GAC during microwave regeneration.

The overall objective of the second laboratory microwave research was to study the feasibility of using the microwave-induced reaction of SO_2 with GAC to destroy SO_2 generated from H_2S oxidation. It was also our goal to investigate the feasibility of decomposing the H_2S in the GAC bed by microwave energy. The H_2S can easily be oxidized in the microwave catalytic oxidizer to produce SO_2. Since the composition of gas desorbed from saturated GAC varies significantly, it is difficult to maintain stoichiometric air required for the oxidation of impurities in the microwave catalytic oxidizer. It is simpler to pass the gas flowing out from the microwave regeneration unit to the GAC bed to destroy H_2S prior to oxidizing the biogas impurities in the microwave oxidizer. Excess air will consume GAC in the microwave field forming CO_2. The specific objectives of the second part of the laboratory program are numerated as follows:

1. Conduct a series of microwave experiments using a laboratory microwave reactor system to obtain experimental data on the SO_2–carbon reaction for the various sweep gas superficial velocities or residence times and microwave power levels.
2. Capture the elemental sulfur generated from the SO_2 and carbon reaction.
3. Select the superficial gas velocity and microwave power that destroys greater than 95 percent of the SO_2.
4. Conduct a series of microwave experiments using a laboratory microwave reactor system to investigate the decomposition rate of H_2S in the GAC bed by microwaves for the various sweep gas superficial gas velocities and microwave power levels.
5. Monitor the outlet gas for H_2S concentration.
6. Determine the efficiency for microwave-induced decomposition of H_2S into the elemental sulfur and hydrogen.
7. Select the sweep gas velocity and microwave powers that destroy 95 percent of the H_2S.
8. Measure the GAC adsorption capacity for siloxanes.
9. Determine the microwave regeneration efficiency for GAC saturated with siloxanes.

2.2.1 Analysis of Biogas

A Tedlar bag sample of biogas at Carson Energy was taken on September 2, 2008. Laboratory analysis showed it consists of about 58.6 percent Methane, 36 percent Carbon Dioxide, 4 percent Nitrogen, and 1.3 percent Oxygen. Biogas samples for siloxanes were taken periodically during the demonstration. Analysis data for four sample periods are provided in Table 1. Note that the siloxane concentration varies greatly over time but D5 and D4 are present in the highest concentration in this biogas. The variation of the inlet siloxane concentration influences the

adsorber outlet concentration significantly, causing difficulties of interpreting data on the siloxane removal efficiency.

Hydrogen Sulfide (H_2S) in the biogas was measured using a handheld sensor or Draeger tubes. Concentration varied depending on the maintenance schedule of the iron sponge treatment system at the SRWWTP and was typically between 12 ppm and 30 ppm.

Table 1: Siloxane Concentrations in Biogas at the Carson Energy Site

	9/2/2008	4/1/2009	5/11/2009	7/12/2010
Description	**ppmv as Si**	**ppmv as Si**	**ppmv as Si**	**ppmv as Si**
Tetramethyl silane	<0.1	<0.1	<0.1	<.02
Trimethyl silanol	<0.1	<0.1	<0.1	<.02
Hexamethyldisiloxane (L2)	<0.1	<0.1	<0.1	<.02
Hexamethylcyclotrisiloxane (D3)	<0.1	0.09	<0.1	.044
Octamethyltrisiloxane (L3)	<0.1	<0.1	<0.1	<.02
Octamethylcyclotetrasiloxane (D4)	1.36	0.90	0.74	1.24
Decamethyltetrasiloxane (L4)	0.10	<0.1	<0.1	<.02
Decamethylcyclopentasiloxane (D5)	10.06	2.25	3.23	11.14
Dodecamethylpentasiloxane (L5)	<0.1	<0.1	<0.1	<.02
Dodecamethylcyclohexasiloxane (D6)		0.16	1.13	.41
Others (as L2)	6.73	0.15	0.72	.06
Total as Si, ppmv	18.25	3.55	5.82	12.89
Total (Si, mg/M^3)	22.88	4.45	7.30	15.28

2.2.2 Laboratory Microwave Regenerating Testing and Selection of Media

The media adsorber with a 3.5-cubic feet capacity was used to collect siloxanes and VOCs on the test media at Carson Energy. For this test, the top 50 lb of media was the test media and segregated from the lower media with a filter pad. The lower media remained in the adsorber as a support during the test. This would ensure that the bypass of the biogas through the test media could not occur. The level of the media inside the adsorber was marked prior to the first adsorption test. The media adsorber was configured for top down flow.

After the initial test to confirm the operation of the system, each batch of the test media was weighed and placed in the adsorber for exposure to 24 hours of biogas flow. The saturated batch would be weighed, packaged, and shipped to the CHA laboratory in Laramie, WY for testing. After testing and regeneration, the media would be shipped back to Carson Energy.

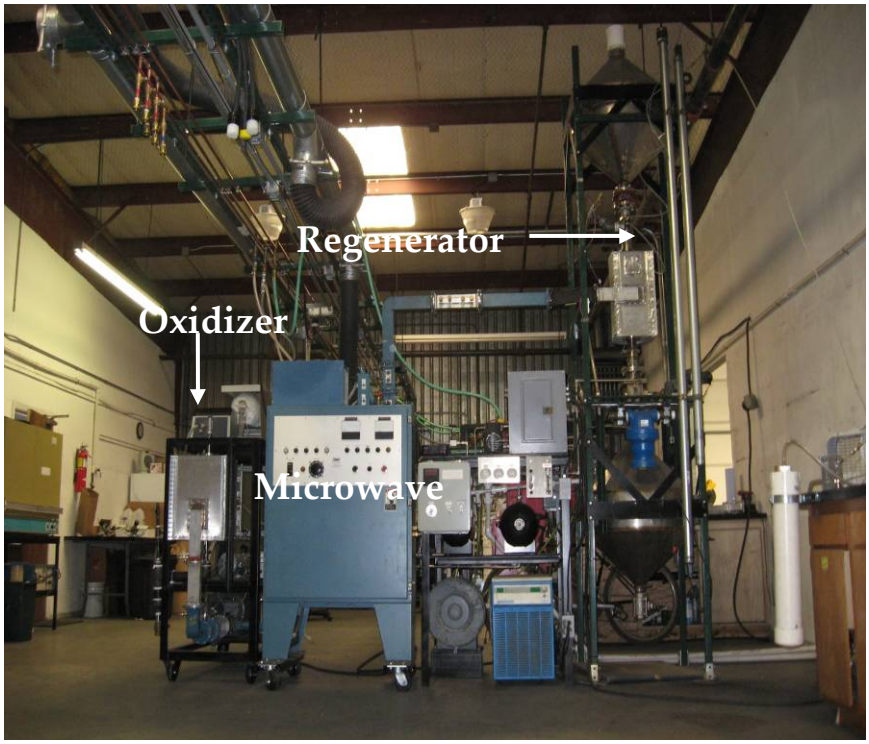
The laboratory microwave regeneration testing included the following steps;

1. Saturate about 50 pounds of CTC-70 GAC with biogas.
2. Regenerate the GAC saturated with biogas impurities in a 50-lb/hr prototype microwave regenerator.
3. Monitor the outlet gas from the microwave oxidizer for total hydrocarbon concentration.
4. Measure the adsorption capacity of regenerated GAC using the Carbon Tetrachloride (CTC) number or Butane number.
5. Re-saturate the regenerated GAC with biogas impurities.
6. Repeat the adsorption/regeneration cycle (steps 1 through 5) several times.

2.2.2.1 Microwave Regeneration Prototype Unit

CHA has a 50-lb/hr prototype microwave regeneration unit that is installed in the CHA laboratory and also a 100-lb/hr mobile microwave unit that was modified for the field demonstration at Carson Energy Plant for upgrading biogas. Figure 9 shows a photograph of the 50-lb/hr microwave carbon regeneration system that was modified for this program.

Figure 9: Existing 50-lb/hr Microwave GAC Regeneration System



This microwave GAC regeneration system consists of a 3-inch quartz tube microwave reactor, top and bottom hoppers, water-cooled heat exchanger, 6-kW Cober microwave generator, knockout pot, 3-kW microwave-SiC oxidizer, pneumatic conveyor, and compressor. The saturated media is pneumatically transported into the feed hopper. The media moves through the quartz tube reactor by gravity and its rate is controlled by the star valve located at the bottom of the quartz tube. The vapor desorbed from the media is carried by a nitrogen sweep

gas and is condensed in the water-cooled heat exchanger. The condensed liquid is collected in the knockout pot. The nitrogen and uncondensed vapor flow into the microwave-SiC oxidizer. Any VOCs and siloxanes are oxidized by microwaves in the SiC bed and then flow into the filter. The SiO_2 produced from siloxanes is captured by the filter and remaining gas is vented into the atmosphere. A 3-kW Gerling microwave generator supplies microwave energy to the oxidizer.

The 50-lb sample is transferred to the top hopper for microwave regeneration. A sample of the saturated media was taken for the CTC number measurement. The star valve was set at 30-lb/hr regeneration rate, which was lower than the pilot plan design capacity because of higher water content of the saturated media. Approximately 1.0 standard cubic feet per minute (scfm) nitrogen flow was used as the sweep gas. Also, 1.0-scfm air flow was supplied to the microwave oxidizer to oxidize hydrocarbons including siloxanes desorbed from the media. The detailed test procedure is presented in Appendix A: Laboratory Test Plan.

2.2.2.2 Laboratory Regeneration Testing Results

CTC-70 GAC Adsorption Media

As described above, 50 lbs of CTC-70 GAC was saturated for 24 hours with biogas at Carson Energy site and shipped to CHA Lab for microwave regeneration. CHA regenerated four samples for Batch 1 and Batch 2 totaling eight 50-lb GAC treatments using 50-lb/hr microwave regenerator shown in Figure 9. Appendix B presents all laboratory microwave regeneration testing data. Figure 10 and Figure 11 present respectively the CTC number of regenerated media and the amount of liquid recovered for Batch 1 media. Figure 12 and Figure 13 show respectively the CTC number of regenerated media and the amount of recovered for Batch 2 sample.
As shown in Figure 10 and Figure 12 the first cycle of microwave regeneration did not restore the fresh GAC CTC number of 70. The four samples from first and second cycle adsorption tests were much more saturated with water and hydrocarbon liquid than third and fourth adsorption cycles as shown in Figure 11 and Figure 13.

The regeneration of first adsorption cycle samples for Batch 1 and Batch 2 showed a great improvement in the CTC number as well as a large amount of liquid recovered. However, in the subsequent regeneration cycles the improvement in CTC and the amount of liquid recovered decreased as seen in Figure 11 and Figure 13. These figures show the number of regenerations on the X-axis. Some of the samples were regenerated as many as four times with varying mass and volumetric flow rates. The optimal condition for regeneration was found to be at 5-kW of power with a low flow rate (0.6-0.8 ft^3/hr).

Figure 10: Batch 1 Regeneration Showing CTC # Improvement

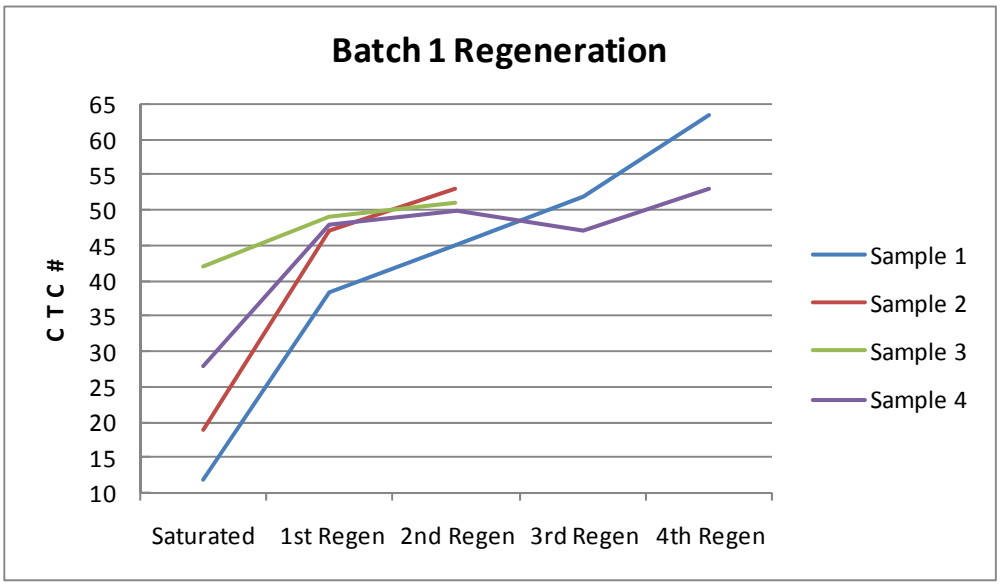


Figure 11: Batch 1 Liquid Recovered

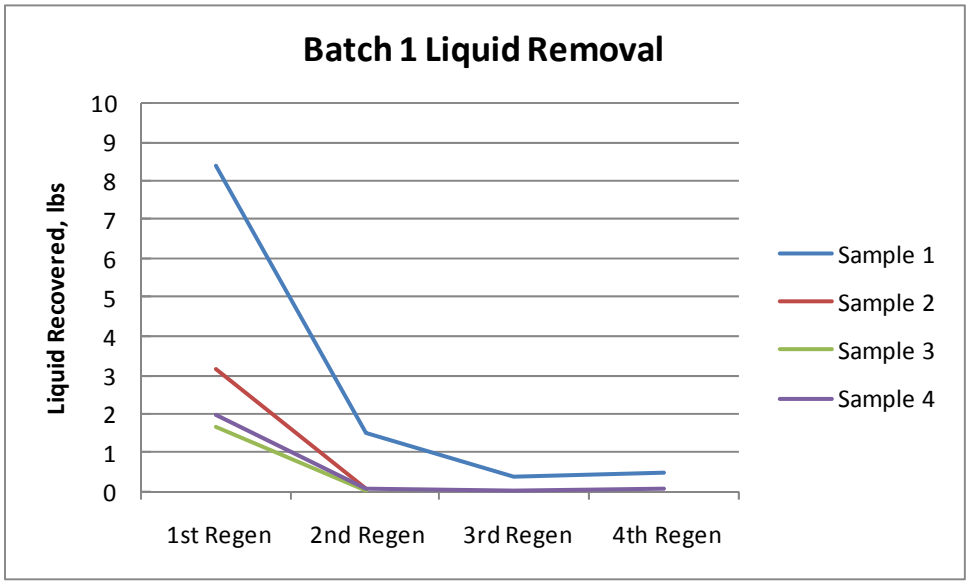


Figure 12: Batch 2 Regeneration Showing CTC # Improvement

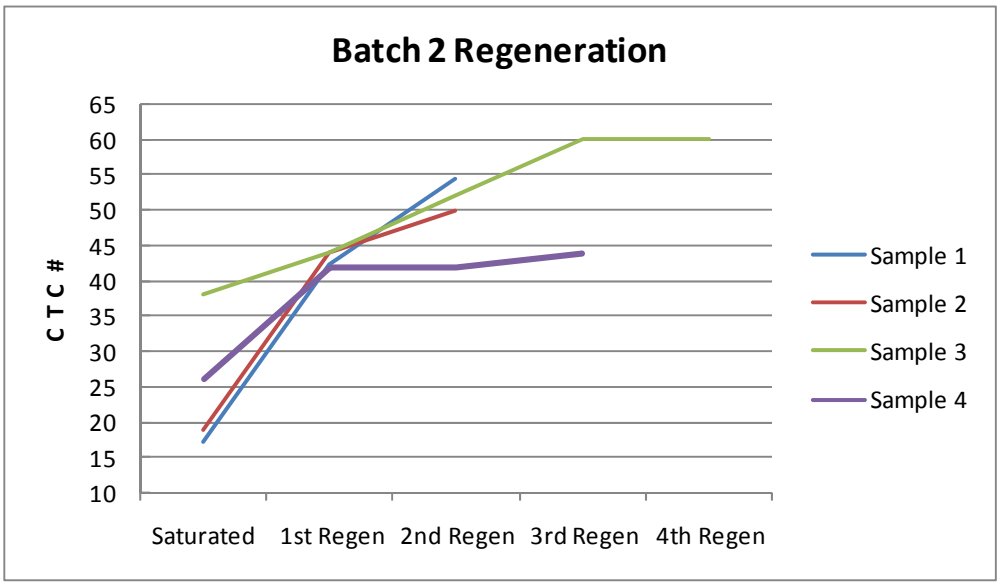
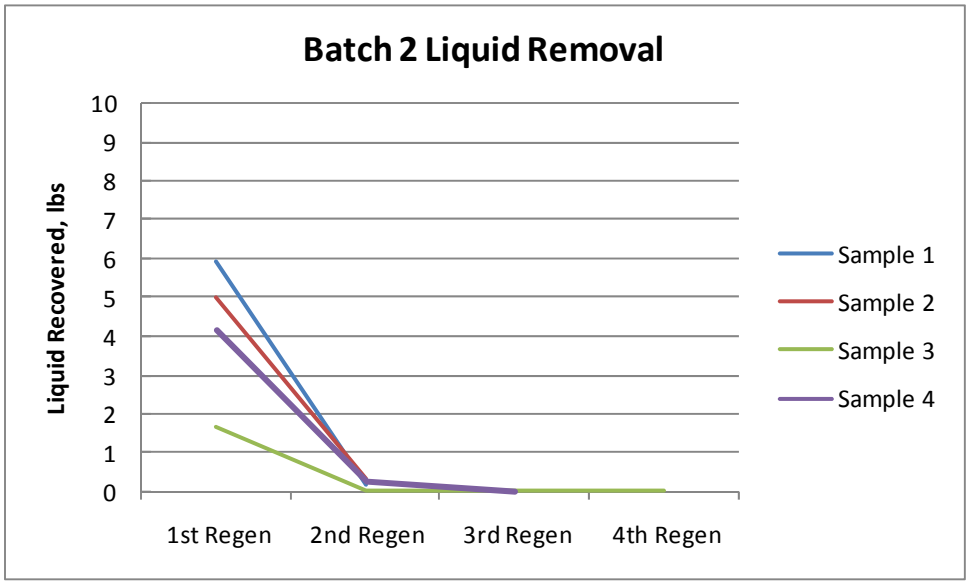


Figure 13: Batch 2 Liquid Recovered



It is not clear why third and fourth saturation tests produced higher CTC number GAC. The condition of biogas is dependent on the weather. Rainy days would produce biogas with high moisture. It appears that first four saturation tests were conducted with biogas having higher moisture contents.

Four cycles of adsorption and regeneration results show clearly that the CTC-70 GAC is not a suitable regenerable adsorbent for removing siloxanes and VOCs from biogas. Consequently,

the team decided to terminate further field adsorption and lab microwave regeneration tests using CTC-70 GAC.

CTC-80 GAC & HOX Mixture

After completing the small scale tests on the CTC-70 GAC discussed above, AFT suggested different media and provided 50 pounds each of CTC-80 GAC and HOX. CHA staff conducted laboratory tests using D5 and CTC-80 GAC and found that CT-80 GAC was much better adsorbent for D5 siloxane. Also, the adsorption and microwave regeneration tests were conducted using D5 and the mixture of CTC-80 and HOX (equal volume). The team ran four cycles of adsorption and regeneration. The results showed that microwave regeneration restored the D5 adsorption capacity of the mixture of fresh CTC-80 and HOX. The advantage of using CTC-80 GAC over CTC-70 GAC is a larger pore size.

Because of favorable D5 adsorption and regeneration test results, staff tested the mixture of CTC-80 GAC and HOX at Carson Energy. The mixed adsorbent had equal volume of CTC-80 GAC and HOX. This mixed batch weighed about 56-lbs and was saturated for 25 hours. CHA received the saturated sample and regenerated it under the optimal conditions. The Butane number was measured to calculate the CTC number for a fresh sample of the mixture and also for the regenerated adsorbent. The fresh adsorbent had a CTC number of 40.3 while the regenerated adsorbent yielded a CTC number of 56.3. The results were encouraging because microwave regeneration actually increased the CTC number and thus the adsorption capacity of the GAC and HOX mixture. Additionally, 7.62-lbs (3,750-mL) of liquid were recovered from the batch which is amongst the highest ever recorded. Of the liquid recovered 4.85-lbs (2,200-mL) was water and 2.77-lbs (1,550-mL) was hydrocarbon liquid. The specific gravity of the recovered hydrocarbon liquid was 0.792. A sample of the hydrocarbons recovered was sent to a lab for analysis. They were primarily C6 through C12 hydrocarbons and also contained siloxanes. Analysis results are shown in Table 2 and Table 3.

Table 2: Liquid Hydrocarbon Analysis

Hydrocarbons	Weight %
Other C4-C5 compounds	1.51
n-Pentane	0.37
Other C5-C6 compounds	3.32
n-Hexane	0.81
Benzene	0.32
2-Methylhexane	0.76

3-Methyl hexane	0.70
Hydrocarbons	**Weight %**
2,2,4-Trimethyl pentane	0.82
Other C6-C7 compounds	3.51
n-Heptane	0.87
Toluene	2.84
Other C7-C8 compounds	8.32
n-Octane	0.90
m,p-Xylenes	1.04
o-Xylene	1.07
Other C8-C9 compounds	8.45
n-Nonane	1.22
1,2,4-Trimethyl benzene	1.78
Other C9-C10 compounds	9.80
n-Decane	2.44
Cymenes	2.98
Other C10-C11 compounds	17.0
n-Undecane	3.44
Other C11-C12 compounds	19.5
C12 plus compounds	6.16

Table 3: Siloxane Analysis of Liquid Hydrocarbon

Organic Siloxanes	Weight %
Trimethyl silane	<0.01
Trimethyl silanol	0.003
Hexamethyldisiloxane (L2)	0.36
Hexamethylcyclotrisiloxane (D3)	0.022
Octamethyltrisiloxane (L3)	<0.01
Octamethylcyclotetrasiloxane (D4)	1.57
Decamethyltetrasiloxane (L4)	0.007
Decamethylcyclopentasiloxane (D5)	1.41
Dodecamethylpentasiloxane (L5)	<0.01
Dodecamethylcyclohexasiloxane (D6)	0.035
Others (as L2)	0.030
Total	3.43

Assuming the gas flow rate of 150-scfm and using VOC concentration data, we estimated the amount of VOCs entered into the adsorber for 25 hours to be 0.46 pound. After consulting with SRWWTP staff, it is believed that the sources of the larger hydrocarbons are industrial waste streams and seasonal runoff from streets and parking lots that enter the digesters. Note that these hydrocarbons comprise potential fuel that is currently disposed of with single use media. Capture of condensable hydrocarbons will need to be included in the demonstration system.

The average gas temperature of vapor from the microwave regenerator was 60 °F when the mixture of CTC-80 and HOX was regenerated. The average temperature of vapor from the microwave reactor during regeneration of CTC-70 GAC was 80 °F. This indicates that the bed temperature of the mixed adsorbent was lower than bed temperature of CTC-70 GAC.

In conclusion, the GAC-80 and HOX mix produced much better laboratory results than the CTC-70 GAC and was selected for the field demonstration tests.

2.2.3 Small- Scale Laboratory Investigation

The overall objective of the second laboratory microwave research was to study the feasibility of using the microwave-induced reaction of SO_2 with GAC to destroy SO_2 generated from H_2S oxidation. It was also our goal to investigate the feasibility of decomposing the H_2S in the GAC bed by microwave energy. The H_2S can easily be oxidized in the microwave catalytic oxidizer to produce SO_2. Since the composition of gas desorbed from saturated GAC varies significantly, it is difficult to maintain the stoichiometric air required for the oxidation of impurities in the microwave catalytic oxidizer. It is simpler to pass the gas flowing out from the microwave regeneration unit to the GAC bed to destroy H_2S prior to oxidizing the biogas impurities in the microwave oxidizer. Excess air will consume GAC in the microwave field forming CO_2. The specific objectives of the second part of the laboratory program are numerated as follows:

1. Conduct a series of microwave experiments using a laboratory microwave reactor system to obtain experimental data on the SO_2–carbon reaction for the various sweep gas superficial velocities or residence times and microwave power levels.
2. Capture the elemental sulfur generated from the SO_2 and carbon reaction.
3. Select the superficial gas velocity and microwave power that destroys greater than 95 percent of the SO_2.
4. Conduct a series of microwave experiments using a laboratory microwave reactor system to investigate the decomposition rate of H_2S in the GAC bed by microwaves for the various sweep gas superficial gas velocities and microwave power levels.
5. Monitor the outlet gas for H_2S concentration.
6. Determine the efficiency for microwave-induced decomposition of H_2S into the elemental sulfur and hydrogen.
7. Select the sweep gas velocity and microwave powers that destroy 95 percent of the H_2S.
8. Measure the GAC adsorption capacity for siloxanes.
9. Determine the microwave regeneration efficiency for GAC saturated with siloxanes.

2.2.3.1 Lab-Scale Microwave Reactor System

An existing lab-scale microwave reactor was modified for the planned experiments. Figure 14 shows a picture of the modified lab-scale microwave reactor system that was used to conduct all experiments.

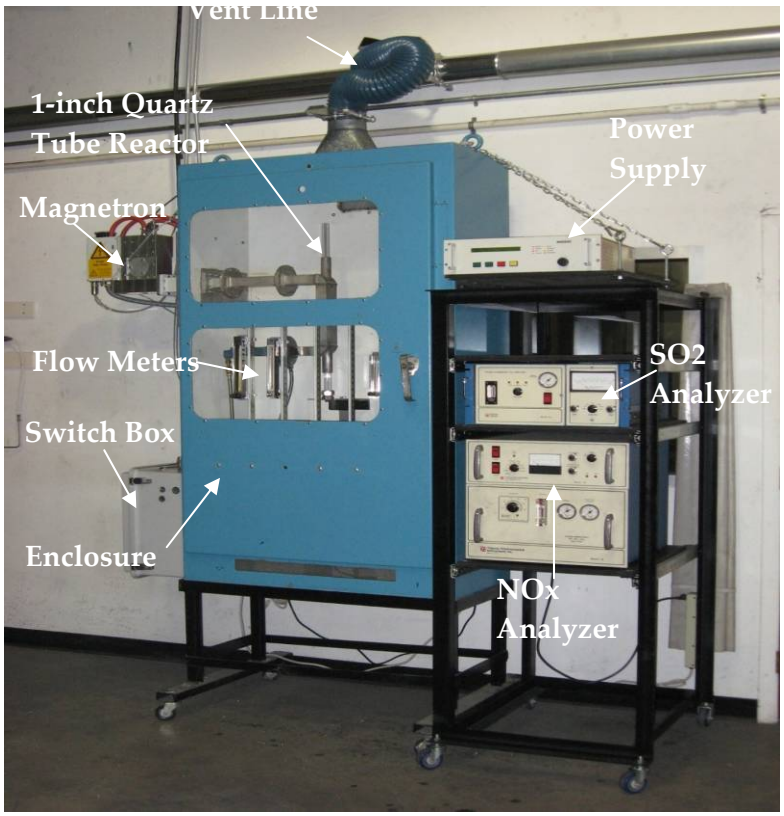
It consists of an aluminum waveguide that houses a 1-inch quartz tube. The waveguide is attached to a variable-power Cober microwave generator. The microwave generator is capable of producing 0-3 kW microwave power, but was run at powers less than 1.5 kW for the testing. The concentration of H_2S in the inlet gas was calculated but outlet concentration was measured. Also, SO_2 concentration of the outlet gas was monitored by the SO_2 Analyzer.

Following is a list of items that were used for experimental investigation:

- H_2S gas cylinder

- SO_2 lab calibration gas cylinder
- Decamethylcyclopentasiloxane (D5) liquid bottle
- Total Hydrocarbon (THC) Analyzer
- H_2S Sensor
- Particulate filter to capture the elemental sulfur
- THC calibration gas
- One glass rotameter for H_2S (14-140 cc/min)
- Two rotameters for N_2 gas (0-50 scfh) and N_2-SO_2 gas mixture
- SO_2 Analyzer
- NOx Analyzer
- Siloxane (D5) sparger

Figure 14: Picture of Lab-Scale Microwave Reactor System



To minimize the possibilities for personnel exposure to the H_2S, the entire lab-scale reactor system was located inside an enclosure that was ventilated continuously during testing. All analyzers were located outside of this enclosure. The H_2S cylinder was located inside the enclosure but SO_2 and N_2 cylinders were located outside the enclosure.

The 22-mm quartz tube was charged with approximately 50 grams of GAC that was not changed until all of the experiments presented were complete. The H_2S sensor, Model PT295, made by Pem-Tech did not function properly. It appeared that the H_2S sensor did not detect the H_2S in the moving gas stream. As a result, we decided to use H_2S Draeger detection tubes made by RAE Systems. The following describes the test procedure.

1. Perform the series of experiments varying the microwave power level, N_2 flow rate, and the oxygen flow rate. H_2S flow rate remained constant at 26.5-cc/min and the second series at approximately 10-cc/min.
2. Measure the H_2S concentration in the outlet gas with a continuous H_2S gas analyzer to assess the conversion efficiency. Also, use a H_2S Draeger tube to check data measured by the continuous H_2S sensor.
3. Calculate the H_2S conversion using outlet gas H_2S concentration data measured by the H_2S sensor or Draeger tube and inlet H_2S concentration calculated from flow rate data.

2.2.3.2 Small-Scale Laboratory Reactor Testing Results

Microwave-Induced H_2S Destruction

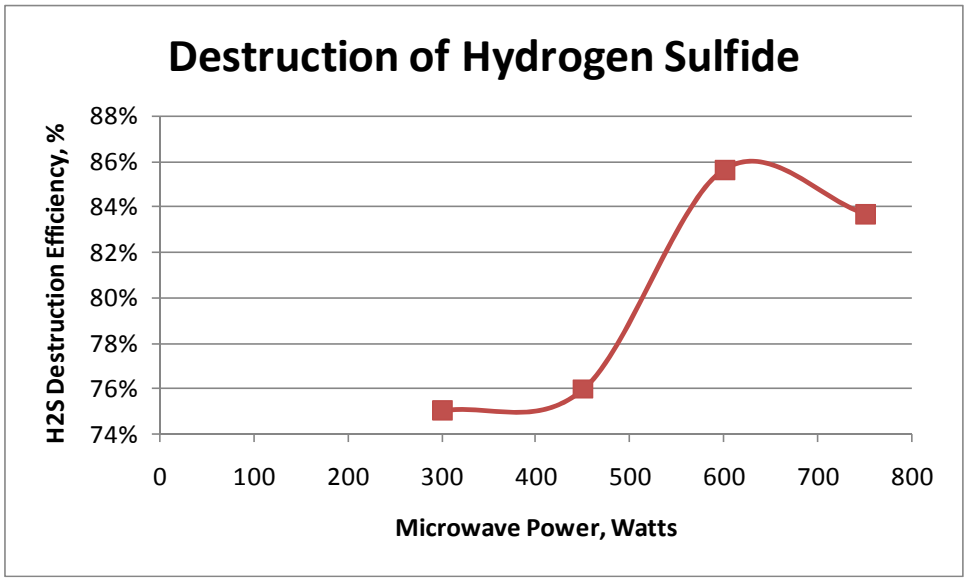
First we focused our effort to investigate the microwave-induced H_2S decomposition reaction in the GAC bed. A series of preliminary experiments were conducted to check the experimental system and find correct experimental conditions. During the preliminary experiments, we observed that plasma was formed when only 81 cc/min H_2S was flowing through the GAC bed at 1,000-W microwave power. However, the plasma stopped when either the power was reduced to 450-W or nitrogen was introduced into the reactor.

A series of microwave tests were conducted to measure the microwave-induced H_2S dissociation. The H_2S inlet flow control valve was not good enough to maintain the H_2S flow rate constant. As a result, the H_2S flow rates changed for Test #3 and #4. Each of the four tests were run for two hours and repeated. Table 4 presents experimental results and Figure 15 shows the average H_2S destruction efficiency as a function of microwave power.

Table 4: Test Results for H_2S Destruction in GAC Bed by Microwave Energy

Test #	H2S Flowrate	N2 Flowrate	MW Power	Inlet H2S	Outlet H2S	H2S Destr.	Average
0	cc/min	cc/min	Watts	Conc., ppm	Conc, ppm.	Efficiency, %	
1	10.7	8498.1	300	1257.5	315	75%	75%
1A	11.1	8498.1	300	1304.5	325	75%	
2	11.1	8498.1	450	1304.5	300	77%	76%
2A	10.7	8498.1	450	1257.5	315	75%	
3	7.8	8498.1	600	917.0	100	89%	86%
3A	8.6	8498.1	600	1011.0	180	82%	
4	8.6	8498	750	1011.0	140	86%	84%
4A	8.6	8498.1	750	1011.0	190	81%	

Figure 15: H_2S Destruction Efficiency as a Function of Microwave Power



The H_2S is dissociated into hydrogen and elemental sulfur in a GAC bed by microwave energy. However, this reaction reaches equilibrium unless an oxidation agent is added to consume hydrogen. Figure 15 shows that the H_2S dissociation efficiency increased as the microwave power increased but reached equilibrium at a microwave input power of 600-W. The H_2S dissociation efficiency at equilibrium was 86 percent. In order to increase the H_2S dissociation efficiency to greater than 86 percent, it is necessary to introduce a chemical compound that provides oxygen for the hydrogen oxidation.

The equilibrium of microwave-induced H_2S destruction may be broken by the presence of oxygen as shown in the following reaction:

$$H_2S + 1/2O_2 \rightarrow H_2O + S$$

$$H_2S + 3/2O_2 \rightarrow H_2O + SO_2$$

Next, a series of experiments were conducted to determine the effect of oxygen on the H_2S destruction by microwave energy to find the feasibility of using air for the microwave destruction of H_2S. The mixture of H_2S, oxygen, and nitrogen flows into the microwave GAC reactor. The nitrogen flow rate was kept constant at 8,498-cc/min. The H_2S concentration of the outlet gas was measured to calculate the H_2S destruction efficiency. Appendix B presents the data obtained from these series of experiments.

Figure 16 shows the H_2S destruction efficiency as a function of microwave power at three different ratios of H_2S flow to oxygen flow rate. The data shown in Figure 15 are also plotted in Figure 16 for comparison. Figure 16 show that adding oxygen increased the H_2S destruction efficiency significantly. The H_2S destruction efficiency increased with increasing microwave power. The H_2S destruction efficiency increased as the ratio of the oxygen flow rate to the H_2S

flow rate increased, reached maximum at equal H_2S and oxygen flow rates, and then decreased with further increase in the oxygen flow rate.

Microwave–Induced SO_2 – Carbon Reaction

If the H_2S is not easily destroyed by the microwaves in the GAC bed, SO_2 is produced from H_2S when impurities desorbed from the GAC are oxidized. Also, the upgraded biogas containing low H_2S concentration (<600-ppm) can be combusted in an engine for power generation. In this case, the SO_2 has to be removed and destroyed before the oxidizer outlet gas or engine exhaust gas can be vented to the atmosphere.

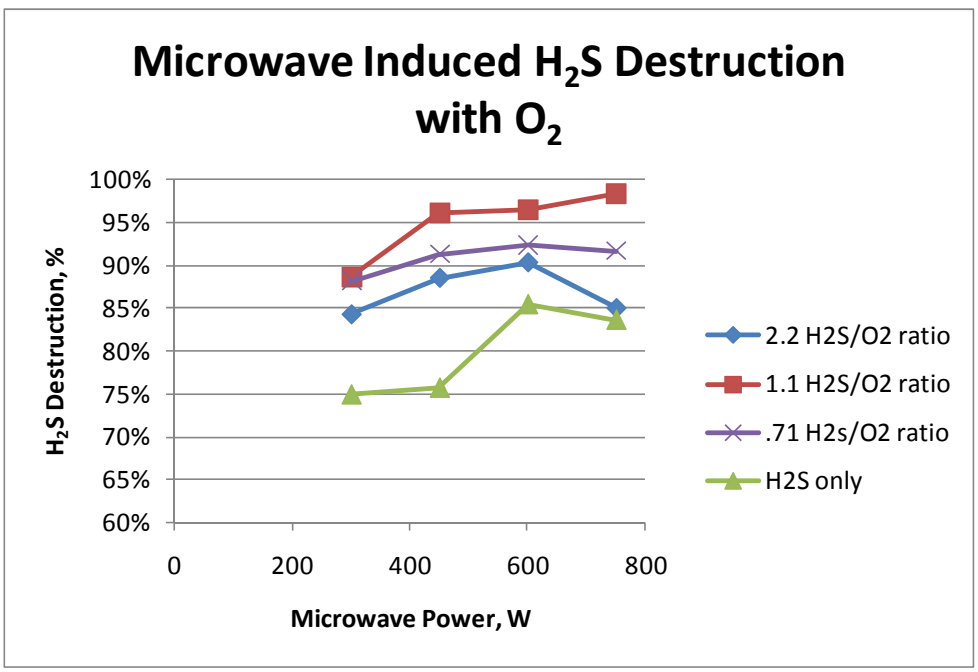
The SO_2 reacts with carbon by microwaves to produce the elemental sulfur and carbon dioxide as follows:

$$C + SO_2 \rightarrow CO_2 + S$$

The main objective of this task was to measure the conversion efficiency for the SO_2-carbon reaction by microwaves. The conversion efficiency was measured as a function of microwave power, gas flow rate, and SO_2 concentration in the inlet gas. The SO_2-N_2 gas mixture was used for all tests, which was run for two hours and duplicated.

The quartz tube was packed with 47g of CTC-70 GAC. The SO_2 was supplied by the gas mixture containing 1 percent SO_2 and 99 percent nitrogen. After the GAC bed was preheated with microwaves for about 20 minutes, the N_2 and SO_2 gas mixture was introduced into the GAC bed. The outlet gas was continuously monitored by the SO_2 analyzer.

Figure 16: H_2S Destruction Efficiency at Various Ratios of H_2S to O_2



A number of difficulties were encountered during testing. The maximum scale on the SO_2 analyzer is 5,000-ppm. Consequently, we were not able to measure the destruction efficiency if the SO_2 concentration in the outlet gas was greater than 5,000-ppm. For microwave powers lower than 450-W, a part of the SO_2 introduced into the reactor was adsorbed by the GAC. Consequently, we were not able to measure the SO_2 destruction efficiencies for 300-W and 450-W for the higher inlet SO_2 concentrations. For 750-W of microwave power so much sulfur was produced that it plugged up the filter quickly and increased the bed pressure rapidly. Consequently, we were not able to run the experiments using 750-W except for the first series of tests. Table 5 presents results obtained from microwave-induced SO_2-Carbon reaction tests.

Table 5: Test Results for SO_2-Carbon Reaction

MW Power	1% SO2/N2 Gas	N2 Flowrate	Total Flowrate	Inlet SO2	Outlet SO2	Residence	SO2 Destr.
W	Flowrate, LPM	LPM	LPM	Conc., ppm	Conc., ppm	Time, Sec	Eff., %
450	10	0	10	10,000	>5000	0.58	
600	10	0	10	10,000	2,572	0.58	74.3
750	10	0	10	10,000	282	0.58	97.2
300	6	2.83	8.83	6,795	5,000	0.66	26.4
450	6	2.83	8.83	6,795	2,838	0.66	58.2
600	6	2.83	8.83	6,795	2,765	0.66	59.3
450	4	5.66	9.66	4,141	3,238	0.60	21.8
600	4	5.66	9.66	4,141	1,580	0.60	61.8
300	4	8.50	12.50	3,200	2,800	0.46	12.5
450	4	8.50	12.50	3,200	1,638	0.46	48.8

The SO_2 destruction efficiencies were much lower than expected, probably due to insufficient gas residence time. Also, the data indicate that at least 750-W of microwave power needed to be applied to obtain destruction efficiencies greater than 90 percent. Consequently, we need to conduct SO_2 destruction experiments using longer residence times and a better elemental sulfur collection system.

As a comparison, in separately funded research project to simultaneously destroy SO_2 and NOx in a GAC bed by microwave energy, no SO_2 was detected with 0.58 second gas residence time and 450-W microwave power when the mixture of SO_2 and NOx in nitrogen stream was introduced into the GAC bed.

2.2.3.3 Microwave Reactivation Tests of GAC Saturated with Siloxane

The main objective of this task was to demonstrate that the microwave-induced reactivation restores 95 percent of GAC original adsorption capacity of siloxane. Also, it was our objective to prove that the microwave reactivation would not produce SiO_2. Decamethylcyclopentasiloxane (D5) was used to represent siloxanes since it is the predominate siloxane species in the biogas produced from Sacramento Regional Waste Water Treatment Plant.

The quartz tube was packed with about 50g of adsorbent. The heated D5 sparger was used to generate the D5-N_2 mixture gas. D5 was introduced into the D5 sparger using the syringe

pump. A part of the nitrogen flow passed through the heated D5 sparger. Then this D5-N_2 mixture gas was mixed with 0.4-scfm nitrogen to obtain the 264-ppm D5 inlet concentration. The outlet D5 concentrations in the nitrogen were measured by the THC analyzer. Since the THC analyzer is calibrated with a methane gas standard, 264-ppm D5 the concentration in nitrogen should be read at about 2,640-ppm on the THC Analyzer. During the adsorption test we measured GAC weight every 10 minutes.

When the THC concentration in the outlet gas increased greater than about 26-ppm, the adsorption test was terminated and D5-saturated GAC was regenerated with microwave energy. The saturated GAC was regenerated with microwaves until the total hydrocarbon concentration in the sweep gas stream was less than 100 ppm.

Three different adsorbents, CTC-70 GAC, CTC-80 GAC, and HOX, were used for testing. The following section presents the test results of these three adsorbents.

Saturation and Regeneration of CTC 70 GAC Using D5 Siloxane

Four cycles of D5 adsorption and regeneration tests were completed for CTC-70 GAC. Figure 17 shows the D5 breakthrough curves for four cycles of adsorption. Table 6 presents a summary of the four tests.

As shown in Figure 17, the initial breakthrough time decreased as the adsorption and regeneration cycles increased. Figure 18 shows the GAC weight gain as a function of adsorption time for four adsorption and regeneration cycles. Figure 18 clearly shows that CTC-70 GAC adsorbs D5 siloxane continuously after the D5 broke through the GAC bed. Consequently, the ultimate adsorption capacity of the CTC-70 GAC was much greater than the adsorption capacity at time when D5 broke through the GAC bed.

Figure 17: D5 Breakthrough Curves for CTC-70 GAC

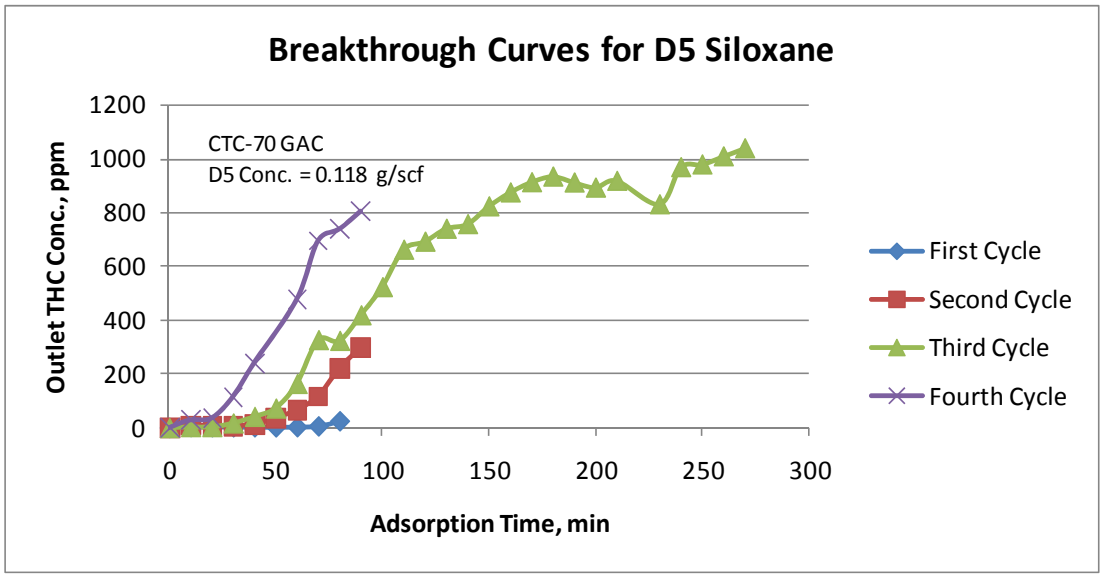
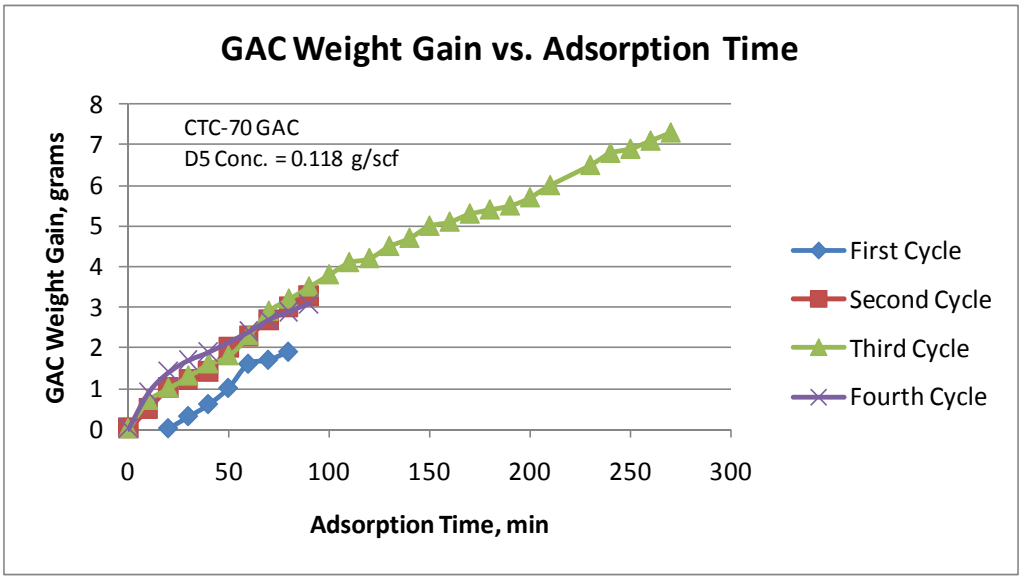


Table 6: Summary of D5 Adsorption Tests for CTC-70 GAC

Cycle #	Total Ads. Time, min	Breakthrough Time, min	D5 Injected g	GAC Weight Gain, g	GAC Weight Gain at Breakthrough	Ads. Capacity gD5/100g GAC
1	80	80	2.9	1.9	1.9	3.8
2	90	50	3.8	3.3	2	4
3	270	40	12.7	7.3	1.6	3.2
4	90	20	4.6	3.1	1.4	2.8

Figure 18: GAC Weight Gain as a Function of Adsorption Time



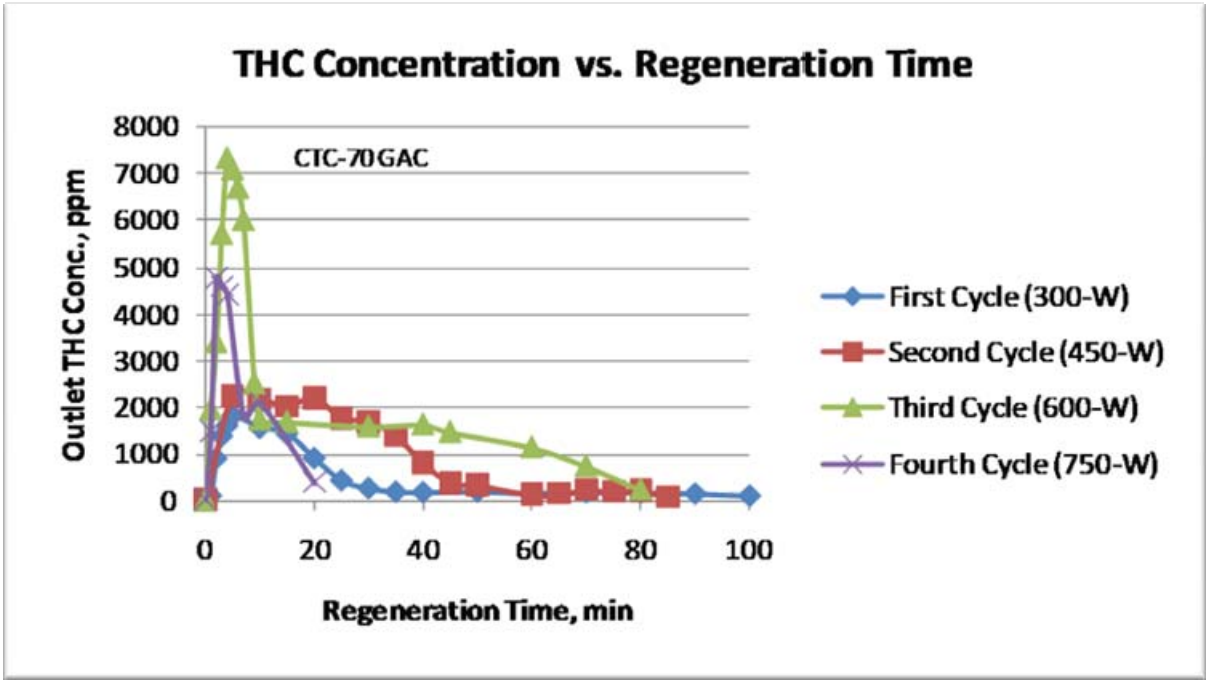
For the first adsorption cycle the fresh GAC adsorbed 1.9g of D5 when the D5 broke through the bed. This saturated GAC was regenerated with 300-W for 150 minutes but the weight loss was only 1.0g. The microwave power was increased to 450-W and regenerated for an additional 70 minutes. Finally, the microwave power was increased to 600-W and regenerated for another 10 minutes. Table 7 presents the microwave powers applied, regeneration time, and GAC weight loss.

Table 7: First Cycle Regeneration Test for D5-Saturated GAC

Microwave Power, W	Regeneration Time, min	GAC Weight Loss, g
300	140	1.0
450	70	0.5
600	10	1.4
	220 total	2.9 total

CTC-70 GAC saturated with D5 siloxane was not easily regenerated with microwaves and required higher microwave power than other common solvents. It is not clear why the total weight loss was 1.0g greater than the weight gain of 1.9g during D5 adsorption. Figure 19 shows the THC concentration as a function of regeneration time for four cycles of microwave regeneration.

Figure 19: THC Concentration of Outlet Gas During Microwave Regeneration



As shown in Figure 19, higher microwave power provided a faster regeneration rate but did not restore the initial breakthrough time. Table 8 presents a summary of the microwave regeneration for CTC-70 GAC. This table shows that higher microwave powers and longer regeneration times provide greater weight loss. After four cycles of adsorption and regeneration, 95 percent of the D5 adsorbed was desorbed.

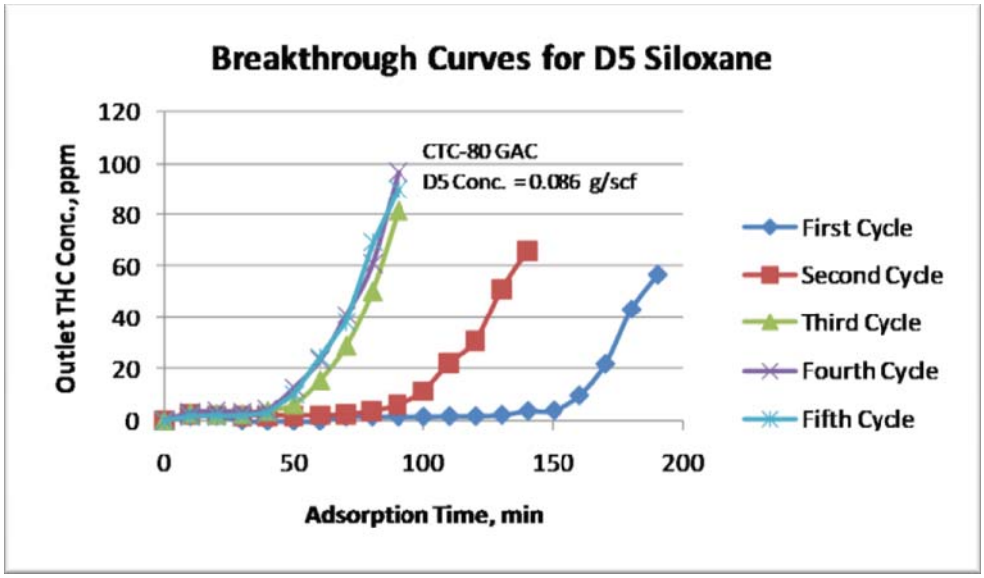
Table 8: Summary of Microwave Regeneration of CTC-70 GAC

Cycle #	MW Power	Reg. Time	GAC Wt. Loss	Wt. Loss/
	W	min	g	Wt. Gain
1	300-600	230	2.9	1.53
2	450-600	85	2.4	0.73
3	600	80	6.8	0.93
4	750	30	2.7	0.87
Total			14.8	0.95

Saturation and Regeneration of CTC-80 GAC Using D5 Siloxane

CTC-80 GAC has larger pore size than CTC-70 GAC and should be better suited for larger sized molecules such as D5 siloxane. The following presents the test results obtained from the adsorption and regeneration tests using CTC-80 GAC.

Figure 20: Breakthrough Curves from CTC-80 GAC Adsorption Tests



Five cycles of adsorption and regeneration were performed. Figure 19 shows the breakthrough curves for the CTC-80 GAC adsorption tests as a function of adsorption and regeneration cycle.

The initial breakthrough time decreased as the adsorption and regeneration cycle increased for the 1st through the 3rd cycle. However, after the 3rd cycle the initial breakthrough time remained constant at 60 minutes. Also, the GAC weight gains were the same for the 3rd, 4th, and 5th cycles which was very different from the CTC-70 GAC tests. The microwave regeneration restored the GAC working adsorption capacity. Table 9 presents a summary of the adsorption tests.

Table 9: Summary of CTC-80 GAC D5 Adsorption Tests

Cycle #	Total Ads. Time, min	Breakthrough Time, min	D5 Injected g	GAC Weight Gain, g	Ads. Capacity gD5/100g GAC
1	190	180	7.1	6.7	15.6
2	140	110	4.6	4.1	9.5
3	90	60	3	2.8	6.5
4	90	60	3.1	2.8	6.5
5	90	60	3.3	2.8	6.5

The 1st cycle of microwave regeneration was conducted for 120 minutes with 450-W followed by 60 minutes using 600-W. The 1st cycle regeneration was completed by applying 750-W of microwave power for 60 minutes. The GAC weight loss was 5.0g for first 60 minutes using 450-

W but additional regeneration increased the weight loss by 0.2g. Using higher powers of 600-W and 750-W for 120 minutes provided only 0.7g of weight loss. Therefore, the microwave regeneration was almost completed after 60 minutes.

For the 2nd cycle regeneration using 450-W, the GAC weight loss was 2.9g after 30 minutes, 3.0g after 60 minutes and 3.1g after 120 minutes, indicating the microwave regeneration was almost completed after 30 minutes.

Figure 21 shows the THC concentration of the outlet gas as a function of regeneration time. Table 10 presents a summary of the CTC-80 GAC regeneration.

Figure 21: THC Conc. of Outlet Gas as a Function of Regeneration Time (CTC-80 GAC)

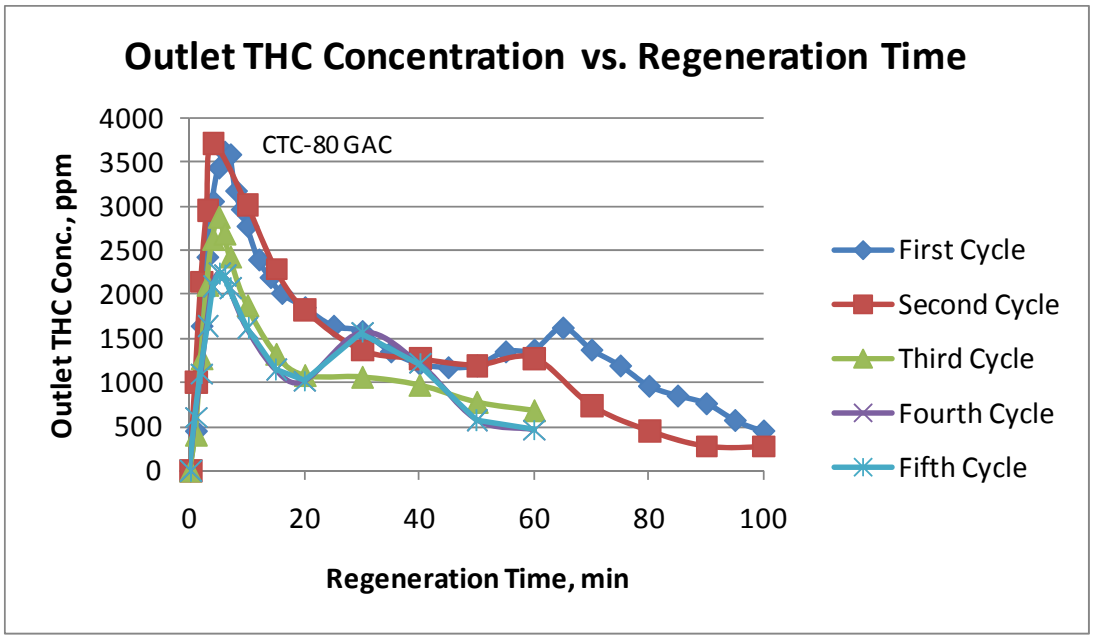


Table 10: Summary of CTC-80 GAC Regeneration Test Results

Cycle #	MW Poer	Reg. Time	GAC Wt. Loss	Wt. Loss/
	W	min	g	Wt. Gain
1	450-750	210	5.9	0.88
2	450	130	3.1	0.76
3	600	60	2.8	1.00
4	600	60	2.5	0.89
5	600	60	2.8	1.00
Total			17.1	0.89

The microwave regeneration was practically complete after 30 minutes and the GAC weight loss was about the same for the 3rd, 4th, and 5th cycles. Therefore, we concluded that CTC-80 GAC is preferable for the biogas upgrading.

Comparison of CTC- 80 GAC with CTC- 70 GAC

To compare the CTC-80 GAC with the CTC-70 GAC, we plotted the breakthrough curves for the fresh GAC and 4th regenerated GAC. Figure 22 shows the 1st cycle of breakthrough curves for CTC-70 and CTC-80 GACs. Figure 23Figure 23 shows breakthrough curves for 4th cycle of adsorption for CTC-70 and CTC-80 GAC. These two figures demonstrate clearly that CTC-80 GAC performs much better than CTC-70 GAC for the removal of siloxanes from biogas and for multiple microwave regeneration.

Figure 22: 1st Cycle Breakthrough Curves for CTC-70 and CTC-80 GAC

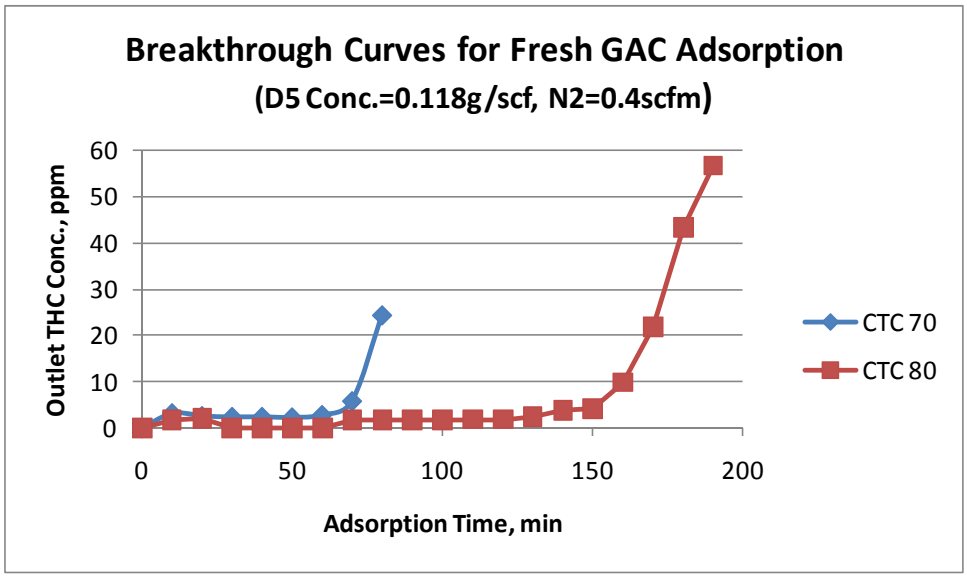
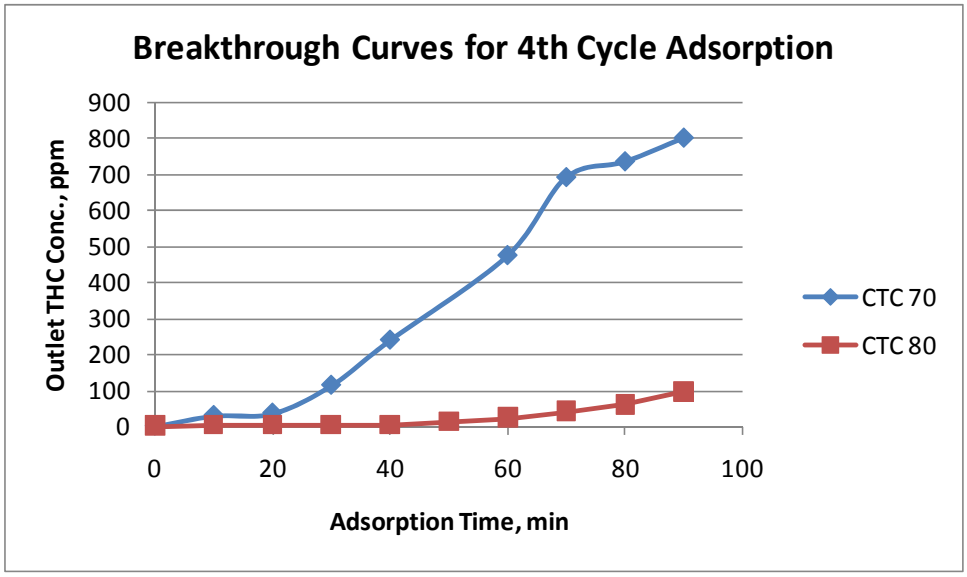


Figure 23: 4th Cycle Breakthrough Curves for CTC-70 and CTC-80 GAC



D5 Saturation and Regeneration of Mixture of CTC-80 GAC and HOX

HOX is a silica-based adsorbent used to remove the moisture and siloxanes in a gas stream. AFT uses layers of HOX and GAC in commercial contaminant removal applications. AFT provided 50-lbs each of HOX and CTC-80 GAC for testing. The following presents the results of the D5 adsorption and microwave regeneration of the media consisting of equal volume of HOX and CTC-80 GAC (50-50 mix).

The quartz tube was packed with 60.6g HOX and saturated with D5 for three hours. The nitrogen flow rate and the D5 injection rate were 0.4-scfm and 2-g/hr, respectively. After 3-hour saturation, the GAC was weighed at 60.6g. No HOX weight gain indicated that water contained in the HOX was displaced by D5. The amount of D5 injected was 6g which was much closer to the amount of water contained in the HOX (6.6g).

HOX saturated with D5 was regenerated with 450-W of microwave power for 60 minutes. The weight loss was only 2.9g, indicating that less than one-half of the D5 adsorbed in the HOX was desorbed. We mixed this HOX (57.7g) with 43g CTC-80 GAC (equal volumes of HOX and GAC). One half of this mixture was regenerated with 450-W microwave power for 30 minutes. The weight loss was 1.9g after 30 minutes. The other half of the mixture was also regenerated with 450-W of microwave power that produced a weight loss of 2.0g. This clearly showed that HOX did not absorb microwave energy and microwave regeneration was not effective to regenerate HOX. Note that silica gel (HOX) is regenerated with hot inert gas in commercial applications.

The second test was conducted by packing the quartz tube with 60g of HOX. The HOX was dried with 450-W of microwave power for 30 minutes, producing 6.4g water. This 53.6g of dried HOX was saturated with D5 in 0.4-scfm nitrogen for 850 minutes. The THC concentration of the outlet nitrogen was 4-ppm after 850 minutes of D5 adsorption. The HOX weight gain was 28.3g, indicating that the D5 adsorption capacity of HOX was 52.8g D5 per 100g HOX at D5 breakthrough.

Forty grams of D5 saturated-HOX was mixed with 20g of CTC-80 GAC to provide about equal volumes of these two adsorbents. This media contains 26.18g HOX free of D5 and water and 19.36g of dried GAC. The media was regenerated with 450-W of microwave power for 60 minutes. Then four cycles of adsorption and regeneration tests were completed using this 50-50 mix. Figure 24 shows the adsorption capacity of this media at the time of the initial D5 breakthrough. This figure demonstrates that microwave regeneration restored the D5 adsorption capacity of fresh media.

Figure 24: D5 Adsorption Capacity at Various Ads./Reg. Cycles

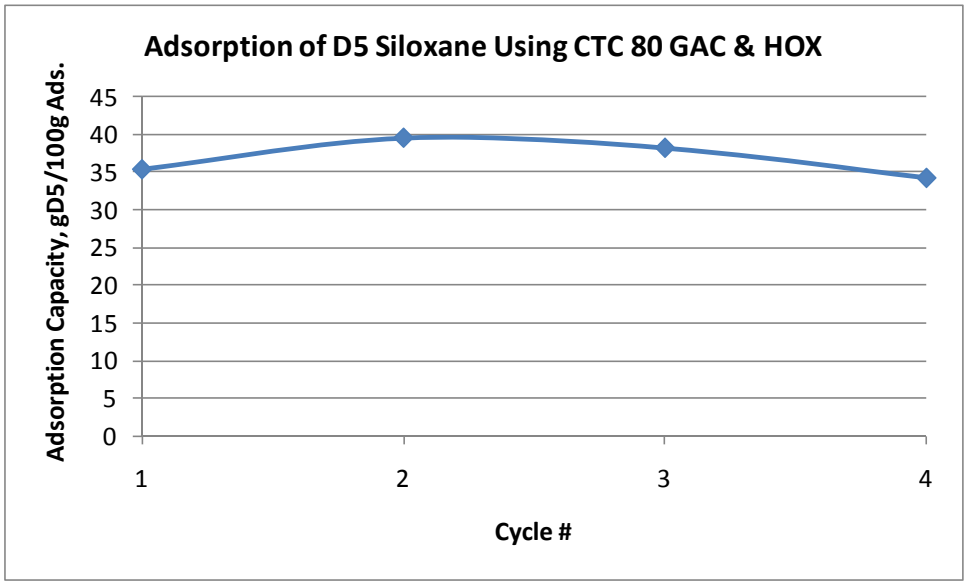
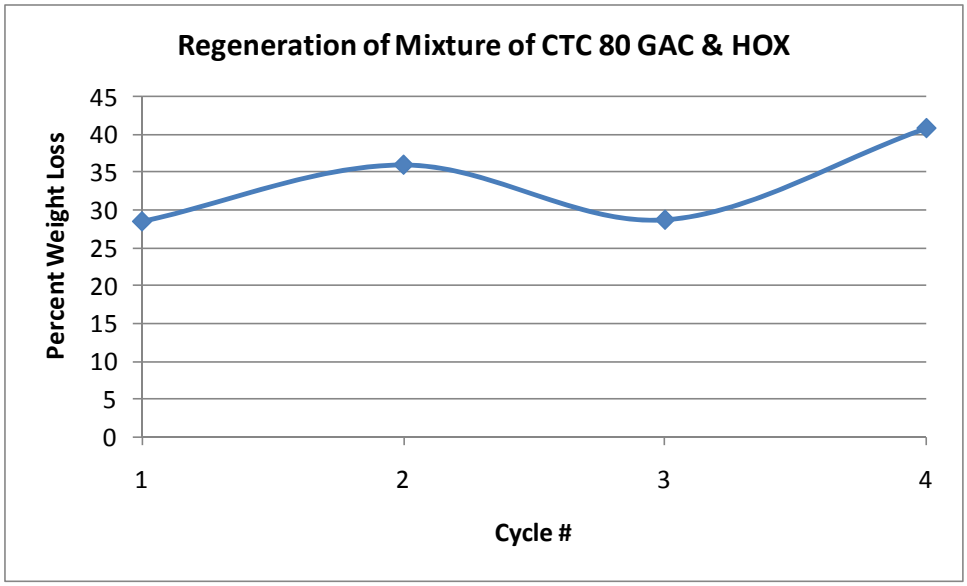


Figure 23 shows the weight loss of the media as a function of the adsorption/regeneration cycle. The weight loss remained almost constant, indicating that the microwave regeneration removed about same amount of D5 adsorbed.

Apparently the CTC-80 GAC pellet absorbs the microwave energy during regeneration and thermally regenerates the adjacent HOX pellet. Figure 24 and Figure 25
Figure 25 clearly demonstrate that the 50-50 mix of HOX and CTC-80 will be regenerated with microwave energy and is the best adsorbent choice for this project. Consequently, the team decided that that the siloxane adsorption field test at Carson Energy be conducted using the media consisting of equal volume of HOX and CTC-80 GAC.

Figure 25: Weight Loss as a Function of Ads/Reg Cycles



2.2.3.4 System Specifications for Field Demonstration

The results obtained from Task 2 work led to the following specifications for the field demonstration of the microwave technology for removing siloxanes and H_2S from biogas at Carson Energy Plant.

1. Media consisting of equal volumes of CTC-80 and HOX should be used for removing siloxane and H_2S.
2. The microwave carbon reactor should be installed before the microwave oxidizer to destroy H_2S in the desorbed gas during the saturated media regeneration to avoid the production of sulfur dioxide (SO_2) in the microwave oxidizer.
3. Because of the high concentration of petroleum gas in the biogas, the vapor desorbed from the adsorbent should be condensed to separate any hydrocarbon liquid prior to the microwave carbon reactor.
4. Since the breakthrough curve for VOCs could not be obtained during field adsorption tests, a method to determine time for the media change-out needs to be developed to prevent the siloxane breakthrough.
5. Gas samples should be taken for siloxane analysis at different adsorption times during the adsorption testing.

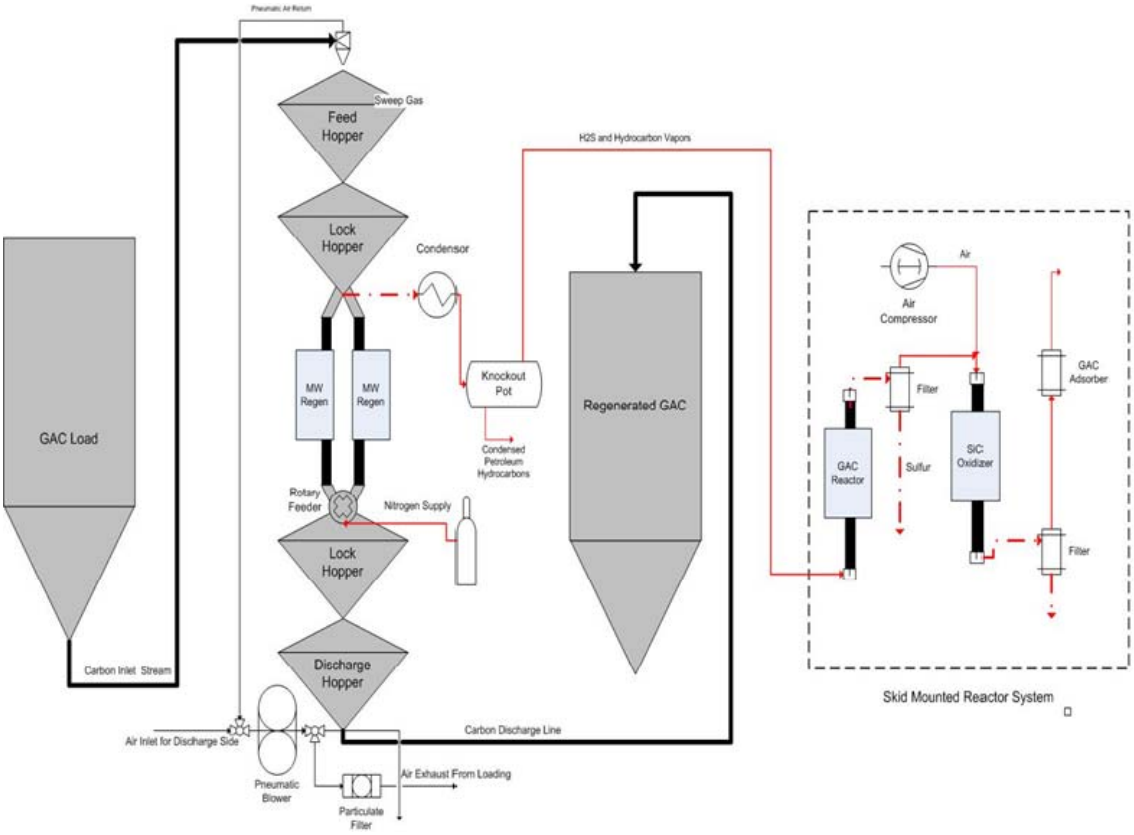
CHA modified the existing mobile microwave unit and constructed the microwave carbon reactor and microwave oxidizer system to accommodate the specifications listed above.

2.3 Modification of Existing 100-lb/hr Portable Microwave Unit (Task 3)

The 100-lb/hr trailer mounted microwave media regenerator was originally constructed to treat GAC saturated by soil vapor extraction systems. The mobile microwave reactivating unit utilizes two 50-lb/hr quartz reactors to process media at an overall rate of 100-lb/hr. The media hoppers are arranged in an airlock configuration to allow for continuous processing of large amounts of media. It also allows the use of smaller and lighter hoppers to reduce the weight of the unit. The original mobile microwave unit had a two-stage vapor condensing system with total recycling of sweep gas flow system. The second condensing system was removed and total recycling was modified to one-pass through sweep gas flow system to oxidize biogas impurities desorbed from media during the microwave regeneration.

Figure 26 presents the overall GAC reactivation Process Flow Diagram (PFD) for the modified 100-lb/hr portable microwave unit.

Figure 26: PFD for Modified 100-lb/hr Microwave Unit



The media loaded with siloxanes, VOCs, and H_2S is fed by a feed hopper at the top and exits through a tapered rotary valve at the bottom of the microwave vapor desorber or media regenerator. The microwave vapor desorber operates as a moving-bed and regenerates the used media via microwave energy. The microwaves cause the siloxanes, VOCs, and H_2S to rapidly desorb from the media and return to the vapor phase. The siloxanes, VOCs, and H_2S are removed from the top of the regenerator by a constant stream of nitrogen purge gas injected at the bottom of the regenerator. This sweep gas containing siloxanes, VOCs, and H_2S then flows into the condenser. The regenerated media flows into the bottom hopper and will be transferred into 5-gallon buckets for adsorption tests.

During laboratory testing performed under Task 2, it became apparent that the GAC used for biogas upgrading at Carson Energy contains a significant amount of petroleum hydrocarbons. To fully oxidize these hydrocarbons would require a larger, more powerful, oxidizer than we proposed originally. This is because our oxidizer was sized based on the gas TO-15 VOC analysis, which does not analyze for the higher molecular weight compounds found in biogas.

To handle this situation, the first stage of the condensing system on the original mobile unit was retained. Doing so reduces the load on the microwave oxidizer to a level so we can use our existing equipment. A consequence of not removing the refrigeration system is that there is not enough room to add the H_2S carbon reactor, microwave oxidizer, filters, or electronics to the existing unit. Consequently, the microwave oxidizer was installed on a small dedicated skid.

The skid was designed so it could be easily loaded into the back of a pickup truck with a forklift. The unit incorporated nearly all of the changes that were originally going to be made to the mobile unit.

The only changes made to the 100-lb/hr carbon regenerator were the removal of the sweep gas compressor, the removal of the second knockout pot, and the second heat exchanger. The gas outlet from the first knockout pot was extended to tie into the inlet of the H_2S-carbon reactor. The coolant lines from the second heat exchanger were extended to supply the cooling water for the microwave generators in the new oxidizer skid.

The mobile microwave oxidizer system containing a microwave oxidizer and microwave carbon reactor was constructed with two 3-kW microwave generators and two microwave reactors. Total hydrocarbon analyzer and SO_2 analyzer were installed in this system. Figure 27 shows a picture of this mobile microwave oxidizer system.

The first microwave reactor in the oxidizer system contains GAC. The gas leaving the condenser containing H_2S and non-condensable VOCs flows into the microwave carbon reactor. In this reactor H_2S is decomposed into hydrogen and elemental sulfur. Since the air increases the H_2S decomposition efficiency, we introduced a small amount of air into the microwave carbon reactor if the outlet H_2S concentration was greater than 6-ppm (10 percent of H_2S concentration of gas entering microwave carbon reactor).

If organic halides are present, the GAC in this reactor can be supplanted with NaOH-impregnated GAC. The impregnant will react with the acid gasses formed by organic halide decomposition, yielding sodium halide salts and water vapor. The gas leaving the microwave carbon reactor flows into a particulate filter to separate elemental sulfur and other solid particles.

The H_2S-free gas leaving the microwave carbon reactor contains non-condensable VOCs and siloxanes. This gas flows into the microwave oxidizer and VOCs and siloxanes are then oxidized in the silicon carbide (SiC) bed by microwave energy. A particulate filter following this reactor will capture SiO_2 generated during the oxidation. A part of the clean gas leaving the filter may be recycled back through the regeneration reactor. Any excess clean gas is vented to the atmosphere through a final GAC adsorber to ensure there are no contaminant emissions from the system.

Figure 27: Picture of Mobile Microwave Oxidizer Unit

2.4 Adsorption Field Test Plan (Task 6)

The adsorption field test was planned to be conducted in three phases. In the first phase, breakthrough of H_2S and siloxane was determined for this biogas to provide a basis to calculate the change-out period for the media. The second phase will confirm the adsorption capacity of the media through multiple regeneration cycles. The third phase will provide performance data for the microwave regeneration system.

2.4.1 Determine H_2S and Siloxane Breakthrough Curves (Test 1A)

The main objective of adsorption Test 1A was to determine H_2S and siloxane breakthrough curves. These breakthrough curves will be used to determine the media change-out time. Since there is no practical method to determine the siloxane concentration in real time in the field, the breakthrough curves for siloxanes need to be estimated from laboratory siloxane analysis data of gas samples taken various adsorption times.

The biogas entering the adsorber has about 59 percent methane (CH_4) and 20-ppm H_2S. In the laboratory, CHA Corp used a THC analyzer (max. 100,000-ppm) to determine the breakthrough curves for hydrocarbons (VOCs). The THC analyzer cannot be used to determine the VOC breakthrough in a biogas stream because the methane overwhelms the readings of the THC.

H_2S levels can be measured in real time in biogas. The lab data shows that the breakthrough of H_2S in the selected media occurs earlier than the breakthrough of Siloxane. Therefore, H_2S should be detected coming through the media before siloxane breakthrough and the amount of H_2S coming through the media can be used as a predictor of change-out time.

The H_2S molecular weight is much lower than siloxane molecules. If we decide the media change-out time based on the H_2S breakthrough curves, the siloxanes will not breakthrough adsorbers. We hoped that a reasonable correlation could be obtained by taking samples of the adsorber outlet gas at various adsorption times for siloxane analyses in the laboratory. These siloxane analysis data would be compared with H_2S measurements to develop the correlation.

The H_2S and siloxane concentrations of biogas at Carson Energy site were 19.76-ppm and 18.25-ppm as Si, respectively. The H_2S detection tubes made by RAE Systems were used to monitor the H_2S concentration in the adsorber outlet gas.

The H_2S, siloxanes, and VOCs are adsorbed onto the media when the biogas flows through media bed. Water vapor is also adsorbed onto the media. The media weight gain during the saturation is the sum of H_2S, siloxanes, VOCs, and water adsorbed on the media surface.

2.4.1.1 Test Procedure

1. Prepare the 75-lbs media by mixing 31 lbs of CTC-80 GAC with 44 lbs of HOX.
2. Load the adsorber with this 2.4 ft^3 of CTC-80 and HOX mix media.
3. Connect the adsorber to the biogas supply and return line.
4. Start gas flow through adsorber.
5. Measure inlet and outlet pressures and the gas flow rate.
6. With the H_2S tube, measure H_2S concentration of the adsorber inlet gas.
7. Take feed biogas sample for siloxane analysis.
8. Monitor the H_2S concentration of the adsorber outlet gas using the H_2S tube.
9. Record H_2S concentration every 30 minutes.
10. Take adsorber outlet gas sample when H_2S concentration reaches 10 percent, 30 percent, 50 percent, 70 percent, and 90 percent of the inlet H_2S concentration.
11. Take a gas sample from the adsorber outlet for VOC analysis.
12. Flow biogas through the media until H_2S concentration of the adsorber outlet gas reaches 90 percent of the inlet concentration.
13. Shut off blower. Close inlet and outlet valves. Vent any pressure in system.
14. Open the adsorber top. Allow one minute for purging before accessing the adsorbent.
15. Prepare six 5-gallon buckets for saturated adsorbent (each bucket should be numbered and weighed).
16. Remove all adsorbent from the adsorber using 5-gallon buckets. Note condition of media (color, odor, moisture).
17. Weigh each of the 5-gallon buckets filled with saturated media removed from the adsorber.
18. Transport 5-gallon buckets to the mobile microwave unit.
19. Complete test log.

Because of too early H_2S breakthrough, this adsorption test did not produce any meaningful data and demonstrated that H_2S breakthrough did not correlate with Siloxane breakthrough. However, the CTC number of the regenerated media represents the effectiveness of microwave regeneration.

2.4.2 Measure Adsorption Capacity of 1st Regenerated Media (Test 2A)

The media saturated with biogas during the first adsorption test was regenerated in the mobile microwave regeneration unit. The main goal of the second adsorption test was to measure the adsorption characteristics of the microwave regenerated media. If microwave regeneration restores the adsorption capacity of fresh media, the CTC number of the regenerated media should be close to the CTC number of fresh media. The 2nd adsorption test procedure was similar to Test 1A procedure and is presented below.

2.4.2.1 Test Procedure

1 Load the adsorber with the regenerated media from 1st regeneration test.

1. Connect the adsorber to the biogas supply and return line.
2. Start gas flow through adsorber.
3. Measure inlet and outlet pressures and record the gas flow rate.
4. With the H_2S tube, measure H_2S concentration of the adsorber inlet gas.
5. Monitor the H_2S concentration of the adsorber outlet gas using the H_2S tube.
6. Record H_2S concentration every 30 minutes.
7. Run adsorption test for 24 hours.
8. Shut off blower. Close inlet and outlet valves. Vent any pressure in system.
9. Open the adsorber top. Allow one minute for purging before accessing the adsorbent.
10. Remove all adsorbent from the adsorber using 5-gallon buckets. Note condition of media (color, odor, moisture).
11. Weigh each of the 5-gallon buckets filled with saturated adsorbent removed from the adsorber.
12. Transport 5-gallon buckets to the mobile microwave unit for regeneration.
13. Complete test log.

Two additional adsorption tests (Test 3A - 5A) were conducted following the Test 2A procedure to find the effectiveness of microwave regeneration.

2.4.3 Prepare Saturated Media for Microwave Regeneration Tests (Test 6A-9A)

The main goal of Test 6A-9A was to generate about 300 lbs of saturated media for various throughput microwave regeneration tests. The test procedure is given below.

2.4.3.1 Test Procedure

1. Load the adsorber with the regenerated media from regeneration test or fresh equal volume of CTC-80 and HOX mix.
2. Connect the adsorber to the biogas supply and return line.
3. Start gas flow through adsorber.
4. Measure inlet and outlet pressures and set the gas flow rate at the predetermined value.

5. With the H_2S tube, measure H_2S concentration of the adsorber inlet and outlet gas.
6. Record H_2S concentration every 30 minutes.
7. Flow biogas through the media for 24 hours.
8. Shut off blower. Close inlet and outlet valves. Vent any pressure in system.
9. Open the adsorber top. Allow one minute for purging before accessing the adsorbent.
10. Remove all media from the adsorber using 5-gallon buckets. Note condition of media (color, odor, moisture).
11. Weigh each of the 5-gallon buckets filled with saturated media removed from the adsorber.
12. Transport 5-gallon buckets to the mobile microwave unit for regeneration.
13. Complete test log.

2.5 Microwave Regeneration Field Test Plan (Task 7)

The goal of Task 7 was to setup, operate, and test the microwave regeneration unit. The regeneration conditions were selected to obtain a consistent CTC number of the regenerated media. Specific objectives of Task 7 were to demonstrate items listed below:

- Microwave regeneration of media saturated with biogas restores working adsorption capacity of fresh media.
- More than 90 percent of H_2S entering the carbon bed can be destroyed by microwave energy.
- Heavy hydrocarbons in desorbed gas are condensed and recovered as liquid.
- Elemental sulfur produced from H_2S and SiO_2 produced from siloxane oxidation are collected by the particulate filters.
- No air pollutants are produced from the microwave regeneration system.

The results obtained from laboratory study investigating microwave-induced H_2S decomposition in the GAC beds showed that greater than 90 percent of H_2S could be decomposed into elemental sulfur and water vapor by microwave energy with the oxygen having the same flow rate as H_2S.

The microwave regeneration shall restore the working adsorption capacity. Depending on the chemicals and media, the working adsorption capacity for siloxane and H_2S may not be the same as the capacity of fresh media. Media consisting of equal volume of CTC-80 and HOX was tested in the lab-scale microwave reactor. Results obtained from four cycles of adsorption and regeneration showed that microwave regeneration restored the working adsorption capacity for D5 siloxanes, which was the same as the fresh media adsorption capacity.

The effectiveness of microwave regeneration was determined by comparing the CTC number of fresh media with the CTC number of regenerated media. The CTC number was determined from the butane desorption method.

The first microwave reactor in the mobile microwave oxidizer unit was filled with GAC to destroy H_2S prior to the microwave oxidizer. The second microwave reactor was filled with the mixture of silicon carbide (SiC) and oxidation catalyst.

The regeneration test number corresponds to the adsorption test number. For example, Test 1R is to regenerate the saturated media generated from Test 1A.

2.5.1 Determine Effectiveness of Microwave Regeneration (Test 1R)

The main objective of Test 1R was to measure the effectiveness of microwave regeneration of the media consisting of equal volume of CTC-80 and HOX that was saturated with biogas from the adsorption Test 1A. It was also the goal of Test 1R to determine the effectiveness of microwave destruction of H_2S in desorbed gas from the microwave regeneration reactor. We needed to find the air flow rate to the microwave carbon reactor that provided the H_2S destruction efficiency greater than 90 percent. The air flow rate to the microwave carbon reactor shall be the same as the H_2S inlet flow rate that was equivalent to the rate of H_2S desorbed from the saturated media.

2.5.1.1 Regeneration Test Procedure

1. Fill the quartz tube of the microwave regenerator with media consisting of equal volume of fresh CTC and HOX.
2. Transfer media saturated with biogas under Test 1A from 5-gallon buckets to the top hopper of the microwave reactor.
3. Set the star valve speed at 35-lb/hr.
4. Conduct the visual inspection of the mobile microwave regeneration and oxidizer units to make sure the system is ready for start-up.
5. Start nitrogen sweep gas flow at 1.5-scfm for microwave regenerator.
6. Start the air compressor and set the air flow at 1.0-scfm for the oxidizer.
7. Set the air flow rate to microwave carbon reactor at 26-cc/min.
8. Start the 3-kW microwave generators in the mobile oxidizer and preheat the microwave oxidizer system for about 30 minutes.
9. Start one of two 6-kW microwave generators and increase the microwave power to 5-kW.
10. Start the star valve and regenerate media in the microwave reactor using 5-kW microwave power.
11. Measure H_2S concentration of the feed gas to the microwave carbon reactor using the H_2S tube.
12. If H_2S concentration is different from 600-ppm, adjust the air flow rate to the microwave carbon reactor by the concentration ratio to 600-ppm.
13. Monitor THC concentration of the oxidizer outlet gas with THC Analyzer and record THC concentration every 10 minutes.
14. Measure and record THC concentration of oxidizer inlet gas every 20 minutes with THC Analyzer.
15. Stop the star valve when the top hopper becomes empty.
16. Shut down all microwave generators.
17. Shut down air compressor in the oxidizer unit.
18. Stop nitrogen flow 20 minutes after shutting down microwave generators.
19. Remove media from the bottom hopper into 5-gallon buckets.
20. Weigh regenerated media.

21. Take about 100 grams sample of regenerated media for CTC number measurement.
22. Drain and weigh the condensate.
23. Add the fresh media to makeup the loss during transfer.
24. Transport 5-gallon media buckets to the adsorber.
25. Complete test logbook.
26. Ship the regenerated media sample to CHA Corp lab.

It was very difficult to remove all media from the microwave regeneration system and make accurate weight comparisons but the CTC number represents the working adsorption capacity of the regenerated media. Therefore, the change in CTC numbers would indicate the microwave regeneration efficiency.

2.5.2 Determine Consistency of Microwave Regeneration (Test 2R-5R)

The CTC number of regenerated media may decrease with the increase in the regeneration cycle. However, results obtained from laboratory D5 saturation and regeneration tests using media consisting of equal volume of CTC-80 and HOX indicated that the microwave regeneration restored the D5 initial breakthrough time for this media.

The main goal of first four regeneration tests was to determine if the microwave regeneration restored the fresh media adsorption capacity for siloxanes in biogas. Also, it was the goal of these regeneration tests to demonstrate that the effectiveness of microwave-induced H_2S destruction and non-condensable hydrocarbon oxidation.

The procedure for Test 2R-5R was the same as the test procedure shown in Test 1R. After Test 5R was complete, we reviewed the regeneration data including the CTC numbers of regenerated media and amount of recovered hydrocarbon liquid and water. Also, we should review the adsorption test data, especially initial breakthrough times. Then, we could determine if five cycles of adsorption and regeneration tests provided sufficient information for determining the consistency of microwave regeneration. However, the H_2S initial breakthrough time could not be used because of too quick breakthrough.

2.5.3 Test Various Regeneration Throughputs (Test 6R-9R)

The mobile unit was designed for regenerating 100-lb/hr of GAC saturated with toluene. Since the regeneration throughput producing repeatable CTC number of regenerated media is dependent on the media and chemicals in biogas, we needed to find the effect of regeneration throughput on the working adsorption capacity of media for biogas. We prepared about 300 lbs of saturated media for conducting regeneration tests with various regeneration throughputs. The following shows the planned regeneration throughput for four regeneration tests:

Test 6R40-lbs/hr

Test 7R50-lbs/hr

Test 8R60-lbs/hr

Test 9R80-lbs/hr

If results from Test 1R-4R show that the microwave regeneration unit operates without any problems and produces the repeatable CTC number of regenerated adsorbent, we will run only one microwave regeneration reactor.

2.5.4 Conduct 6-hr Regeneration Test (Test 10R)

After Test 9R was complete, we selected the regeneration throughput that produced the repeatable CTC number of regenerated media. Using this regeneration throughput, we conducted a 6-hr microwave regeneration test to identify mechanical problems that need to be solved in order to commercialize the microwave biogas upgrading technology successfully. Also, we measured the electric power consumption during the 6-hr microwave regeneration tests. It took many days to prepare saturated media for this long regeneration test. Consequently, we conducted Test 10R using only one microwave regeneration reactor. The test procedure for Test 10R was the same as Test 1R procedure.

2.6 Prepare Commercialization Plan (Task 8)

AFT engineered and installed more than 100 adsorption systems for biogas upgrading. It is logical to provide media regeneration services using the microwave technology. Consequently, we evaluated the merits of a mobile microwave regeneration system that will travel to service a number of sites in California or other locations. Also, we evaluated a field installed system dedicated to each site.

Based on field testing results, we developed the process flow diagram (PFD) for the mobile microwave system and the field installed integrated microwave system that combines with the adsorption unit. Using the PFDs, we developed major equipment list for these two systems. Then, we estimated capital and operating costs for these two microwave biogas upgrading systems.

Using the capital and operating costs, we estimate the total annualized costs for these two biogas upgrading systems using 15 year life time of the installed equipment. Also, we would identify trained man-power requirements to commercialize the microwave biogas upgrading technology successfully.

We need to identify specific requirements and characteristics of the dairy farms, landfill sites, and waste water treatment facilities. Then, we can determine the microwave process systems that will provide the best options to meet specific requirements. Also, we can evaluate near term and long term microwave processing scenarios for biogas upgrading.

2.7 Production Readiness Plan

The goal of the plan is to determine the steps that will lead to the manufacturing of the technologies developed in this project or to the commercialization of the project's results. We will develop the market plan for upgrading biogases produced from landfill sites, wastewater treatment facilities, food processing and dairy farms in California. The upgraded biogas will be used for power and heat generation. We will investigate economic and environmental

advantages to install microwave onsite reactivation facilities at SMUD's customers and AFT's customers in California.

CHAPTER 3:
Project Outcomes

3.1 Field Testing of Biogas Adsorption and Microwave Regeneration

A two-month field testing of biogas adsorption and microwave regeneration of saturated media started on April 13, 2009 at Carson Energy Facility in Elk Grove, California. Due to mechanical problems with the steam turbine at the Carson Energy, we stopped the field testing temporarily on May 31 and postponed until October. Only one week of field testing work needed to be completed when we stopped the field testing work. CHA personnel returned to the Carson Energy site on October 4th and completed the rest of field testing on October 9th. The following presents results obtained from the field testing work.

The media consisting of 50 percent HOX and 50 percent CTC-80 was used for all of the field adsorption and regeneration tests. The picture of this media is shown in Figure 28.

Figure 28: Picture of 50% HOX and 50% CTC-80 GAC Mix Media

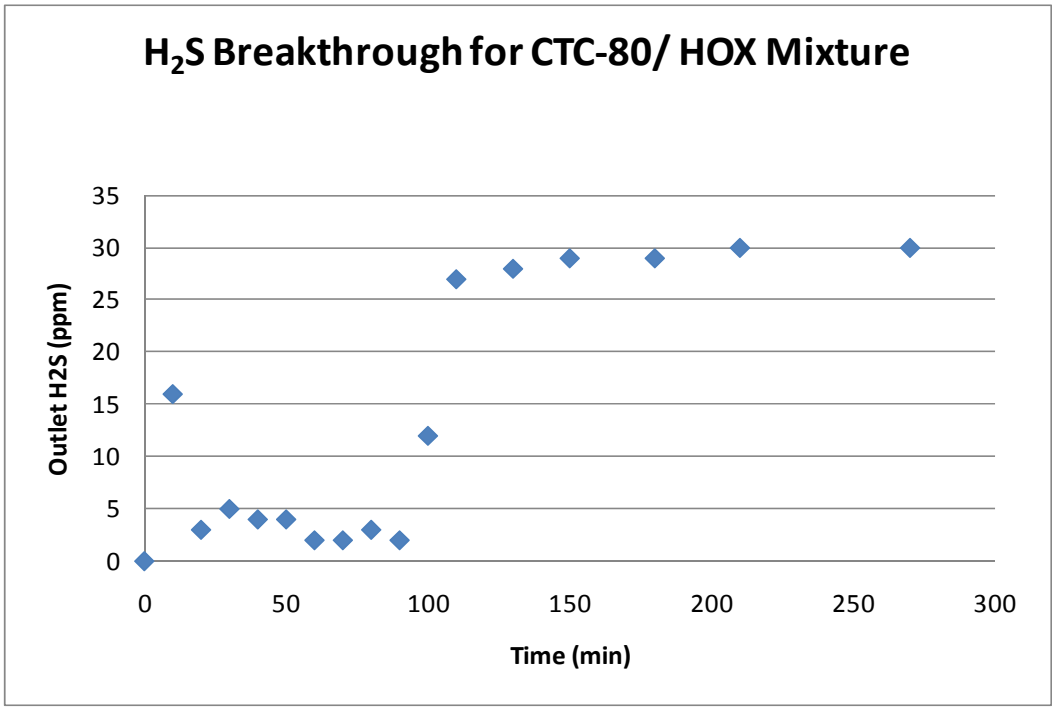
3.1.1 H_2S Breakthrough Curve Using HOX-GAC Media

Because there is no analyzer to measure siloxane concentration of biogas in real time on-line, we were hoping to measure the H_2S breakthrough curve and use the initial H_2S breakthrough time to estimate the media change-out time for siloxanes. We checked the H_2S concentration of the biogas with a Draeger tube made by RAE Systems. The H_2S broke through just after ten minutes of adsorption time. Consequently, we decided that the H_2S initial breakthrough time could not be used to determine the media change-out time.

SMUD provided a Landtec portable biogas analyzer to measure H_2S concentration of the biogas. In October a complete H_2S breakthrough curve for biogas generated from SRWWTP was measured when we prepared saturated media for 6-hour long microwave regeneration test.

The adsorber was loaded with 80 lbs of HOX and CTC-80 GAC mix media and run for 24 hours at 130-scfm biogas flow rate. Figure 29 presents this complete H_2S breakthrough curve for the biogas at Carson Energy. As shown in this figure, H_2S broke through at 10 minutes of adsorption time and its concentration reached 16-ppm but decreased to 3-ppm at 20 minutes and stayed at low concentrations until 90 minutes. Then, the H_2S concentration increased steadily after 100 minutes of adsorption time. Approximately 0.035 lbs of H_2S was adsorbed for 100 minutes of adsorption time.

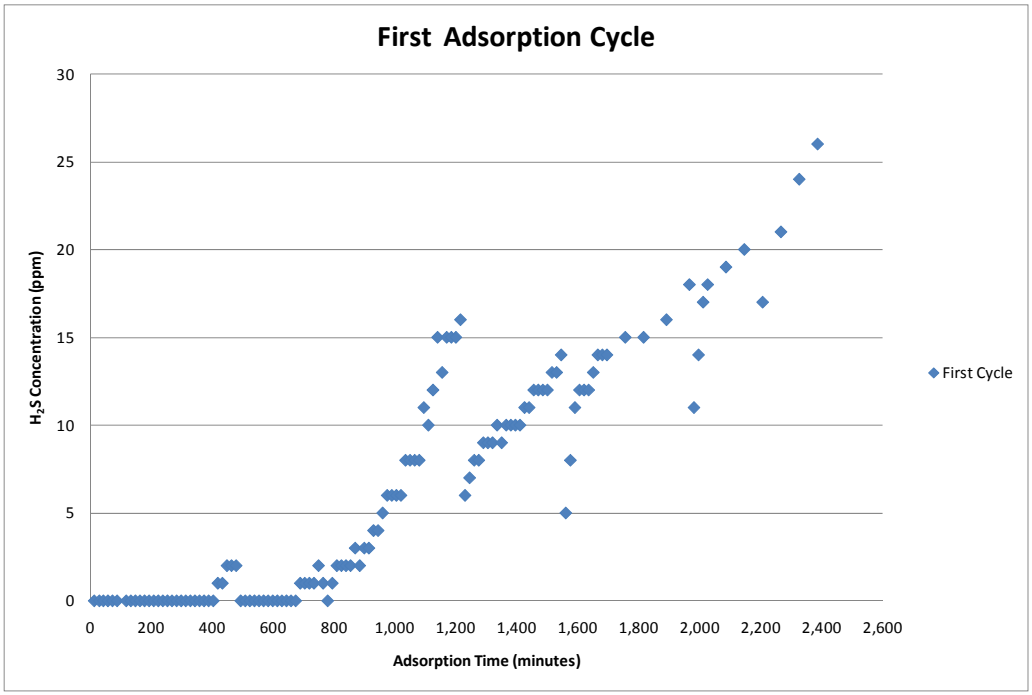
Figure 29: H_2S Breakthrough Curve for SRWWTP Biogas Using HOX-GAC Mix



The HOX material does not adsorb H_2S; only CTC-80 activated carbon adsorbs H_2S. The breakthrough time for H_2S of 100 minutes for this media compares unfavorably to the estimated breakthrough time of 24 hours for Siloxane. This indicates that this media is not efficient in complete H_2S removal and monitoring H_2S is not a good indicator of siloxane breakthrough for this media.

In a separately funded project, The H_2S adsorption test was also conducted using the media consisting of 20 lbs CuO-impregnated GAC (Sulfusorb) and 23.41 lbs of HOX that started the last week of October 2009 and was completed on November 4th. The adsorption test was run for six days to record H_2S concentration of the adsorber outlet gas every 15 minutes. Figure 30 presents H_2S breakthrough curve obtained from this test.

Figure 30: H_2S Breakthrough Curve Using HOX-Sulfusorb Mix



As shown in Figure 30, the H_2S broke through after 800 minutes of adsorption time. A comparison of Figure 30 with Figure 29 shows that the initial H_2S breakthrough time was more than ten times longer for the Sulfusorb-HOX mix. For the same amount of Sulfusorb impregnated GAC the initial breakthrough time of the Sulfusorb-HOX mix bed would be 16 times longer than the HOX-GAC-80 mix media.

Figure 30 shows that when the H_2S adsorption test was restarted after about 16 hours, the H_2S concentration of the adsorber outlet was about 10-ppm lower than the previous concentration when the test was temporally terminated previous day. This suggests that the H_2S adsorbed by the carbon reacted with CuO to produce CuS over night, which created an additional H_2S adsorption sites on the carbon and increased the H_2S adsorption capacity and rate when the test was started again next day.

A demonstration to identify a regenerable media for efficient H_2S removal was separately funded by SMUD and conducted near the end of this project. This separate demonstration also examined both H_2S and Siloxane removal using landfill biogas. The results of this separate study show that H_2S can be effectively removed with a CuO-impregnated media that absorbed the H_2S after siloxane and hydrocarbons were removed. The impregnated GAC (Sulfusorb) was regenerated in a separate microwave process and reused to remove H_2S. The final report of this separate demonstration to remove H_2S from biogas is attached as Appendix E to this report.

3.1.2 Determine the Consistency of Microwave Regeneration (Test 2R-5R)

Two batches of fresh media were prepared for tests to investigate the consistency of microwave regeneration. Each batch had about 75 lbs of the media consisting of equal volume of HOX and CTC-80 GAC. The media in these two batches designated Batch 1 and Batch 2 were separately

saturated with biogas for 24 hours and then regenerated with microwaves at about 35-lb/hr. Media in these two batches were not mixed until this series of tests were completed. Consequently, each cycle consisted of the adsorption for 24 hours and about two hour microwave regeneration. Four cycles of adsorption and microwave regeneration were completed for two batches. Only one microwave reactor was used for regeneration since it took almost one hour to reach steady state operating conditions. Table 11 and Table 12 present saturation and regeneration results, respectively. During the cycle 2 microwave regeneration tests of Batch 1 and Batch 2 the vapor take-off screen was plugged, causing much lower liquid recovery and media weight loss. As a result, CTC numbers of regenerated media were lower than other cycles of regeneration tests. The vapor take-off screen was removed and cleaned after the second cycle regeneration of two batches.

Table 11: Saturation Data for 75 lb Batch Tests

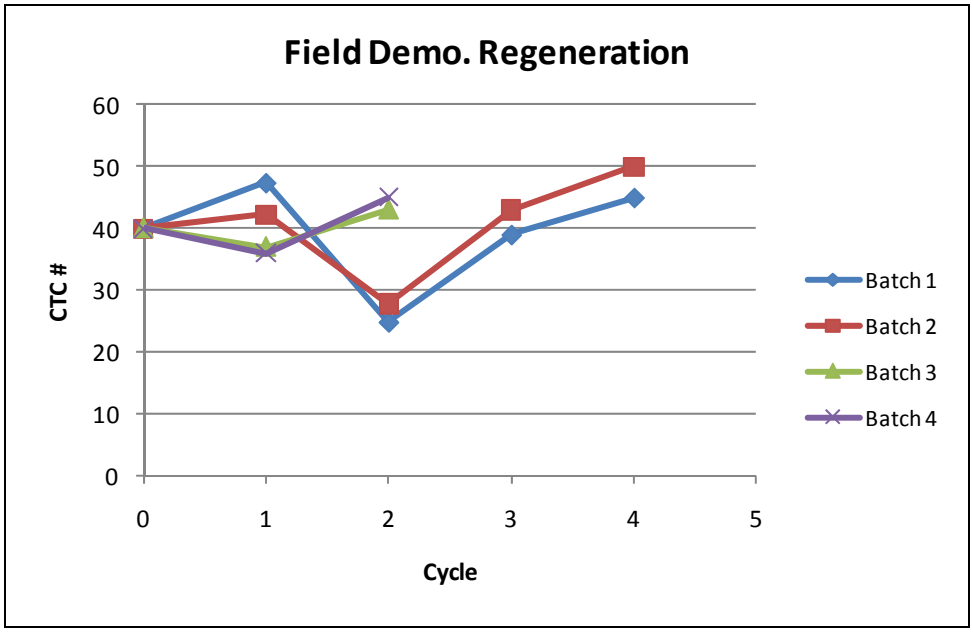
Batch #	Cycle #	Intial Weight (lb)	Final Weight (lb)	Weight Gain (lb)	CTC #
1	0	72.00			40
2	0	75.00			40
1	1	72.00	81.33	9.33	
2	1	75.00	84.75	9.75	
1	2	68.5	75.89	7.39	
2	2	72.81	79.41	6.60	
1	3	73.02	79.54	6.52	
2	3	78.41	82.62	4.48	
1	4	67.05	72.35	5.30	
2	4	70.78	75.94	5.16	

Table 12: Regeneration Data for 75 lb Batch Tests

Batch #	Cycle #	Intial Weight (lb)	Final Weight (lb)	Weight Loss (lb)	Liquid Recovered (lb)	CTC #
1	1	79.00	68.50	10.50	7.23	47
2	1	83.44	72.81	10.63	7.26	42
1	2	76.74	73.02	3.72	0.29	25
2	2	80.99	78.14	2.85	0.23	28
1	3	76.93	67.05	9.88	8.98	39
2	3	83.44	70.78	12.66	10.34	43
1	4	73.31	67.23	6.08	4.51	45
2	4	74.44	68.63	5.81	3.56	50

Figure 31 shows the CTC number of regenerated media as a function of adsorption and regeneration cycle to see the consistency of microwave regeneration. Data from Batch 3 and 4 are also included in this figure. These 150-lbs media batches were prepared for tests investigating the effect of regeneration rate on the microwave regeneration efficiency.

Figure 31: CTC # of Regenerated Media at Various Adsorption/Regeneration Cycle



The CTC number of the fresh media was 40. After the first cycle of regeneration the both Batch 1 and Batch 2 CTC numbers increased to 47 and 42, respectively. Except cycle 2 both batch CTC

numbers are equal or greater than the fresh media CTC number, indicating that the microwave regeneration of 35-lb/hr restored the media adsorption capacity.

Figure 32 shows the percent weight gain of the media during saturation. The media weight gain decreased as the adsorption cycle increased. Because the feed hydrocarbon concentration was not constant, it was not clear what caused the decrease in the media weight gain.

Figure 32: Media Weight Gain during Biogas Adsorption vs. Cycle

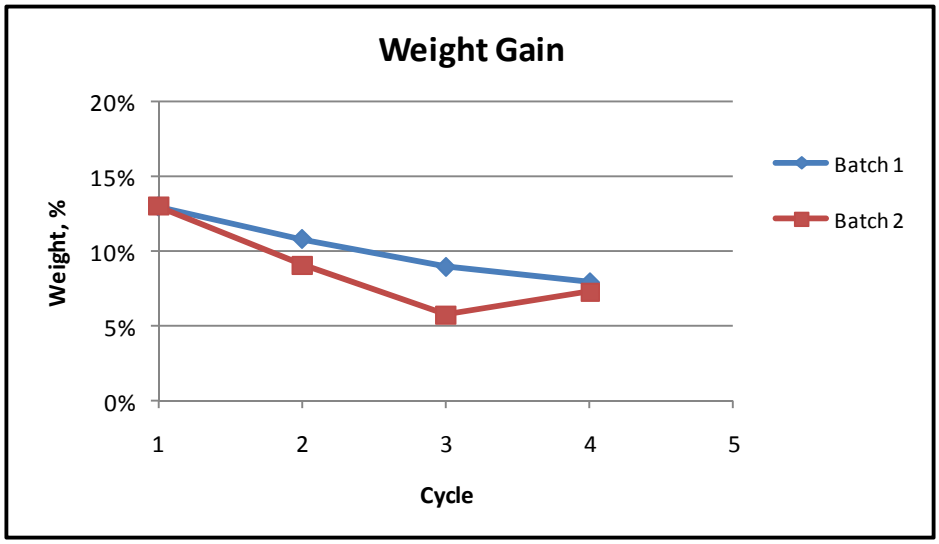


Figure 33 presents the media weight loss by microwave regeneration. The lower weight losses of two batches for the cycle 2 microwave regeneration were caused by the plugged vapor take-off screen. Higher weight losses at the 3rd cycle regeneration indicated that some of hydrocarbon liquid was not removed from the media during the 2nd cycle regeneration. However, if the average weight losses of 2nd and 3rd cycles were used, the media weight loss decreased also as the adsorption/regeneration cycle increased. Total weight gain from eight batches of adsorption was 54.53 lbs, which is close to total media weight loss of 62.13 lbs during regeneration.

Figure 33: Media Weight Loss by Microwave Regeneration vs. Cycle

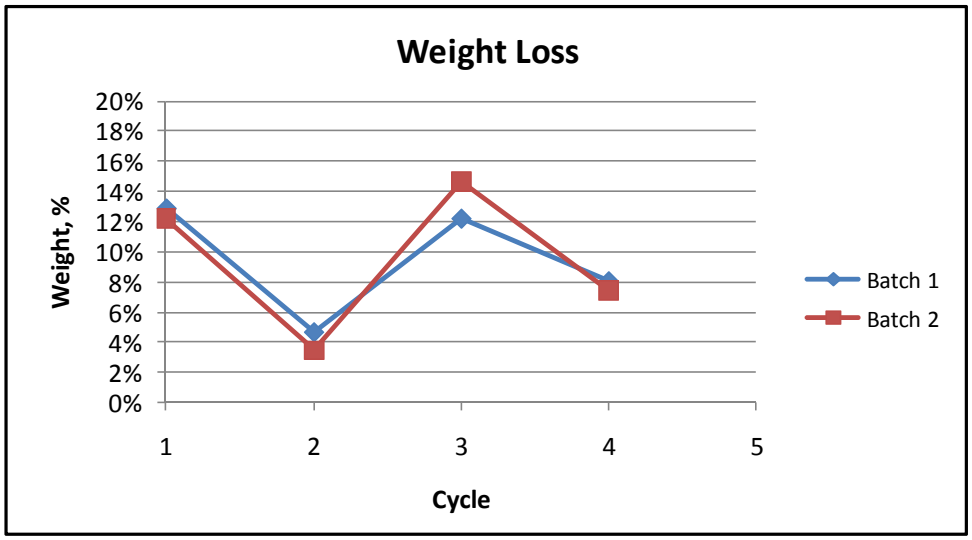


Figure 34 presents the amount of liquid recovered as a function of the adsorption/regeneration cycle. The amount of liquid recovered followed the media weight loss curve shown in Figure 33 decreased as the cycle increased.

Figure 34: Liquid Recovered During Regeneration vs. Cycle

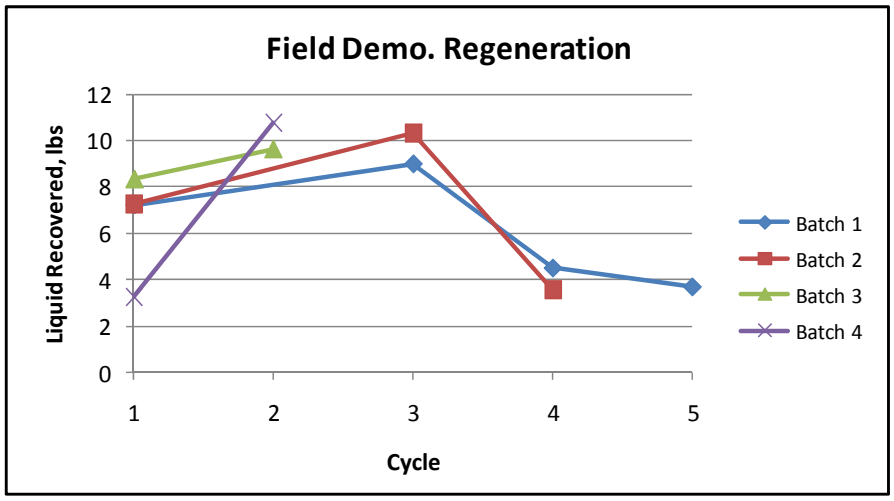
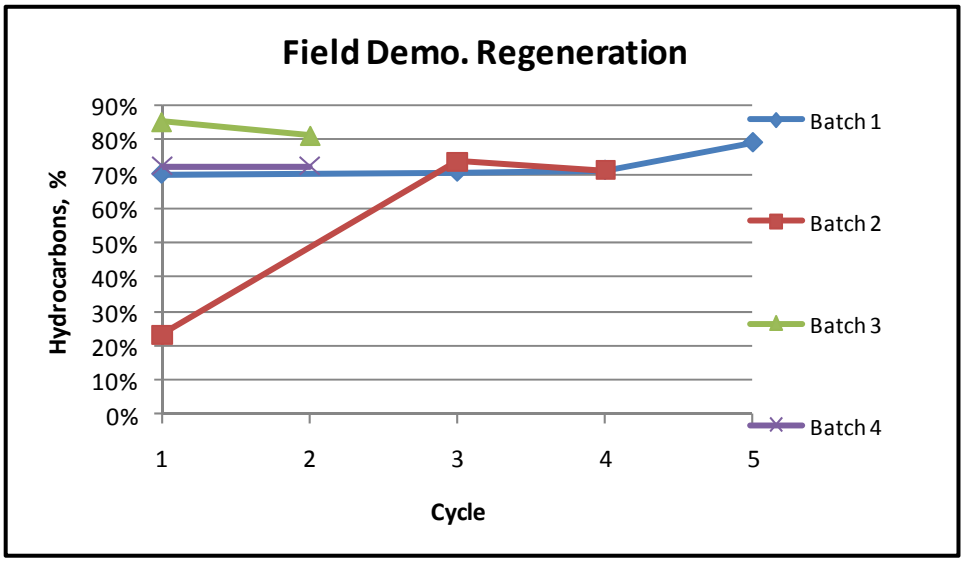


Figure 35 shows the percent of hydrocarbons in the recovered liquid as a function of the regeneration cycle. Except the first cycle of Batch 1 more than 70 percent of liquid recovered were hydrocarbons as shown in this figure. The average amount of hydrocarbon liquid per pound of regenerated media was 0.05 lbs. For microwave regeneration of one SMUD adsorber containing 9,000 lbs media could produce 450 lbs of hydrocarbon liquid, equivalent to 8,250-scfm methane.

Figure 35: Percent Hydrocarbon Liquid in Reovered Liquid vs. Cycle



The H_2S in the sweep gas was decomposed in the GAC bed by microwave energy and produced elemental sulfur was captured by the filter. The picture of elemental sulfur and carbon dust collected in the filter is shown in Figure 36. Also, siloxanes in the sweep gas were oxidized to produce silicon dioxide that was captured by the filter with ash. Figure

Figure 37 shows the picture of silicon dioxide captured in the filter.

Figure 36: Picture of Sulfur Collected in Filter

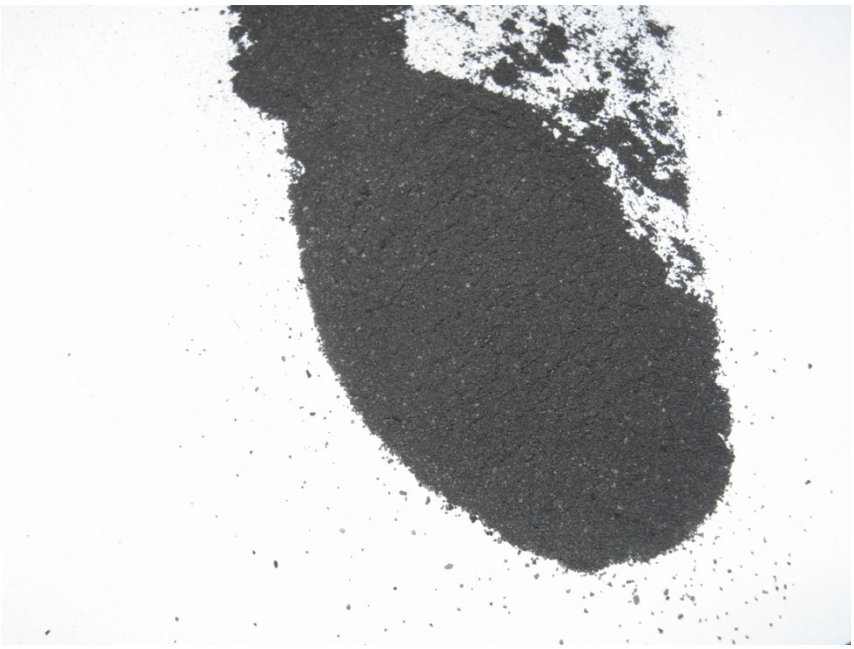


Figure 37: Picture of Silicon Dioxide Collected in Filter

3.1.3 Test Various Microwave Regenerator Throughputs (Test 6R-9R)

Higher microwave regenerator throughput tests require more than 75 lbs of HOX and CTC-80 GAC mix. We prepared 150 lbs Batch 3 sample by mixing 75 lbs of Batch 1 regenerated media with 75 lbs of virgin media and 150 lbs Batch 4 sample by mixing 75 lb of Batch 2 regenerated media with 75 lbs of virgin media. Then, we saturated Batch 3 and Batch 4 with biogas for 24 hours. The first cycle adsorption required four adsorption batches. We regenerated the Batch 3 saturated media with 50-lb/hr regenerator throughput using two microwave reactors. We regenerated Batch 4 saturated media with 40-lb/hr throughput. Then, we saturated regenerated Batch 3 and Batch 4 samples again with biogas for 24 hours. The Batch 3 saturated media was regenerated with 80-lb/hr throughput and Batch 4 with 60-lb/hr throughput. Table 13 and Table 14 present adsorption and microwave regeneration test results, respectively.

Table 13: Saturation Data for 150 lb Batch Tests

Batch #	Cycle #	Intial Weight (lb)	Final Weight (lb)	Weight Gain (lb)
3	1	143.63	159.20	15.57
4	1	144.51	154.70	10.19
3	2	145.33	159.87	14.54
4	2	144.99	154.02	9.03

Table 14: Regeneration Data for 150 lb Batch Tests

Batch #	Cycle #	Intial Weight (lb)	Final Weight (lb)	Weight Loss (lb)	Liquid Recovered (lb)	Regeneration Rate (lb/hr)	CTC #
3	1	156.76	145.33	11.43	8.32	50	37
4	1	149.17	144.99	4.18	3.27	40	36
3	2	160.91	139.91	21.00	9.63	80	43
4	2	176.14	157.96	18.18	10.76	60	45

Figure 38 presents the CTC number of regenerated media as a function of the regenerator throughput. The CTC number of regenerated media increased from 36 at 40-lb/hr, reached 45 at 60-lb/hr, and then decreased to 43 at 80-lb/hr. However, the CTC numbers of regenerated media were close to the virgin media CTC number of 40. Figure 38 indicates that the optimum throughput was 60-80 lb/hr for two microwave regenerators or 30-40 lb/hr for each microwave regenerator.

Figure 38: CTC # of Regenerated Media vs. Microwave Regenerator Throughput

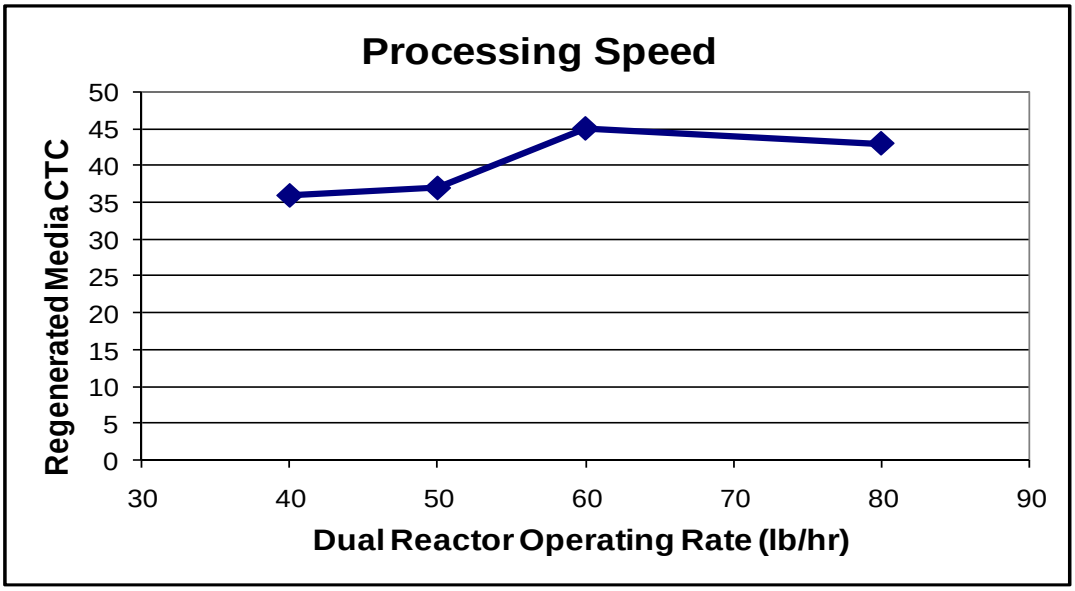


Figure 39 and Figure 40 present the media percent weight gain after adsorption and percent weight loss after regeneration, respectively, for two adsorption/regeneration cycles of Batch 3 and Batch 4. It is not clear why Batch 3 had higher weight gains and also higher weight losses. The amount of liquid recovered after regeneration is shown in Table 14. More than 70 percent of recovered liquid was hydrocarbon liquid.

Figure 39: Media Weight Gain after Saturation vs. Ads/Reg Cycle

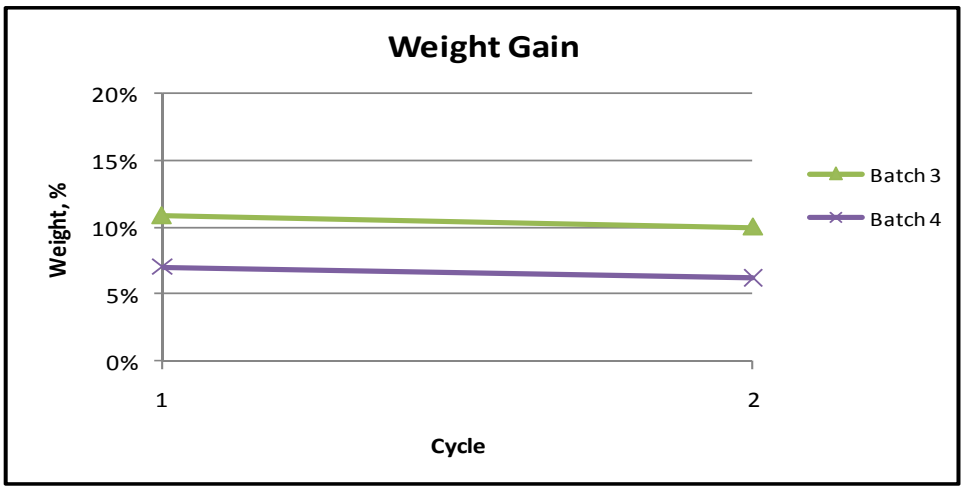


Figure 40: Media Weight Loss after Regeneration vs. Ads/Reg Cycle

3.1.4 6-hr Long Microwave Regeneration Test (Test 10R)

Approximately 350 lbs of saturated media was prepared to conduct a 6-hr long microwave regeneration test. Approximately 200 lbs of saturated media was prepared in May before the temporary power plant shut-down and 150 lbs was saturated on October 4th through 6th after the power plant was back online. We started a 6-hr microwave regeneration test early morning of October 9th. Because of trouble with the chiller we passed the regenerator sweep gas over an ice and water mixture. Only one microwave reactor was used with the 50-lb/hr regenerator throughput. Table 15 presents results from the 6-hr microwave regeneration test. The hydrocarbon liquid recovered from this 6-hr regeneration test was much smaller than the previous tests.

The H_2S and siloxanes can be destroyed in the GAC bed by microwave energy. If H_2S and siloxanes can be destroyed in the GAC bed, the microwave oxidizer can be eliminated and non-condensable desorbed gas can be recycled to recover heating value of hydrocarbon gases. In order to investigate this possibility, the mixture of oxidation catalyst and SiC in the second microwave reactor was replaced by GAC so that two microwave reactors acted as one GAC reactor. For the first three hours of regeneration period, air was not added to the microwave GAC reactor 1. For the remainder of the regeneration period, air was added to GAC reactor 1 at 1.5-L/hr. Gas samples were taken from the knockout pot outlet, MW GAC Reactor 2 outlet after three hours and six hours of regeneration. Table 16 presents the H_2S concentrations of the GAC Reactor 1 and GAC Reactor 2 outlets.

Table 15: 6-hr Microwave Regeneration Test Results

Saturated Media Weight	352.52 lbs
Regenerated Media Weight	310.1 lbs
Liquid Recovered	16.98 lbs

Water Recovered	13.24 lbs
Hydrocarbon Recovered	3.74 lbs
Average CTC # of Regenerated Media	38

Table 16: H_2S Concentration of MW GAC Reactor Outlet Gases (6-hr Test)

	Regenerator 1			MW GAC Reactor 1			MW GAC Reactor 2	
	MW	Reg.	Outlet	Reactor 1	Outlet	H2S	Outlet	H2S
Time	Power	Throughput	H2S Conc.	Power	H_2S Conc.	Destr. Eff.	H_2S Conc.	Destr. Eff.
[min.]	[kW]	[lbs/hr]	[ppm]	[kW]	[ppm]	%	[ppm]	%
0	0	0	0	2.55	0		0	
1	3	60	680	2.55	0	100%	0	100%
30	5.4	60	550	2.55	0	100%	0	100%
60	5.4	50	580	2.55	325	44%	0	100%
90	5.4	50	630	2.55	360	43%	0	100%
120	5.4	50	700	2.55	325	54%	0	100%
150	5.4	50	680	2.55	440	35%	1	100%
180	5.4	50	775	2.55	425	45%	1	100%
210	5.4	50	>800	2.55	480	>40%	3	>99.6
240	5.4	50	>800	2.55	300	>40%	9	>98.9
270*	5.4	50	>800	2.55	300	>40%	22	>97.3
300	5.4	50	>800	2.55	475	>40%	61	>92.4
330	5.4	50	>800	2.55	490	>40%	60	>92.5
360	5.4	50	>800	2.55	350	>40%	NA	

* 1.5 L/hr of air added to MW GAC Reactor 1

The biogas analyzer was not calibrated to measure the H_2S concentration greater than 800-ppm. After 210 minutes of regeneration time the H_2S concentration of the knockout outlet gas was greater than 800-ppm. Consequently, the overall H_2S destruction efficiency could not be calculated. The H_2S was completely destroyed in the GAC reactors by microwave energy for the three hours of the microwave regeneration without air. Table 16 clearly indicates that H_2S desorbed from saturated media can be completely destroyed by microwaves if approximately 1.5 seconds gas residence time is used.

Gas samples were taken in Tedlar bags and shipped to Analytical Solution, Inc. in Chicago, Illinois for siloxane analysis. Table 17 presents siloxane analysis results for the knock pot outlet, GAC Reactor 2 outlet with and without air addition. It should be noted that the knock pot outlet contained non-condensable desorbed gas from the microwave regenerator.

Table 17: Siloxane Analysis Results from 6-hr Microwave Regeneration Test

	Knock out Pot Outlet		GAC Reactor Outlet w/o Air		GAC Reactor Outlet with Air	
Organic Silicon (Siloxane)	**ppmv as Si**	**ppmv**	**ppmv as Si**	**ppmv**	**ppmv as Si**	**ppmv**
Tetramethyl silane	<0.1	<0.1	0.35	0.35	0.63	0.63
Trimethyl silanol	2.18	2.18	<0.1	<0.1	<0.1	<0.1
Hexamethyldisiloxanes (L2)	0.38	0.188	<0.1	<0.05	<0.1	<0.05
Hexamethylcyclotrisiloxane (D3)	41.76	13.92	<0.1	<0.03	1.58	0.53
Octamethyltrisiloxane (L3)	0.54	0.18	<0.1	<0.03	<0.1	<0.03
Octamethylcyclotetrasiloxane (D4)	12.81	3.20	0.09	0.023	0.34	.084
Decamethyltetrasiloxane (L4)	<0.1	<0.02	<0.1	<0.02	<0.1	<0.02
Decamethylcyclopentasiloxane (D5)	4.07	0.81	0.10	0.19	0.18	0.037
Dodecamethylpentasiloxane (L5)	<0.1	<0.02	<0.1	<0.02	<0.1	<0.02
Dodecamethylcyclohexasiloxane (D6)	0.14	.024	0.15	0.025	0.19	0.031
Sub-total	61.88		0.69		2.92	
Others (as L2)	1.59	0.8	1.70	0.85	22.34	11.17
Total	63.47		2.39		25.26	

Table 17 clearly shows that 98.9 percent of siloxanes were destroyed in the GAC reactor by microwaves when air was not added. When air was added to the GAC reactor, other silicon component as L2 increased from 1.7-ppm as Si to 22.34-ppm as Si. This suggests that some of siloxanes were oxidized to produce SiO_2, which was included in the concentration of "Others as L2". Anecdotal experience from other biogas engineers suggest that some the Si in the "Others as L2" reported by some laboratories is actually entrained SiO_2. .Consequently, if other silicon components reported as L2 are entrained SiO_2 the efficiency of siloxane removal is actually higher than measured.

Since 99 percent of H_2S and siloxanes contained in the microwave regenerator outlet gas were destroyed, and both Sulfur and SiO_2 can be removed as a solid, the microwave oxidizer can be replaced by a microwave GAC reactor and the low volume outlet gas from the GAC reactor can be filtered and recycled to the untreated biogas, which will utilize the heating value of non-condensable hydrocarbon gases. Also, the biogas instead of nitrogen can be used as sweep gas that will avoid the addition of nitrogen to treated biogas stream. Finally, if the condensed liquid hydrocarbons were introduced into the microwave GAC reactors, these hydrocarbons can be cracked to methane and hydrogen and put back into the untreated biogas stream. The significance of this process is that the fuel value of the hydrocarbons can be recovered and no vent or flare would be required for the regenerated gasses.

Table 18 presents the composition of outlet gas from the microwave GAC reactor with and without air addition. Adding air to the GAC reactor increased concentration of hydrogen and lower molecular hydrocarbon gases as well as CO_2 and CO concentrations. This suggests that air addition increased the decomposition of higher hydrocarbons.

Table 18: GAC Reactor Outlet Gas Analysis for 6-hr MW Regeneration Test

Gas Component	GAC Reactor Outlet Gas w/o Air Addition, Volume %	GAC Reactor Outlet Gas with Air Addition, Volume %
Hydrogen	0.13	0.75
Carbon monoxide	0.33	0.56
Nitrogen	90.6	93.9
Oxygen	6.18	0.38
Hydrogen sulfide	ND	ND
Carbon dioxide	0.154	0.467
Methane	1.55	2.81
Ethylene	0.174	0.266
Ethane	0.158	0.215
Propylene	0.179	0.222
Other C4s	<0.005	<0.005
i-Butane	0.028	0.023
n-Butane	0.021	0.018
Other C5s	0.010	0.019
i-Pentane	0.010	<0.005
n-Pentane	0.015	0.011
Other C6s	0.198	0.200
Hexane plus	0.157	0.117
Total	100.0	100.0

3.1.5 Siloxane and Other Gas Analysis

The siloxane samples were taken from adsorber inlet, adsorber outlet, microwave regenerator outlet, microwave GAC reactor outlet, and microwave oxidizer outlet using Tedlar bags. These gas sample bags were shipped to the Analytical Solutions, Inc. or the AFT lab for siloxane and other gas analysis. Additional samples at the adsorber were taken using the methanol impingement method and delivered to the Air Toxics Laboratory. The main objectives of this task were to determine the siloxane initial breakthrough time, adsorber performance for removing siloxanes and H_2S from biogas, and the performance of microwave GAC reactor and oxidizer.

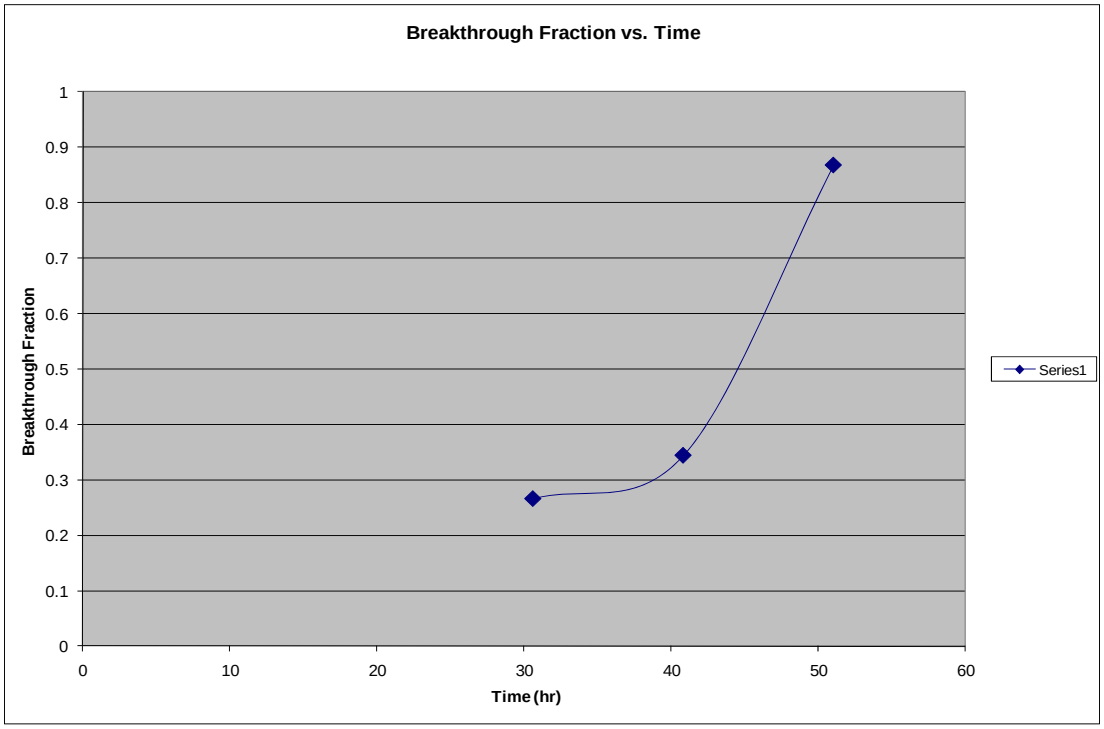
Table , presented previously, shows total siloxane concentration of SRWWTP biogas at Carson Energy was different for four different sample times.

In April 2009, gas samples were taken from the inlet and adsorber outlet at 18, 24, and 30 hours of adsorption time for siloxane analysis. The adsorber had 44 lbs of media. Table 19 presents siloxane analysis results of these samples. Concentrations of trimethyl silane, trimethyl silanol, L2, L3, L4, L5 were reported lower than the 0.1-ppmv reporting limit and not shown in this table. This table shows that the siloxanes already broke through the adsorber after 18 hours of adsorption time. From data shown in Table 19 total siloxane concentration in terms of the fraction of inlet concentration as Si is plotted in Figure 41 as a function of adsorption time adjusted to 75-lb of media in the adsorber. Note that the concentration of D3, D6 and others as L2 in the adsorber outlet are sometimes reported at higher concentrations than the inlet. The anomaly of a higher outlet concentration of certain siloxane species reoccurs in additional analyses presented in this project.

Table 19: Adsorber Siloxane Concentrations of Biogas at Carson Energy Site (4/2/ 2009)

	Biogas Inlet	**18-hr Outlet**	**24-hr Outlet**	**30-hr Outlet**
Organic Silicon (Siloxane)		ppmv as Si	ppmv as Si	ppmv as Si
Hexamethylcyclotrisiloxane (D3)	.09	0.47	0.59	0.06
Octamethylcyclotetrasiloxane (D4)	.90	0.34	0.37	0.14
Decamethylcyclopentasiloxane (D5)	2.25	0.15	0.16	0.50
Dodecamethylcyclohexasiloxane (D6)	.16	0.11	0.13	1.47
Others (as L2)	.15	0.13	0.22	0.60
Total as Si	3.55	1.20	1.47	2.77
Removal Efficiency		66%	59%	22%

Figure 41: Siloxane Breakrough Curve for 50-lb Adsorber



Because of the smaller quantity of media and very low concentrations of siloxane species, it was very difficult to determine the initial breakthrough time from data presented in Table 19. Figure 42 shows that the adsorber outlet siloxane concentration may not decrease below 20 percent of the inlet concentration. However, we estimated the initial siloxane breakthrough time for a 75-lb adsorber to be 24 hours of the adsorption time by extrapolating this curve. Consequently, we decided to run the adsorption for 24 hours using 75 lbs of HOX and CTC-80 mix.

On May 11th and 12th 2009, a series of siloxane tests were taken on the inlet and outlet of the adsorber containing 75 lbs of HOX and CTC-80 GAC mix. Siloxane concentrations were measured using the Air Toxics Labs methanol impingement method. Results from this test method are typically available in 24 to 48 hours. Carson Energy has used this siloxane analysis method to determine siloxane concentration of the cleaned gas from the existing 9,000 lbs GAC adsorbers. The test adsorber outlet gas samples were also taken in Tedlar bags at the same time for a side by side comparison of laboratory analyses. Tedlar bags were sent to Analytical Solutions Laboratory in Illinois for siloxane analysis. Siloxane analysis results obtained by the Analytical Solutions Lab and Air Toxics Labs are compared in Table 20.

Table 20: Siloxane Analysis Results

Compound	Inlet (ppbv)		Outlet 24 hr (ppbv)		Outlet 48 hr (ppbv)	
	ATL	AnSol	ATL	AnSol	ATL	AnSol
D4	290	185	ND	16	ND	26
D5	1,600	650	ND	12	ND	146
D6	0	190	ND	17	ND	4
Other as L2	NA	360	NA	270	NA	380
Total	1,890	1,385	ND	298	ND	556
Removal Efficiency			100%	84%	100%	71%

Table 20 shows clearly that the Air Toxics Labs methanol impingement method did not agree with siloxane analysis results obtained by the Analytical Solution, Inc. We ran four adsorption tests to determine siloxane initial breakthrough time. Because the siloxanes concentration data based on the Air Toxic Labs showed no siloxanes in the adsorber outlet gas, we completed four adsorption tests and concluded that 75-lbs HOX and CTC-80 mix media was adequate to remove all siloxanes in biogas and the siloxane removal goals of the project had been met. By the time we received siloxane analysis data from the Analytical Solutions Lab two weeks later, we had to stop field testing because the Carson Energy power plant was shut down for an extended period. We should have conducted additional adsorption tests to determine the initial siloxane breakthrough time and demonstrate that HOX and CTC-80 GAC mix media is capable of removing siloxanes from biogas completely.

Table 21 compares the siloxane concentration as Si of the adsorber outlet gas at 24 and 48 hours of adsorption times with the biogas inlet concentration. Total siloxanes in the adsorber outlet were 26 percent at 24 hours and 62 percent at 48 hours. If L2 is not included, total siloxanes in the adsorber outlet were 19 percent and 56 percent of the inlet concentrations at 24 and 48 hours, respectively. This suggests that the initial siloxane breakthrough time could be shorter than 24 hours of adsorption time according to analysis data obtained by the Analytical Solutions Lab.

Table 21: Siloxane Concentrations as Si for Inlet, 24-hr, and 48-hr Samples

	Biogas Inlet	24-hr Outlet	48-hr Outlet
Description	**ppmv as Si**	**ppmv as Si**	**ppmv as Si**
Tetramethyl silane	<0.1	<0.1	<0.1
Trimethyl silanol	<0.1	<0.1	<0.1
Hexamethyldisiloxane (L2)	<0.1	<0.1	<0.1
Hexamethylcyclotrisiloxane (D3)	<0.1	<0.1	0.09
Octamethyltrisiloxane (L3)	<0.1	<0.1	<0.1
Octamethylcyclotetrasiloxane (D4)	0.74	0.06	0.1
Decamethyltetrasiloxane (L4)	<0.1	<0.1	<0.1
Decamethylcyclopentasiloxane (D5)	3.23	0.06	0.73
Dodecamethylpentasiloxane (L5)	<0.1	<0.1	<0.1
Dodecamethylcyclohexasiloxane (D6)	1.13	0.87	2.02
Others (as L2)	0.72	0.54	0.76
Total as Si, ppmv	5.82	1.53	3.61
Total (Si, mg/M^3)	7.30	1.92	4.52
Removal Efficiency		73.7%	37.9%

(Tedlar Bag Sample Taken on May 11th and 12th 2009)

Siloxane analysis data measured by the Air Toxic Labs showed siloxanes did not breakthrough after 24 hours but data obtained by Analytical Solutions Lab showed that siloxanes already broke through the 75-lbs adsorber after 24 hours. Therefore, the adsorption tests should be repeated to determine the siloxane initial breakthrough time to demonstrate that the 50-50 HOX and CTC-80 GAC mix media remove siloxanes from biogas completely. The Air Toxics Labs methanol impingement method is much more convenient but is apparently not applicable to measure very low concentration of siloxane species. It is very difficult to determine the initial breakthrough time from data shown in

Table 21 because of the concentration of other siloxane species concentration as L2 is much higher than any known siloxane species concentrations.

Table 21 show that the D6 and others as L2 concentrations of the inlet gas were 1.13 and 0.72 ppmv, respectively. After 48 hours of adsorption, the concentrations of D6 and others as L2 increased to 2.02 and 0.76 ppmv, respectively. This suggests that there were some problems with the siloxane analytical method used by the Analytical Solutions Lab. It should be noted that if we do not include D6 and L2, the siloxane removal efficiency after 24 hours of adsorption increases to 97 percent from 74 percent.

Although the test results from the ATL impingement method indicated complete siloxane removal in the adsorber, this conclusion was not supported by the results from the tedlar bag samples taken at the same time. From this data, the goal of 99 percent removal of siloxane by the media in the adsorber could not be conclusively verified.

During the technical transfer activities related to this project, other companies providing commercial siloxane removal systems with thermally regenerated media revealed that they regenerate prior to breakthrough in the range of 15 percent of the adsorption capacity of the media. This range was apparently selected to prolong media life and provide warrantable siloxane removal efficiency.

In July 2010, the test adsorber was reinstalled to conduct further tests of siloxane removal efficiency. Based on previous tests, if siloxane breakthrough was estimate approximately 24 hours for 75 lbs of media, then 4 hours would represent the commercial media exposure time before regeneration.

Another theory for measuring siloxane removal efficiency below the project goal is the size of the adsorber and relatively high flow rate of the biogas resulting in bypass of biogas past the media, especially along the smooth container walls. The 0.85 second contact time in the test adsorber is much shorter than a well-designed commercial adsorber. A 1-hour test was scheduled to determine if lab results would indicate that bypass was a significant factor.

On July 12, 2010, 75 lbs of media was placed in the adsorber. Tedlar bag samples of the adsorber outlet were taken at 1 hour and 4 hours and the adsorber inlet biogas was sampled at 4 hours. Samples were sent to both the AnSol Lab and a separate lab sponsored by AFT. Results are shown in Table 22.

As shown, the siloxane analyses from the two labs have no correlation. Removal efficiency increased from 1 hour to 4 hours. Note that the concentration of L5 increased significantly in the adsorber in the AFT lab results. Because of the large variation of reporting in the different lab analyses, no conclusion concerning the siloxane removal efficiency, adsorber bypass or project goals could be reached.

Table 22: Siloxane Analysis of Samples from Additional Adsorption Test on 7/12/2010

Siloxane Component	Inlet Biogas 7/12/2010		I hour Outlet 7/12/2010		4 hour Outlet 7/12/2010	
	AnSol	**AFT**	**AnSol**	**AFT**	**AnSol**	**AFT**
TMS	<.02	-	<.02	-	<.02	-
L2	<.02	0.0047	<.02	ND	<.02	0.0011
D3	0.044	0.0083	0.022	0.0011	0.0016	0.0018
L3	<.02	0.0029	<.02	ND	<.02	ND
D4	1.24	1.4	0.256	0.0062	0.22	0.0085
L4	<.02	0.0031	<.02	ND	<.02	ND
D5	11.14	0.0048	0.185	0.11	0.094	ND
L5	<.02	0.0028	<.02	0.11	<.02	0.95
D6	0.41	ND	0.088	ND	0.043	ND
Other as L2	0.06	-	0.02	-	0.02	-
Total as Si ppmv	12.89	1.58	0.57	0.237	0.39	0.987
Total (Si, mg/M^3)	15.28	-	0.68	-	0.46	-
Removal Efficiency (Si ppmv)			95.58%	85.00%	96.97%	37.53%

Notes:

ND = Non Detected at reporting limits

Test Adsorber is 75 lbs of carbon/HOX media @ 120 CFM

Recent siloxane test results were also obtained from a fourth lab used by the Carson Energy operations staff where three 9,000 lb carbon adsorbers are now used in series to remove siloxane from the biogas. Table 23 shows the inlet siloxane concentrations and Table 24 shows the adsorber outlet results for three different situations and four different labs.

Table 23: Inlet Siloxane Concentrations Measured by Different Laboratories

Siloxane Component	Inlet Biogas 5/11/2009		Inlet Biogas 7/12/2010		Inlet Biogas 6/17/2010
	AnSol	ATL	AnSol	AFT	Lab D
TMS	<.01	-	<.02	-	0.007
L2	<.01	ND	<.02	0.0047	0.0009
D3	<.01	-	0.044	0.0083	0.00217
L3	<.01	ND	<.02	0.0029	0.0124
D4	0.74	0.29	1.24	1.4	0.238
L4	<.01	-	<.02	0.0031	0.015
D5	3.23	1.6	11.14	0.0048	0.607
L5	<.01	-	<.02	0.0028	-
D6	1.13	ND	0.41	ND	-
Other as L2	0.72	-	0.06	-	-
Total as Si ppmv	5.82	1.89	12.89	1.58	0.883
Total (Si, mg/M^3)	7.3	2.85	15.28	-	-

Table 24: Siloxane Concentration after Test Adsorber

Siloxane Component	48 hr outlet 5/12/2009		4 hour outlet 7/12/2010		Existing Carbon Adsorbers (3) 6/17/2010
	AnSol	ATL	AnSol	AFT	Lab D
TMS	<.01		<.02	-	0.06
L2	<.01	ND	<.02	0.0011	0.00006
D3	<.01	-	0.0016	0.018	0.00089
L3	<.01	ND	<.02	ND	0.00012
D4	0.1	ND	0.22	0.0085	0.00826
L4	<.01	-	<.02	ND	0.00021

Siloxane Component	48 hr outlet 5/12/2009		4 hour outlet 7/12/2010		Existing Carbon Adsorbers (3) 6/17/2010
	AnSol	ATL	AnSol	AFT	Lab D
D5	0.73	ND	0.094	ND	0.0071
L5	<.01	-	<.02	0.95	-
D6	2.02	ND	0.043	ND	-
Other as L2	0.76	-	0.02	-	-
Total as Si ppmv	3.61	0	0.39	0.987	0.01724
Total (Si, mg/M^3)	4.52	0	0.46	-	-
Removal Efficiency (Si ppmv)	37.97%	100.00%	96.97%	37.53%	98.05%

Notes:

ND = Non Detected at reporting limits

Test Adsorber is 75 lbs of carbon/HOX media @ 120 CFM

Existing 3 carbon Adsorbers are 9,000 lbs of carbon each in series @ about 1200 CFM.

Age of carbon in existing adsorbers is estimated at one to three months.

One of the four laboratories reported 100 percent removal efficiency. Tests on the existing siloxane removal system reported 98 percent removal efficiency. No further conclusions could be reasonably drawn on siloxane removal efficiency in the test adsorber from comparing the results of these analyses. In addition, the inlet siloxane concentration of 0.883 ppmv was much lower than the siloxane concentration of 12.89 ppmv measured on July 12th on June 17th, causing more difficulties drawing any conclusion regarding the siloxane concentration goal. The project team did conclude that the test adsorber could not replicate performance of a commercial sized adsorber and siloxane testing at low concentrations may be subject to significant variation between labs and from sample to sample.

On May 20th, Dr. Matthew Summers performed sampling for independent system verification. The procedures developed for the Independent Verification Test Plan for Removing Siloxane and H_2S from Biogas were followed. Samples were taken at the outlet of the microwave regenerator and the outlet of the microwave GAC reactor and microwave oxidizer.

Table 25 presents the siloxane analysis results of gas samples taken on May 20 from the outlet of microwave reactors at the portable microwave regeneration unit.

Following conclusions were drawn from siloxane analysis data shown in Table 25:

- 50 percent of siloxanes were destroyed in the GAC reactor by microwaves; some decomposed into lighter molecule siloxane and some could react with water vapor to produce SiO_2 and hydrocarbon gases.
- 97 percent of siloxanes entered into the microwave oxidizer were oxidized by microwaves and air.
- One half of remaining siloxanes (1.0 percent) was captured by the GAC guard bed.
- 99 percent of siloxanes desorbed from saturated media were removed from the sweep gas.

The concentration of "others as L2" in the GAC Reactor outlet is 23.97 ppmv as Si, indicating that SiO_2 is included in this concentration data.

Table 25: Siloxane Analysis Results of Microwave Reactor Outlets

	MW Reg. Outlet		GAC Reactor Outlet		Oxidizer Outlet		GAC Guard Bed	
Description	**ppmv as Si**	**ppmv**	**ppmv as Si**	**ppmv**	**ppmv as Si**	**ppmv**	**ppmv as Si**	**ppmv**
Tetr. silane	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Tri. silanol	5.82	5.82	2.28	2.28	<0.1	<0.1	<0.1	<0.1
L2	2.81	1.41	1.20	0.60	<0.1	<0.05	<0.1	<0.05
D3	52.03	17.34	15.52	5.17	0.11	0.036	0.07	0.023
L3	2.29	0.76	<0.1	0.024	<0.1	<0.03	<0.1	<0.03
D4	30.99	7.75	12.28	3.07	0.20	0.051	0.16	0.04
L4	0.21	<0.025	<0.1	<0.025	<0.1	<0.1025	<0.1	<0.025
D5	11.38	2.28	0.47	0.094	0.13	0.027	0.52	0.105
L5	<0.1	<0.02	<0.1	<0.02	<0.1	<0.02	<0.1	<0.02
D6	0.37	0.062	0.15	0.025	0.08	0.013	0.06	0.009
Others (as L2)	5.72	2.86	23.97	11.98	1.08	0.54	0.03	0.015
Total as Si	111.6		55.88		1.61		0.84	
Total (Si, mg/M^3)	132.3		66.25		1.91		0.99	

Table 26 presents other gas analysis results of samples taken on May 20th by Dr. Summers. Based on the heating value, 93 percent of hydrocarbons were oxidized and only 1 percent of hydrocarbons were discharged into the atmosphere. Also, the gas leaving the GAC guard bed contained only 0.3-ppm H_2S, negligible carbon monoxide and no sulfur dioxide. Also, about 60 percent of H_2S was destroyed in the GAC bed by microwaves.

Table 26: Regenerator and Oxidizer Outlet Major Gasses (Volume %)

Gas Compound	MW Regenerator Outlet Gas	MW GAC Reactor Outlet	MW Oxidizer Outlet	GAC Guard Bed Outlet
Hydrogen	1.76	1.84	<0.01	<0.01
Carbon monoxide	0.41	0.56	<0.01	<0.01
Nitrogen	94.2	93.8	90.7	86.5
Oxygen	0.134	0.393	4.43	11.05
Hydrogen Sulfide	0.128	0.054	0.020	0.00003
Carbon Dioxide	0.102	0.284	4.33	2.38
Methane	2.03	1.94	0.48	0.11
Ethylene	0.139	0.173	<0.01	<0.01
Ethane	0.135	0.160	0.005	<0.005
Propane	0.088	0.103	<0.005	<0.005
Propylene	0.138	0.175	<0.01	<0.01
Other C4s (C3-C4)	0.047	0.026	<0.005	<0.005
i-Butane	0.030	0.041	<0.005	<0.005
n-Butane	0.030	0.032	<0.005	<0.005
Other C5s (C4-C5)	0.143	0.179	<0.005	<0.005
i-Pentane	0.016	0.017	<0.005	<0.005
n-Pentane	0.029	0.027	<0.005	<0.005
Other C6s (C5-C6)	0.066	0.049	<0.005	<0.005
Hexane Plus	0.377	0.187	<0.005	<0.005
Total:	100.0	100.0	100.0	100.0
Relative density	0.958	0.955	0.995	0.995
Gross HV (dry)-Btu/Scf *	71.4	63.2	5.1	1.1
Gross HV (sat)-Btu/Scf *	70.2	62.1	5.0	1.1

Note:
* 60 °F and 14.73 psia
Additional significance is reported for reference only.
The MDL is no better than 0.01% for minor components.
The accuracy of calculated HV cannot be better than 1 Btu/Scf.

The adsorber inlet and 12-hr gas samples from the adsorber outlet were sampled and submitted to the Analytical Solution for siloxane and other gas analysis. The inlet sample was accidently destroyed during shipping. Table 27 and Table 28 present the concentration of major gases and siloxanes in the adsorber outlet. The H_2S concentration of the adsorber outlet gas (Table 27) was 3.08-ppm, indicating that about 85 percent of H_2S in biogas was removed by the GAC in the Guard bed.

Table 27: 12 hr Adsorber Outlet Major Gasses

Component	Conc. Unit	Concentration
Methane	%	63.9
Carbon dioxide	%	29.7
Nitrogen	%	4.44
Oxygen	%	1.95
Ethane	%	<0.005
Propane	%	<0.005
i-Butane	%	<0.005
n-Butane	%	<0.005
i-Pentane	%	<0.005
n-Pentane	%	<0.005
Hexane +	%	<0.005
Hydrogen sulfide	ppmv	3.08

Table 28: 12 hr Adsorber Outlet Siloxanes (ppmv)

Organic Silicon (siloxanes)	ppmv as Si	ppmv
Tetramethyl silane	<0.1	<0.1
Trimethyl silanol	<0.1	<0.1
Hexamethyldisiloxane (L2)	<0.1	<0.05
Hexamethylcyclotrisiloxane (D3)	<0.1	<0.033
Octamethyltrisiloxane (L3)	<0.1	<0.033
Octamethylcyclotetrasiloxane (D4)	0.08	0.021
Decamethyltetrasiloxane (L4)	<0.1	<0.02
Decamethylcyclopentasiloxane (D5)	0.31	0.061
Dodecamethylpentasiloxane (L5)	<0.1	<0.02
Dodecamethylcyclohexasiloxane (D6)	0.75	0.125
Others as L2	0.16	0.08
Total as Si	1.30	
Total (Si, mg/M^3)	1.55	

A comparison of the adsorber outlet (Table 28) with adsorber inlet (Table 29) indicates that total siloxanes as Si increased from 1.30-ppmv to 1.53-ppmv for 12 hours but increased from 1.53-ppmv to 3.61 when adsorption time increase from 24 hours to 48 hours. Therefore, we may assume the initial breakthrough time of siloxanes was 24 hours after the adsorption started.

3.1.6 Power Used for Operating 100-lb/hr Mobile Microwave Unit

During 6-hr microwave regeneration testing on October 9, Carson Energy personnel measured power used in the microwave oxidizer unit and microwave regeneration truck. We operated only one 6-kW microwave generator for this testing. The following presents power measured:

3-phase 480 VAC, 60 AMP Service/Oxidizer Unit

VAC to Ground

A: 263.3 B: 263.5 C: 264.5

VAC Phase to Phase

A-B: 457 A-C: 458 B-C: 458

AMPS

A: 10.71 B: 12.31 C: 11.01

Power: 8.992 kW

3-Phase 480 VAC, 100 AMP Service/Regeneration Trailer

VAC to Ground

A: 265.1 B: 266.0 C: 264.4

VAC Phase to Phase

A-B: 461 A-C: 459 B-C: 460

AMP

A: 12.05 B: 13.35 C: 12.84

Power: 10.155 kW

With two 6-kW microwave regenerators the mobile unit power requirement would be about 30-kW; 9-kW for two 3-kW microwave generators, 18-kW for two 6-kW generators, and 3-kW for pumps and compressors.

3.1.7 Potential Improvements on Microwave Biogas Upgrading System

This section describes items that caused operational problems during the microwave regeneration tests. These problems must be corrected for the successful commercialization of the microwave biogas upgrading system.

3.1.7.1 Plugging of Media Flow between Feed Hopper and Microwave Reactor

We experienced frequent plugging of media flow into the microwave reactor from the feed hopper, especially when the wet media was feeding into the microwave reactor. We used a

hammer to release the plugged media. This was caused by steam that flowed up and was condensed at the media surface. After we evaluated a couple of possible methods to prevent the media plugging problems, we decided to maintain a continuous flow of nitrogen into the bottom of the feed hopper at 0.5-scfm. We tested this at the 50-lb/hr microwave pilot plant in the CHA laboratory and found that the pilot plant operated for four hours without plugging problems on November 24th.

We installed a nitrogen injection line to the feed hopper at the 100-lb/hr mobile microwave regeneration system on December 4th. After the nitrogen was injected to the bottom of feed hopper, we did not experience any media plugging problems with the 100-lb/hr unit.

3.1.7.2 Cooling System of Microwave Oxidizer Unit

The 100-lb/hr mobile unit was originally constructed with total recycling of nitrogen sweep gas without the oxidation of the desorbed hydrocarbons. After construction of the mobile microwave oxidizer unit, the cooling water was supplied from the refrigeration system of the 100-lb/hr microwave regeneration unit. The 100-lb/hr microwave system worked without overheating in the climate of Laramie, Wyoming. When operating the 100-lb/hr microwave unit at Carson Energy site in Sacramento summer conditions, the microwave oxidizer unit shut down due to overheating after about one hour operation. The mobile microwave oxidation unit was operated using tap water at Carson Energy Plant. A robust cooling water system for the microwave oxidizer unit must be added.

After the field demonstration was completed, the mobile microwave oxidizer unit was transported back to CHA laboratory. A new cooling water supply system will be constructed to supply cooling water to two 3-kW microwave generators installed at the oxidizer unit.

3.1.7.3 Plugging of Vapor Take-off Screen

The vapor take-off screen from the microwave regeneration reactors was plugged with GAC fines and had to be cleaned almost weekly. A method to prevent the vapor take-off becoming plugged with carbon fines needs to be added. The carbon fines are separated by the cyclone when the media is pneumatically conveyed to the feed hopper. A better method of separating carbon fines from media during conveying media pneumatically or a better method of filtering carbon fines from sweep gas should be implemented. Another possibility to avoid plugging of vapor take-off is to install two vapor take-offs and switch them periodically. When the vapor take-off is not used, it can be cleaned by back flushing nitrogen.

3.1.7.4 Automation of Mobile Microwave Regeneration Unit

The 100-lb/hr mobile microwave unit has to be automated to demonstrate a commercial operation of the microwave biogas upgrading technology. The current mobile microwave regeneration unit was not constructed as a routine operational system. CHA plans to rebuild the current 100-lb/hr mobile microwave system and automate the entire system for commercial operation of microwave technology for upgrading biogas or any on-site media regeneration. Once the system is automated, the microwave on-site media regeneration system or biogas upgrading system will be operated without operator attendant.

3.1.7.5 Removal of Halogen and Acid Gasses

The biogas produced from the industrial landfill sites contains chlorinated solvents or other halogen compounds. Consequently, a step to remove these chemicals from the recycle gas or oxidizer outlet gas should be included. If chlorinated solvents are contained in biogas, a sodium or potassium hydroxide-impregnated GAC can be used to remove hydrogen chloride from the recycle gas. A liquid sparger or contact tower with a NaOH solution can also be used.

3.1.7.6 Gasification of Recovered Hydrocarbon Liquid

The best way to dispose recovered hydrocarbon liquid is to gasify the liquid to lower molecular weight hydrocarbon gases that can be introduced into the inlet biogas stream to the adsorber. This will allow recovering the BTU value contained in the hydrocarbon liquid.

3.2 Commercialization Plan

3.2.1 Mobile Microwave Regeneration System

3.2.1.1 Process Flow Diagram

The 6-hr microwave regeneration test results indicated that the microwave oxidizer unit can be replaced with a microwave GAC reactor to avoid the oxidation of non-condensable hydrocarbons desorbed from the regeneration of saturated media. The size of the microwave GAC reactor shown in the 100-lb/hr mobile microwave unit (Figure 26) should be increased to provide twice longer gas residence time and microwave power. In the microwave GAC reactor, H_2S reacts with oxygen to produce water and elemental sulfur and siloxanes are converted into hydrocarbons and SiO_2. Sulfur and SiO_2 are captured by the filter. Siloxane and H_2S-free hydrocarbon gases are recycled to the cleaned biogas stream. All other items are the same as the 100-lb/hr microwave regeneration system shown in Figure 26. Figure 43 presents a PFD for the revised 100-lb/hr mobile microwave regeneration system.

3.2.1.2 Estimated Capital Cost

Table 29 presents a list of major equipment identified from PFD shown in Figure 43. The purchase prices for each of the equipment items are also shown in this table. Storage tanks are not included in the major equipment list. The total equipment cost shown in the major equipment list is $196,300. The installed cost estimate includes costs for site preparation, piping, valves, wiring, conduit, and start up costs. These costs were estimated at $196,300 by applying a 1.0 factor of total equipment purchase cost. The total capital cost for the first commercial mobile microwave unit is the sum of total equipment purchase cost and installation cost that is $392,000. If the second commercial mobile microwave unit will require much lower capital cost.

3.2.1.3 Technical Expertise of Operator

The operator or service provider of the proposed microwave system would need to be a skilled technician with mechanical and electrical expertise with skills compared to an operator of a small generation plant. Specialized training in microwave technology could be provided in about 4 weeks with another 4 weeks of supervised work.

Figure 42: Revised Process Flow Diagram for Mobile Microwave Regeneration System

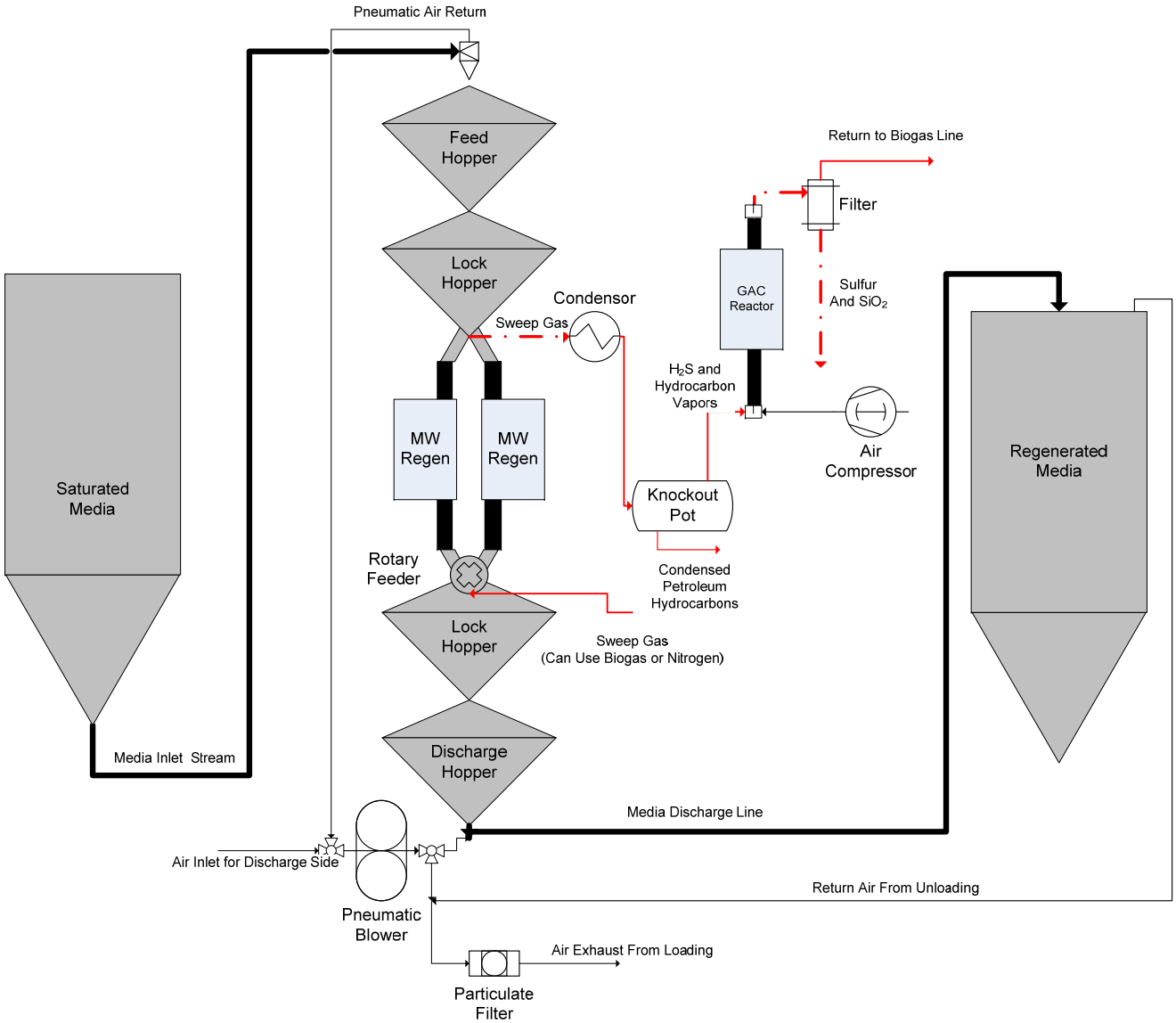


Table 29: Itemized Capital Cost for 100 lb/hr Biogas Media Regeneration Mobile System

Description	Quantity	Unit Cost	Cost
Microwave			
6kW Microwave Power Supply and Remote Magnetron	3	$25,000	$75,000
Slotted Waveguide Antennae	3	$800	$2,400
Mailbox Cavity Applicator	3	$400	$1,200
Reactor			
Quartz Tubes	6	$150	$900
Quartz/Stainless Steel Seal	4	$200	$800
Rotary Feeder	2	$1,200	$2,400
Variable Speed Rotary Feeder drive	2	$450	$900
Outlet Screen/ Tube connector Combo	2	$400	$800
Air Compressor	1	$300	$300
Flow Meter	6	$500	$3,000
Pressure Gauge	3	$200	$600
Condenser System			
1st Stage Condenser	1	$1,500	$1,500
60 gal. Stainless Steel Knockout Pot	1	$2,500	$2,500
Level Indicators	2	$400	$800
Pressure Transducers	2	$200	$400
Teflon Diaphragm Compressor	1	$2,300	$2,300
Thermocouples	10	$100	$1,000
Recirculating Chiller	1	$20,000	$20,000
Electrical			
Panel and Breakers	2	$4,000	$8,000
Main Disconnect	1	$1,000	$1,000
Conduit/Wire	1	$3,000	$3,000
Hoppers			
Feed	2	$1,200	$2,400
Product	2	$1,200	$2,400

Table 29: Itemized Capital Cost for 100 lb/hr Biogas Media Regeneration Mobile System

Description	Quantity	Unit Cost	Cost
Level Indicators	4	$400	$1,600
Valves	4	$1,300	$5,200
Pneumatic Conveying Piping	1	$2,000	$2,000
Vacuum Blower	1	$1,500	$1,500
Bag Filter	1	$400	$400
Structure			
Derrick	1	$4,000	$4,000
Instrument House	1	$5,000	$5,000
Skid	1	$5,000	$5,000
Trailer	1	$15,000	$15,000
Hydraulics	1	$5,000	$5,000
PLC Controller (Includes motor starters and programming)	1	$18,000	$18,000
Total Equipment Cost			**$196,300**
Total Installed Cost			**$392,600**

3.2.1.4 Estimated Operating and Maintenance Cost

The annual operating and maintenance cost was estimated based on the following assumptions.

- Media regenerated per site = 3,500 lbs
- Driving distance = 250 mile average
- Fuel Cost = $3.00 per gallon
- Labor for mobilizing and setting up the unit = 8 hours
- System operates autonomously once set up, processing the media in 35 hours
- Labor for the regeneration operation and demobilization = 16 hours
- Total time on site = 3 days
- Operator Salary = $48,000
- Operator Benefits = $21,600
- Operator per diem = $35,000
- Sites serviced per year = 100
- Electricity Rate = $0.1/kWh
- Annual Sales and Overhead Expenses $50,460
- Capital Depreciation is straight line over 15 years

Table 30 summarizes the annual operating and maintenance costs and equipment depreciation cost for the mobile microwave unit, and gives a cost of $0.72 per pound of reactivated media. Assume the residence time in the media adsorber is about 2 seconds and that each pound of media treats about 1,000 scf of biogas before regeneration, the cost to treat 1,000 SCF of biogas is $0.72. For a 1,000 scfm biogas location and 90 percent utilization, this would result in an annual treatment cost of about $338,000. For an engine or microturbine running at 26 cu ft of biogas per kWh, treatment costs would be about $0.019 per kWh.

Table 30: Annual O&M Cost for 100-lb/hr Mobile Unit

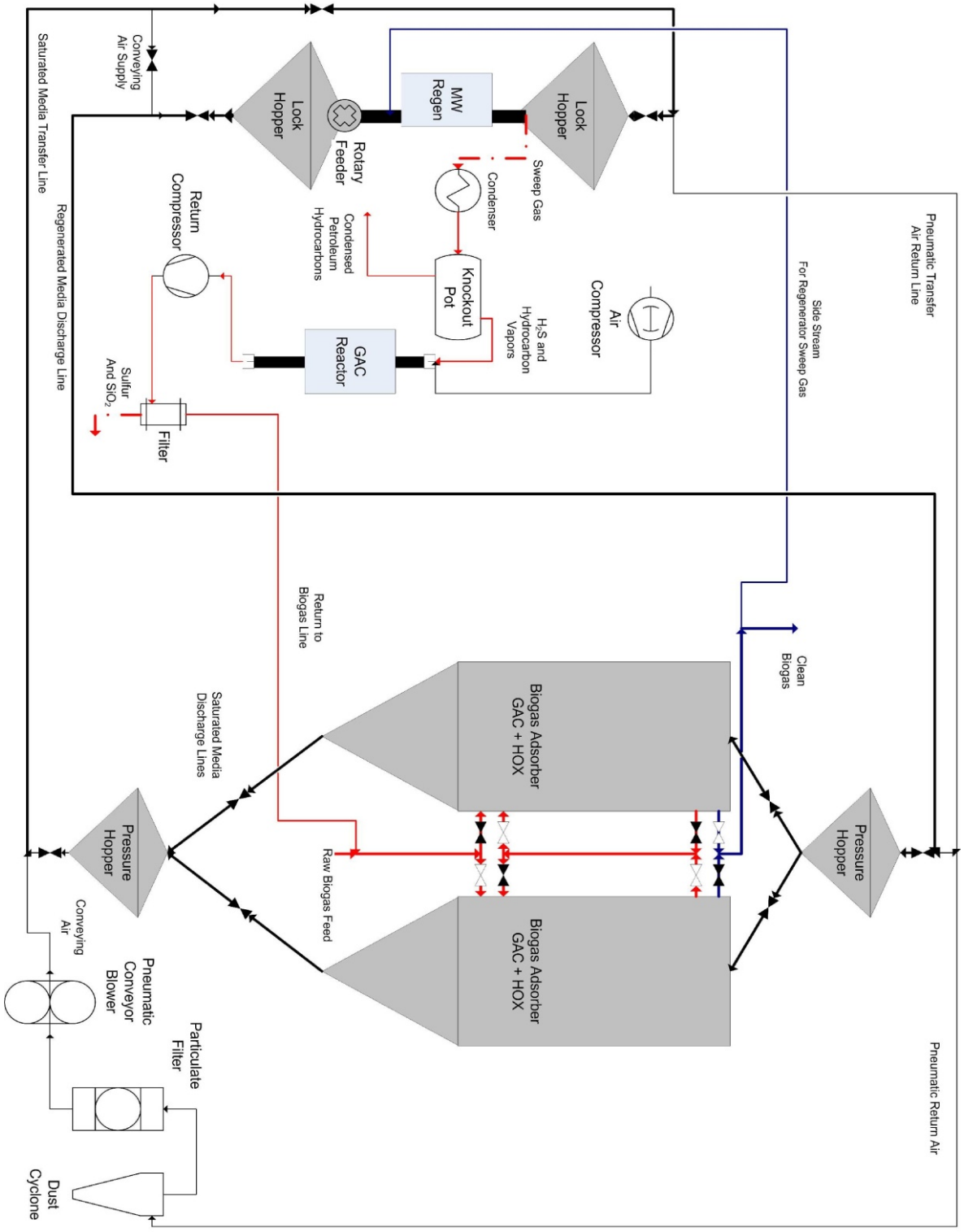
Maintenance Cost (7% of TDC)	$27,480
Labor cost	$84,600
Electricity Cost	$18,420
Operator per diem	$35,000
Travel Fuel Cost	$9,370
Sales Expenses	$42,000
G&A	$8,460
Depreciation	$26,170
Annual O&M Cost	**$225,330**
Total Annualized Cost	**$251,500**
Cost per pound of carbon	**$0.72**

3.2.2 Adsorption and Regeneration Integrated System

3.2.2.1 Process Flow Diagram

Two biogas adsorbers are located above the microwave regeneration reactors. One of two adsorbers is operated to remove siloxanes, H_2S, and other impurities. The adsorber containing saturated media is isolated from biogas to protect from high pressure of biogas. The saturated media in this adsorber is regenerated with microwaves. Raw biogas flows into the bottom of the adsorber and cleaned biogas leaves the top. Regenerated media is fed into the top of microwave reactor and flows by gravity into the bottom hopper. Star valve controls the regeneration rate. The method for applying microwaves to microwave regenerators is the same as the 100-lb/hr microwave system and is shown in Figure 43.

Figure 43: Revised Process Flow Diagram for Integrated Regeneration System



A part of cleaned biogas is used to supply a sweep gas for microwave regenerator. Desorbed vapor flowing out from the microwave regenerators flows into the condenser and knockout pot. The gas leaving the knockout pot flows into the GAC reactor where H_2S and siloxanes are destroyed by microwaves. The sweep gas leaving the GAC reactor is free from H_2S and siloxanes and contains mainly hydrocarbon gases. The elemental sulfur and SiO_2 produced in the GAC reactor are removed by the filter and sweep gas leaving the filter returns to the biogas. Regenerated media is pneumatically conveyed from the bottom hopper to the top of the adsorber.

When the media in the operating adsorber is saturated, the biogas flow is switched to the adsorber containing regenerated media. Then, the saturated media is regenerated with microwaves. The media is transported pneumatically from the bottom hopper to the top of the adsorber after the regeneration is complete. Details of the microwave regeneration system design will be dependent on the composition and flow rate of the biogas.

3.2.2.2 Estimated Capital Cost

Table 31 presents a list of major equipment identified from the PFD shown in Figure 43. The purchase prices for each of the equipment items are also shown in this table. The total equipment cost shown in the major equipment list is $136,650. The installed cost estimate for the first commercial unit includes costs for site preparation, piping, valves, wiring, conduit, and start up costs. These costs for the first commercial unit were estimated at $136,650 by applying a 1.0 factor of total equipment purchase cost. However, the second commercial unit installation cost will be much lower. The total capital cost for the first commercial system is the sum of total equipment purchase cost and installation cost that is $273,300.

3.2.2.3 Estimated Operating and Maintenance Cost

The operating and maintenance cost was estimated based on the following assumptions.

- System operates 12 hr/day autonomously
- Media regenerated per day = 600 lbs
- System Operates 5 days per week, 48 weeks per year
- Normal operation requires 1 hour per day of operating labor
- 80 hours of maintenance time allotted per year
- Loaded labor rate is $55 per hour
- Overhead is 50 percent of loaded labor
- Electricity Rate = $0.1/kWh

Capital depreciation is straight line over 15 years.

Table 31 summarize the annual costs for operating the unit and depreciation, and gives a cost of $0.48 per pound of reactivated media.

Table 31: Itemized Capital Cost for Integrated Biogas Upgrading System

Description	Quantity	Unit Cost	Cost
Microwave			
6kW Microwave Power Supply and Remote Magnetron	2	$25,000	$50,000
Slotted Waveguide Antennae	2	$800	$1,600
Mailbox Cavity Applicator	2	$400	$800
Reactor			
Quartz Tubes	4	$150	$600
Quartz/Stainless Steel Seal	3	$200	$600
Rotary Feeder	1	$1,200	$1,200
Variable Speed Rotary Feeder drive	1	$450	$450
Outlet Screen/ Tube connector Combo	1	$400	$400
Air Compressor	1	$300	$300
Flow Meter	4	$500	$2,000
Pressure Gauge	2	$200	$400
Condenser System			
1st Stage Condenser	1	$1,500	$1,500
40 gal. Stainless Steel Knockout Pot	1	$1,900	$1,900
Level Indicators	2	$400	$800
Pressure Transducers	2	$200	$400
Teflon Diaphragm Compressor	1	$2,300	$2,300
Thermocouples	7	$100	$700
Recirculating Chiller	1	$15,000	$15,000
Electrical			
Panel and Breakers	2	$4,000	$8,000
Main Disconnect	1	$1,000	$1,000
Conduit/Wire	1	$3,000	$3,000
Hoppers			
Adsorber	2	$5,000	$10,000
Feed	1	$1,200	$1,200
Product	1	$1,200	$1,200
Level Indicators	2	$400	$800

Table 31: Itemized Capital Cost for Integrated Biogas Upgrading System

Description	Quantity	Unit Cost	Cost
Valves	2	$1,300	$2,600
Pneumatic Conveying Piping	1	$2,000	$2,000
Vacuum Blower	1	$1,500	$1,500
Bag Filter	1	$400	$400
Structure			
Instrument Enclosure	1	$4,000	$4,000
Skid	1	$5,000	$5,000
PLC Controller (Includes motor starters and programming)	1	$15,000	$15,000
Total Equipment Cost			**$136,650**
Total Installed Cost			**$273,300**

Table 32: Annual O&M Cost Summary for an Integrated System

Maintenance Cost (5% of TDC)	$13,160
Labor cost	$17,600
Electricity Cost	$11,540
Overhead Expenses	$8,800
Depreciation	$18,220
Annual O&M Cost	**$51,100**
Total Annualized Cost	**$69,320**
Cost per pound of carbon	**$0.48**

If each pound of media treats about 1,000 SCF of biogas before regeneration, the cost to treat 1,000 SCF of biogas is $0.48. For a 1,000 SCFM biogas location and 90 percent utilization, this would result in an annual treatment cost of about $224,000. For an engine or microturbine running at 26 cu ft of biogas per kWh, treatment costs would be about $0.012 per kWh.

3.2.3 Replace the Flare on Existing Regenerating Siloxane Removal Systems

Some existing and proposed siloxane removal systems use alternating fixed beds of mixed media and regenerate the beds using hot air. The hot air is typically heated electrically. The contaminated hot air is mixed with supplemental biogas and sent to a flare to incinerate the contaminants. The parasitic losses to heat the bed and operate the flare can exceed 30 percent of

the total energy in the biogas system and the flare requires an air permit. The media is typically regenerated at about 15 percent of contaminant capacity to ensure high removal efficiencies.

Instead of sending the regenerated hot gasses to a flare, they could be routed through a microwave oxidation system to destroy the H_2S and the hydrocarbons. This could eliminate the cost of the flare installation and the use of biogas for supplemental flare fuel.

In this proposed system, the hot gasses from the regenerating bed are introduced into a condenser at about 40 deg. F. where condensable siloxane, hydrocarbons and water are removed. The remaining noncondensed gas flows through the microwave oxidizer to decompose remaining siloxane, hydrocarbons and H_2S. Solid silicon dioxide and sulfur iare removed in the process. The condensed siloxane and hydrocarbons can be separated from the water and decomposed in the microwave reactor but further field testing is necessary to determine the efficacy of the process.

A further improvement of this process would recycle the gasses from the outlet of the microwave reactor back through the regenerating bed to eliminate air emissions. Additionally, air could continue to recycle through the condenser to cool the regenerated bed for return to service.

The estimated cost of the microwave system is about equal to the cost of a flare system but the operating costs and emissions are significantly lower. A pilot system has been proposed with a commercial provider of siloxane removal systems as of the date of this report.

3.3 Technical Transfer Activities

3.3.1 Tours of the Field Demonstration at Carson Energy

The project team provided several tours of the operating system at Carson Energy in 2009. Visitors included staff from the California Energy Commission, California Integrated Waste Management, Sacramento Waste Water Treatment Plant and the San Jose Waste Water Treatment Plant. Additional tours were provided for visitors from SMUD, Technikon, Korea Electric Power Research Institute, Korea East-West Power Co. LTD, Anyang University, Lindh & Associates, and Synagro.

The attendees of the Pacific West Biomass Conference toured the field demonstration unit on display at Technikon, McClellan Field in January 2010.

3.3.2 Technical Presentations

A power point presentation was presented to staff of California Integrated Waste Management, the Sacramento Waste Water Treatment Plant and the San Jose Waste Water Treatment Plant on May 7, 2009

An abstract and power point presentation was submitted, accepted and presented at the Pacific West Biomass Conference, & Expo, Sacramento, January 11-13, 2010. A copy of the presentation is attached as Appendix F.

An abstract was submitted and accepted for a presentation at the Global Waste Management Symposium, scheduled for October, 2010.

A power point presentation was made to the Siloxane working group at the Solid Waste Association of North America (SWANA) conference, San Diego, March 2010. Subsequent individual presentations were made to several SWANA conference attendees.

Technical presentations were made to staff of SMUD, Caterpillar Solar Turbines, Black & Veatch, Venture Engineering, Lindh & Associates, DE Solutions, Calgon and Fortistar Methane Group.

3.4 Production Readiness Plan

AFT has 167 installations of biogas cleanup technology in the US and projects that biogas production will continue to be a growth market. Market drivers include energy security, increasing price for fossil fuels, environmental incentives for reducing greenhouse gas (methane) emissions, utility incentives for purchasing renewable energy, and increased use of efficient combined heat and power systems. Aging waste water treatment plants also need to be upgraded to current environmental regulations and to recover methane for site energy and heat. AFT has reviewed the market potential of the commercialized microwave technology for a regional carbon regeneration system, a mobile regeneration system and on site regeneration systems.

For a regional regeneration system, there is already competition from existing thermal regeneration systems for bulk carbon in the US. These are carefully regulated for transport and regeneration emissions based on the contaminants in the carbon. Single use carbon treatment is no longer the preferred technology for new biogas systems. Because of the lack of growth of new carbon systems, geographic distribution of biogas sites (transportation costs), and the uncertainty of age and contaminants in bulk media from multiple biogas sites, AFT believes that regional microwave regeneration sites for bulk media in the US would be difficult to commercialize.

Viability of a mobile microwave system is based on the proximity of clustered biogas production sites using regenerable media. The current mix of leased and owned systems and the different entities that control these systems would present difficulties to establishing efficient market clusters for a fleet of mobile regeneration system in the US. Emission controls would need to be permitted for multiple jurisdictions.

One application that AFT is exploring is using mobile adsorbers with regenerable media combined with either mobile or regional microwave regeneration. Mobile adsorbers allow several units to be stored onsite lowering frequency of regeneration per site and allow commercial transport of full loads of containerized media. Dedicated adsorbers also prevent cross contamination from different sites and allow tracking the age of the media. A microwave system of 200 to 500 lbs per hour capacity could regenerate all the mobile adsorbers in one or two days for most biogas sites. A regional microwave regeneration system could operate more than one shift to efficiently regenerate the media in the mobile adsorbers. The steps to

manufacture this system include defining a standard design of mobile adsorbers, and designing the microwave media handling system to efficiently remove, regenerate and replace the media in a mobile adsorber.

The current preference for most new biogas treatment systems 1,000 CFM and higher is onsite, thermal regenerable systems with in situ media (fixed bed). AFT, Parker Hannifin and Venture Engineering, three of the largest installers of biogas treatment systems in the US, offer thermally regenerated fixed beds for larger installations. For these systems thermal energy (usually electricity) is applied rapidly to the media bed and the flushed contaminants are sent to a flare supplemented with biogas to destroy the contaminants. Local air quality regulations preclude this flare system in California and other regions of the US. Preliminary estimates show that using a condenser and microwave oxidizing unit to remove flushed contaminants instead of the flare would be cost effective in the installation and operation and result in significantly less air emissions. All three installers have attended technical presentations of the microwave technology and have expressed different levels of interest. Several landfill and waste water treatment operators have also been briefed about this technology. The steps to commercialize and manufacture this system is to first install a pilot condenser and microwave system on an existing regenerable bed system parallel to the flare. Once the operational parameters of the microwave system are established, a full scale system can be designed and built for either an existing or proposed installation.

Each of the above mentioned installer has manufacturing capability. Technikon, the technology demonstration center at McClellan Field is a partner with CHA Corporation for commercialization of microwave technology and has identified several companies in Northern California that can manufacture commercial microwave systems. CHA is also a client of Gerling Applied Engineering, a Northern California designer and manufacturer of microwave systems.

Licenses and project funding would need to be in place before this technology is commercialized. CHA Corporation holds the US rights to the technology and would need to license the system for manufacture and use. CHA Corporation would also need to provide engineering support for design, manufacture, installation and personnel training.

CHAPTER 4:
Conclusions and Recommendations

4.1 Results Compared to Goals

1. **Biogas quality goals:**

   Maximum Siloxane concentration of 0.1 to 0.03 mg/m^3

   This goal is based on the recommended siloxane concentration for a turbine operating on biogas. We could not confirm this goal was met for two reasons; limitations of the test adsorber and variations of siloxane reporting for different laboratories.

   The initially proposed adsorber system was designed to operate at lower pressures and flow rates. However, the blower and pressure regulator could not achieve necessary pressure drop and flow. A new test adsorber was constructed to operate at plant pressure. The new test adsorber was smaller with higher flow rates to allow batches of media to be rapidly saturated with siloxane to evaluate multiple regeneration cycles. The flow rate of biogas in the test adsorber cannot replicate a commercial adsorber and is too high to achieve the stated goal.

   The laboratory reporting of siloxane at low concentration has been an unresolved issue. Three different laboratories were used during this project to try to achieve consistent siloxane removal results. Results from one lab in one test run indicated the goal was met. Results from other labs in the same and different test runs indicated the goal was not met. Some siloxane species at the adsorber outlet were reported at higher levels than in the inlet of the adsorber. The high cost and length of turnaround time to analyze samples precluded further investigation.

   The siloxane concentration of the biogas varied greatly over time, more than an order of magnitude. Since the inlet siloxane concentration affects the adsorber outlet concentration significantly, it was very difficult to compare the outlet siloxane concentration data obtained at different times.

   Maximum H_2S concentration of 10 ppm

   The H_2S in the biogas after treatment by the 50-50 media was measured at 20.3 ppm with an inlet concentration of 23.5 ppm. The 50-50 media is a poor adsorber of H_2S. However, when a second regenerable media of metal impregnated carbon was used after the 50-50 mix, the H_2S levels were reduced to below 10 ppm.

2. **Determine the best (economic and efficacy) combination of media to meet biogas quality goals.**

   A 50-50 mix of CTC 80 carbon pellets and HOX silica gel beads was determined to have excellent Siloxane and Hydrocarbon removal capacity and regeneration properties. Metal oxide impregnated carbon was determined to have excellent H_2S removal capacity and was regenerable in a microwave process by adding air and steam.

3. **Remove 99 percent of the siloxanes, H_2S and VOCs from the biogas with the best combination of media.**

   The 50-50 media removed 88 percent of Siloxanes and 14 percent of H_2S in the slip stream adsorber system. In a commercial system with longer contact time, this media is predicted to remove 99 percent of siloxanes. Combining the 50-50 media with a metal oxide impregnated media was demonstrated to remove 99 percent of H_2S in the biogas. The impregnated media is also regenerable with a microwave system.

4. **Remove 95 percent of the siloxanes, H_2S and VOCs from the media with microwave regeneration.**

   During laboratory trials the 50-50 mix was subjected to four cycles of D5 saturation and microwave regeneration. Average weight loss during regeneration was 91 percent of average weight gain during adsorption. During the field demonstration, the CTC number after the 5th regeneration of the 50-50 mix was 95 percent of new media.

5. **Determine the optimum, flow rate of media, sweep gas and microwave power level to achieve 95 percent removal rate of siloxanes, H_2S and VOCs from the media.**

   The above removal efficiencies were achieved using a media flow rate of 50 lbs per hour and 2.1-scfm nitrogen sweep through the regeneration reactors. The microwave reactor was operated at a 6 kW power level.

6. **Achieve 85 percent of adsorption capacity of new media after five cycles of regeneration with media used to treat the biogas.**

   The adsorption capacity of the media after five cycles of regeneration, as measured by the CTC number, was measured at 95 percent of new media.

7. **Achieve 95 percent oxidation efficiency for siloxanes, H_2S, and VOCs for the microwave-SiC oxidation reactor.**

   During regeneration, the siloxane concentration in the low volume sweep gas was 111.6 ppm. After treatment, siloxane concentration of the vent gas was 1.61 ppm for a removal (destruction) efficiency of 99 percent. Hydrocarbon removal was also estimated at 99 percent removal but could not be measured because of the number of species in the hydrocarbons. H_2S concentration from regeneration was 1,280 ppm and after treatment was measured at 20 ppm or 98 percent removal.

8. **Achieve SO_2 removal efficiency greater than 95 percent in the microwave reduction reactor.**

   No SO_2 was measured during or after microwave treatment. Any SO_2 produced was removed at 99 percent efficiency by GAC guard bed.

9. **Achieve removal rates of 95 percent for SiO_2 and elemental sulfur in the particle filters.**

Removal of at least 95 percent based on analysis of gasses was achieved. The weight of solids in the filters could not be accurately measured in the field. Captured material in the filter included entrained carbon particles and some solids remained in the carbon and silicon carbide beds.

10. **Determine if the operational reliability of the microwave regeneration process can meet a 70 percent availability factor.**

    The 6 hour test demonstrated that the process can operate at steady state for extended time periods.

11. **Document any mechanical and operational issues experienced during field testing of the microwave regeneration, oxidation, and carbon-SO_2 reactors that need to be addressed in the design of a full scale, automated system.**

    Equipment cooling was marginal for the demonstration system and needs to be improved. Carbon fines were generated during movement of material and plugged filters during the demonstration. Further automation is needed for a commercial unit. Careful selection of a lab for siloxane analysis will be needed to confirm operational efficacy.

12. **Identify any environmental and safety issues associated with commercial operation of microwave reactors for treatment of biogas.**

    No environmental or safety issues were identified.

13. **Demonstrate that the microwave regeneration process can treat and recycle media at about $.40 per pound.**

    A small integrated regeneration unit operating at 50/lb per hour of media would regenerate media for about $0.48 per pound.

14. **Demonstrate the capital cost and operational cost to install and operate an automated, full scale system at a landfill or digester site with power production would be about $.01 per kWh produced.**

    For a small stationary system treating biogas for an engine or microturbine running at 26 cu ft of biogas per kWh, treatment is calculated to cost $0.012 per Kwh.

15. **Clean about 64,000 scf of biogas that will replace about 40,000 scf of natural gas at the SMUD Carson Energy plant.**

    A single adsorber with a capacity of 75 lbs of media was used for the project. Flow rates through the adsorber were measured at 150 cfm. Each batch of media that was in the adsorber for 24 hours treated approximately 200,000 scf of biogas. Thirty two batches of media were placed in the adsorber and treated about 6,400,000 scf of biogas. This would replace 4,000,000 scf of natural gas.

16. **Determine the capital cost and operational cost to install and operate an automated, full scale system at an existing landfill or digester site to supplement existing media treatment. Express cost in terms of $/scfm gas treated and $/pound of contaminant removed.**

A small regeneration unit treating 50/lb per hour of media would cost about $0.48 per 1,000 cu ft of biogas or $0.48 per pound of media treated.

17. **Determine the capital cost and operational cost to install and operate a regional microwave treatment system to regenerate and service media at several new and existing landfill or digester sites. Express cost in terms of $/scfm gas treated, $/pound of contaminant removed and $/pound media treated and replaced.**

    A portable microwave regeneration system designed to treat multiple biogas sites and operating at 100 lbs per hour would cost about $0.72 per 1,000 cu ft of biogas or about $0.72 per pound of media treated.

4.2 Conclusions

Microwave laboratory and field testing results obtained from this project clearly demonstrated the effectiveness of microwave technology for upgrading biogas. Following conclusions were drawn from microwave testing data and observations.

- The biogas quality goals **of 0.1 to 0.03 mg/m^3** for siloxanes was not met for two reasons; limitations of the test adsorber and variations of siloxane reporting for different laboratories. The initially proposed adsorber system was designed to operate at lower pressures and flow rates. However, the blower and pressure regulator could not achieve necessary pressure drop and flow. A new test adsorber was constructed to operate at plant pressure. The new test adsorber was smaller with higher flow rates to allow batches of media to be rapidly saturated with siloxane to evaluate multiple regeneration cycles. The flow rate of biogas in the test adsorber cannot replicate a commercial adsorber and is too high to achieve the stated goal. The laboratory reporting of siloxane at low concentration has been an unresolved issue. Three different laboratories were used during this project to try to achieve consistent siloxane removal results. Results from one lab in one test run indicated the goal was met. Results from other labs in the same and different test runs indicated the goal was not met. Some siloxane species at the adsorber outlet were reported at higher levels than in the inlet of the adsorber. The high cost and length of turnaround time to analyze samples precluded further investigation.
- Microwave regeneration of the 50 percent CTC-80 GAC and 50 percent HOX media restored the fresh media adsorption capacity. CTC numbers of regenerated media ranged from 38 to 50 for eight cycles of the adsorption and microwave regeneration, which were very close to fresh media CTC number of 40.
- The media consisting of 50 percent CTC-80 GAC and 50 percent HOX removed siloxanes and H_2S from biogas much better than GAC alone. The initial breakthrough time of D5 siloxane was ten times longer for this media than CTC-70 GAC.
- The siloxane initial breakthrough time for media in the test adsorber was estimated to be 24 hours during the field testing at Carson Energy. After four cycles of adsorption and microwave regeneration, regenerated media demonstrated consistent siloxane removal

capacity. However, consistent siloxane removal efficiency could not be validated due to system design and significant variations in lab reports at low siloxane concentrations.

- Microwave regeneration of the media consisting of 50 percent CTC-80 GAC and 50 percent HOX restored the fresh media adsorption capacity. CTC numbers of regenerated media ranged from 38 to 50 for eight cycles of the adsorption and microwave regeneration, which were very close to fresh media CTC number of 40. Repeatable CTC numbers of regenerated media were obtained during microwave regeneration field testing.
- Microwave regeneration of GAC saturated with biogas did not restore the adsorption capacity of fresh GAC. The initial breakthrough time of D5 siloxane was much longer for HOX than both CTC-70 and CTC-80 GACs. The D5 initial breakthrough time remained constant at about 400 minutes for the CTC-80 GAC and HOX mix for 4 cycles.
- H_2S was converted into hydrogen and elemental sulfur in a carbon bed by microwaves. The conversion efficiency increased with microwave power, reached 85 percent at 600-W, and decreased with additional microwave power input. Adding oxygen into the microwave reactor increased the H_2S destruction efficiency significantly.
- With one second gas residence time and 6-kW microwave power siloxanes and H_2S desorbed from media were completely destroyed by microwaves. Consequently, we can replace the microwave oxidizer by the GAC reactor to destroy siloxanes and H_2S in the desorbed gas and recycle cleaned desorbed gas to biogas stream.
- More than 93 percent of non-condensable hydrocarbon gases were oxidized in the microwave catalytic oxidizer and exhaust gas from the final GAC guard bed contained only 1 percent of non-condensable hydrocarbons.
- Liquid recovered during microwave regeneration was about 5-10 percent of media and 70 percent of recovered liquid was hydrocarbons.
- The CTC number of regenerated media varied from 36 to 45 as the regeneration rate varied from 40 to 80-lb/hr. The regeneration rate range from 60 to 100-lb/hr produced the CTC numbers close to the fresh media CTC number of 40.
- The H_2S broke through the GAC bed within ten minutes but was adsorbed in the GAC bed continuously. The final adsorption capacity of H_2S was about 10 percent by weight.
- Estimated cost of regenerated media was lower than one third of fresh media, indicating that the microwave regeneration is better choice than conventional thermal regeneration.
- Analyzing and reporting siloxane at low concentrations varied greatly between laboratories and sampling methods. Sample cost and analysis time were further limitations to accurately measuring performance during siloxane removal and regeneration operations.

4.3 Recommendations

HOX is a silica-based inorganic adsorbent and has very high adsorption capacity for water and siloxanes. Also, HOX cost is almost one-half of GAC cost. However, HOX does not absorb microwave energy. The media used for the field testing consisted of 50 percent HOX and 50 percent CTC-80 GAC to use microwaves for regeneration. We have not tested various ratios of HOX and CTC-80 GAC. Because of low cost and high siloxane adsorption capacity, we need to find the media consisting of the maximum amount of HOX that still can be regenerated by microwaves efficiently. Therefore, we highly recommend the laboratory and field-testing of adsorption and microwave regeneration using media containing various ratios of HOX and GAC. Results obtained from this study may lead to develop two-fixed bed adsorber systems that are equipped with microwave system to allow the regeneration of media in place. This study can be completed within one year with $300,000.

Results obtained from 6-hr microwave regeneration test suggest that biogas can be upgraded by microwaves directly. This direct microwave upgrading reduces biogas upgrading cost significantly if cheaper microwave supply system is used. We would like to recommend the destruction of siloxanes and H_2S in the GAC bed by microwaves using simulated biogas and pilot-scale reactor in the laboratory first and then tested with real biogas at Carson Energy or landfill site. One-year laboratory study requires about $200,000 and 6-month field testing requires $250,000.

Preparing pipeline quality biogas will require a complete removal of H_2S. Because of limited project funds we have not investigated to find the most economical method to remove and destroy H_2S from biogas. We would like to recommend laboratory and field testing project to find and demonstrate a practical method that can remove H_2S from biogas economically. This project may require two-year study with $500,000.

Because of limited project funding, we have not performed a complete economic feasibility study of using microwave regeneration technology for upgrading site-specific biogas. Because of potential technical and economic advantages of microwave technology, we would like to recommend a detailed economic feasibility study for using microwave methods that will be used for upgrading biogas specifically for dairy farms or landfills or wastewater treatment facilities.

Existing commercial thermal regeneration bed systems require a flare to destroy VOC's, siloxane and H_2S from the regeneration step. The microwave oxidizer could be configured to replace the flare and significantly reduce air emissions from media regeneration. A pilot project to install the microwave oxidizer unit on an existing siloxane removal system with a flare may require one year and $500,000.

4.4 Benefits for California

4.4.1 Reduction of Green House Gas emissions

There are over 2,100 dairies in California with a potential to produce about 40 million cubic feet per day (ft^3/day) of biogas with a potential generation capacity of about 136-140 MW. Assuming 50 percent biogas methane content, this represents a potential reduction of approximately 20 million ft^3/day of methane. The scope of this project was focused on removing siloxanes and H_2S from biogas produced from wastewater treatment facilities but the field testing results are applicable to other biogas systems produced from landfill sites, dairy farms, and food digesters. The undeveloped potential generation capacity at California landfills, wastewater digesters, and food digesters is estimated at 600 MW which represents about 85 million ft^3/day of methane. With this microwave biogas upgrading technology, additional biogas can be utilized to produce electricity and thermal energy to reduce natural gas use in California. Otherwise, the methane will be released to the atmosphere from manures digesters and landfills or flared.

This technology also has the potential to reduce greenhouse gas emissions attributed to the manufacture and use of carbon in many biogas siloxane removal systems. Single use activated carbon is used as the media to remove siloxanes and other contaminants. Carbon is changed out of commercial adsorbers every one to six months. This activated carbon is produced from coal that is first heated to a high temperature to remove VOCs then treated with steam and pressure to activate the pore structure. This process releases significant fossil fuel CO_2 for producing the heat energy needed. The bulk activated carbon must be transported, first from coal mine (typically Asia) to the biogas site, then from the biogas site to the disposal site releasing additional CO_2 from the transport fuel. If the contaminated carbon is disposed by burning (such as in a biomass plant), all the carbon is released as CO_2 to the atmosphere as the carbon is combusted. If the 50-50 media used in the microwave process is regenerated only 10 times before disposal, it will reduce greenhouse gas emissions due to production, transport and disposal of media by at least 90 percent. As a point of reference, Carson Energy uses at least 54,000 pounds of one time use activated carbon annually to remove siloxane from about 1,200 CFM of biogas.

4.4.2 Reduction of Criteria Air Emissions

In one design of a commercialized system, siloxanes and H_2S in the desorbed gas from saturated media can be destroyed in the microwave GAC reactor and remaining hydrocarbon gases can be recycled to the biogas. Then, the microwave oxidizer will be replaced by the microwave GAC reactor, eliminating all air emission attributed to siloxane removal. This revised microwave upgrading technology will be a totally contained system and will not have any air emissions. A part of the cleaned biogas will be used as sweep gas for microwave regeneration and cleaned desorbed gas will return to biogas stream.

Existing commercial thermal regeneration systems require a flare to destroy VOC's, siloxane and H_2S from the regeneration step. The microwave oxidizer could be configured to replace the flare and significantly reduce criteria air emissions from media regeneration. This would have a

significant impact in California where air emission regulations typically preclude the use of uncontrolled flares.

Sulfur in the biogas precludes all commercially available post combustion control using catalyst without reliable and robust H_2S removal. Removing H_2S and siloxanes from biogas will provide a new technology to significantly reduce VOCs and SOx emissions from biogas engines to meet the CARB 2007 emission standards and may enable the use of traditional and new post combustion control technologies.

4.4.3 Creation of Green Jobs

A successful commercialization of microwave biogas upgrading technology will enhance the biogas production from landfills, wastewater treatment facilities, dairy farms, and food processing industries. The microwave technology is expected to reduce the cost of upgrading biogas significantly, increasing the use of biogas for power and fuel production from small biogas sources such as dairy farms and food processing facilities.

The undeveloped potential generation capacity at California landfills, wastewater digesters, and food digesters is estimated at 600 MW. With simpler and cheaper microwave biogas upgrading systems, additional biogas can be utilized to produce electricity and thermal energy to reduce natural gas use in California.

The CHA Corporation has relocated to California in 2010. They are in a position to manufacture simpler and cheaper microwave units to be used for upgrading biogas from small sources. The CHA Corporation sources microwave equipment from Gerling Applied Engineering of Modesto, another California company. As more systems are installed in California, additional service positions will be required to operate and maintain these systems. Successful commercialization of this technology will create California green jobs and reduce state unemployment.

GLOSSARY

AFT	Applied Filter Technology
BACT	Best Available Control Technology
CARB	California Air Resources Board
Cal/OSHA	California Occupational Safety and Health Act
CEC	California Energy Commission
CHA	CHA Corporation
CTC	Carbon Tetrachloride
DREs	Destruction Removal Efficiencies
EPA	Environmental Protection Agency
FTO	Flameless Thermal Oxidizer
GAC	Granular Activated Carbon
HAPs	Hazardous Air Pollutants
HASP	Health and Safety Plan
NETTS	National Environmental Technology Test Site
NIEHS	National Institute of Environmental Health Sciences
NOx	Nitrogen Oxides
OU	Operable Unit
OSHA	Occupational Safety and Health Act
PIER	Public Interest Energy Research
PPE	Personal Protective Equipment
ppm	Part per million
scfm	Standard Cubic Feet per Minute
SWWTP	Sacramento Waste Water Treatment Plant
SMUD	Sacramento Municipal Utility District
THC	Total Hydrocarbon
TFDP	Technology Field Demonstration Plan
VOCs	Volatile Organic Compound