Final Report

Project Title:	Novel Sorbent to Clean Up Biogas for CHPs
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Novel Sorbent to Clean Up Biogas for CHPs

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1. Executive Summary

In this project, TDA Research Inc. (TDA) has developed low-cost (on a per unit volume of gas processed basis), high-capacity expendable sorbents that can remove both the H_2S and organic sulfur species in biogas to the ppb levels. The proposed sorbents will operate downstream of a bulk desulfurization system as a polishing bed to provide an essentially sulfur-free gas to a fuel cell (or any other application that needs a completely sulfur-free feed). Our sorbents use a highly dispersed mixed metal oxides active phase with desired modifiers prepared over on a mesoporous support. The support structure allows the large organic sulfur compounds (such as the diethyl sulfide and dipropyl sulfide phases with a large kinetic diameter) to enter the sorbent pores so that they can be adsorbed and removed from the gas stream.

The new SulfaTrap™ sorbents are capable of removing all sulfur compounds from digester gas, and compared to commercial/conventional sorbents our sorbents have a very high capacity. These sorbents were developed to reduce the total sulfur concentration in the biogas to below the maximum allowable level for fuel cells (typically <30 ppb) and are intended to replace existing sulfur sorbent technologies that suffer from low capacity. They were designed primarily for use as polishing systems which take the effluent from bulk desulfurizers and further reduce the sulfur concentration to an acceptable (very low ppb) level.

In this DOE funded project, testing was performed on three SulfaTrap™ sorbents: SulfaTrap™-R2B, SulfaTrap™-R5D and Sulfatrap™-R8. The SulfaTrap™-R8 media was designed for general sulfur removal, including H_2S and mercaptans. The SulfaTrap™-R2B sorbent was designed for removal of dimethyl sulfide (DMS) but is also effective for other sulfur species except carbonyl sulfide (COS). However, this sorbent is generally not recommended for general sulfur removal as it is much more expensive than the SulfaTrap™-R8 sorbent. The final sorbent developed and tested was SulfaTrap-R5D, which exhibited a very high capacity for COS, even in the presence of high concentrations of moisture.

The new sulfur sorbents developed by TDA during the course of this project have been first tested in the laboratory both ar TDA and FuelCell Energy (FCE), and at the pilot scale to demonstrate their performance for anaerobic digester gas (ADG) fueled fuel cell applications. The tests at FCE were conducted in a vessel with low bed aspect ratios (L/Ds of 1.3 and 2.6) than the recommended L/D of 4: as a result the pre-breakthrough loadings in the tests at FCE were lower than the tests at TDA that were carried out with a L/D of 4 or higher.

Once the sorbent development and bench-top testing were completed, TDA built a fully automated test skid to support the slipstream tests. This unit was designed to house 3 reactors: one 10L vessel to hold the bulk desulfurization sorbent, followed by two 1.3 L polishing reactors that ran in parallel so that two different sorbents could be tested at the same time. We carried out two slipstream demonstrations at the Eastern Municipal Water District (EMWD) and one at the Tulare waste water treatment plant. In these tests, we demonstrated the ability of the sorbents to remove the sulfur compounds and siloxanes, with both very high capacity and removal efficiency. FCE coordinated the installation of TDA's slipstream test units at the EMWD in Moreno Valley, California and the Tulare Wastewater treatment plant in City of Tulare, CA. In these field tests, both SulfaTrap^{TM}-R8 and SulfaTrap^{TM}-R7 were tested successfully, and they provided complete removal of all the sulfur compounds and the sorbents achieved high capacities. SulfaTrap^{TM}-R8 adsorbed over 4% wt. sulfur during the slipstream tests while the capacity of the SulfaTrap^{TM}-R7 was high enough that we never reached breakthrough during these small scale tests (the loading had reached 9.8% wt. sulfur before the test was stopped).

Next, TDA and FCE completed the design and fabrication of a full scale prototype desulfurization skid suitable for a DFC300 (300 kW) power plant, and shipped the unit to the Sacramento South Area Transfer Station (SATS) for testing. The system design used a lead/lag configuration, so that we could change-out the sorbent without interrupting the operation of the unit. Each of the beds was 12 cu ft. in volume and was designed for three months of operation. We compared several designs including the FCE standard sorbent vessel design and a custom design made from standard piping components. We then rated each of the designs against the following criteria: cost, prevention of sulfur breakthrough and meet the TDA recommended L/D ratio. The design that scored the highest used custom vessels in a lead/lag configuration.

Three SulfaTrap™ sorbents, SulfaTrap™-R2B, SulfaTrap™-R5D and SulfaTrap™-R8 were used in the prototype system, which was designed to clean up the ADG so that it met the feed specifications provided by FCE. Each lead/lag stage consisted of an R8 vessel and an R2/R5 vessel. The R8 vessel was positioned upstream of the R2/R5 vessel for removal of H_2S and mercaptans, allowing the SulfaTrap™-R2 and SulfaTrap™-R5 sorbents to be conserved for adsorption of DMS and COS, respectively.

The prototype vessels were constructed from commercially available 304SS piping components, with the exception of the top flange on the R2/R5 vessel. This vessel required a custom flange due to the presence of an internal divider which created two internal sections. The two sections included an annular area where the SulfaTrap™-R2B sorbent was loaded and a center tube for the SulfaTrap™-R5D sorbent. Flow enters through the inlet port on the side of the vessel, flows down through the annular area, up through the center tube and exits through the top of the vessel. The vessels were covered with Reflectix duct insulation to reduce the effect of solar heat on the performance of the sorbent. Bed temperature has a large effect on the breakthrough capacity of the SulfaTrap™ sorbents (as with any physical adsorbent), and temperatures over 40^0C result in a rapidly declining sulfur capacity. The duct insulation provides a reflective surface to maintain internal bed temperatures below 40^0C.

The prototype desulfurization system is designed to process 82 SCFM of ADG at an inlet pressure of 30-40 psig with the ADG exit pressure at 15 psig to meet the DFC300 fuel pressure requirement. The system is loaded with one year's worth of sorbent (6 months per stage) and the design allows sorbent replacement while the unit is in operation. Valves are located throughout the system for diverting flow and switching the order of the lead/lag stages. The skid is also equipped with purge connections for each stage to allow for purging after sorbent replacement. The base supporting the prototype system is made from painted carbon steel and the rest of the prototype system is made of 304SS.

A process hazard analysis was conducted before we shipped the prototype unit to the SATS facility for testing. The hazard analysis led us to add a gas sensor, an emergency-stop button, an automatic shut-off valve and status lights to the system. The gas sensor is interlocked to the automatic shut-off valve to isolate the system in the event of a gas leak. The e-stop button allows for shutting the system down in the event of a potential hazard. The status lights provide indication of normal operation, warning and shut down conditions.

The prototype system was installed at the SATS. The prototype desulfurization system was connected to the existing gas conditioning skid that was already in place at SATS. A section of piping was replaced with a new piece that included valves to divert flow to and from the prototype desulfurization system. Only one stage of the system was filled with sorbent for this demonstration. Unfortunately, the prototype system was never tested because SATS discovered leaks in their large digester tanks, and therefore no gas was available for us to feed into our unit. Several attempts were made to repair the tanks, but the leaks in the digester tanks were never fixed.

We assessed the techno-economic feasibility of using SulfaTrap™ sorbents in FuelCell Energy's commercial DFC power plants. We calculated the annual sorbent replacement cost for total sulfur control (including bulk sulfur and siloxane). We calculated the annual sorbent replacement cost when using TDA's SulfaTrap^{TM} sorbents as $36,470/year for 300 kW$_e$ net power generation, when using our sorbents for both bulk and polishing removal. This is about 12.2% of the value of the electricity generated from biogas (300 kW at $0.12/kWh and 95% time on stream). When using TDA's SulfaTrap^{TM} sorbents just for polishing sulfur/siloxane left in the ADG after bulk desulfurization, we calculated the annual sorbent replacement cost to be $9,960; this is only about 3.3% of the value of electricity generated from the biogas (300 kW at $0.12/kWh and 95% time on stream).

The cost of the sorbents currently used in ADG sulfur polishing systems is $48 per cubic foot of media, but the more useful cost comparison is on a per volume of gas treated basis (at breakthrough). For polishing application, the cost of sulfur removal with the current commercial sorbent is $886/MMSCF of ADG processed, while the cost for using the SulfaTrap™ sorbents is only $145.7/MMSCF; thus using SulfaTrap sorbents in the polishing role cuts the cost of polishing by 83% (cuts the cost by a factor of six). For complete desulfurization (including bulk sulfur removal) the cost of desulfurization using SulfaTrap^{TM} media as both bulk desulfurization and polishing sorbent is $533.6/MMSCF. Thus, SulfaTrap^{TM} sorbents can remove both bulk and trace sulfur for only 60% of the cost of polishing alone with the current commercial sorbents.

While we successfully completed the slipstream testing and demonstrated the technical viability of the technology, the operating data from the full scale prototype demonstration was not complete. Hence, in the future work, we recommend that a test of the full-scale prototype be run at another site.

2. Introduction

Industrial processes generate by-products containing more than 2 quadtrillion Btu of energy per year. This energy is either not used at all or is used in old and inefficient processes. Better use of these under-utilized streams could replace significant amounts of natural gas, thereby reducing the U.S. dependence on foreign energy resources and significantly reducing emissions of carbon dioxide (CO_2), a potent greenhouse gas.

The opportunity fuels can take variety of forms (e.g., crop residues, farm waste, municipal solid waste, food processing wastes, sludge waste and wood waste), but all are derived from carbon based materials contained in living organisms. All these fuels can be processed and combusted in a boiler/steam turbine combination to generate combined heat and power (CHP). These wastes could also be converted into biogas in an anaerobic digester or biomass gasifier and then be used to generate process steam or to fire a prime mover. The relatively small, distributed CHP systems present a realistic, neat-term solution for large energy efficiency improvements and significant reduction in CO_2 emissions. While CHP systems has been used in large applications (greater than 20 MW), the smaller-scale applications between 0.5 to 5 MW range have not been fully exploited, largely due to the lack of cost-effective options in this size range. The scalability of these units to small size is important since most of the biomass-based CHP applications are expected to be highly distributed (even for higher energy types of biomass such as wood, the economic transportation distance is only on the order of 50 miles).

Unlike combustion engines, the fuel cells operate with very high efficiency even at small scale, offering significant benefits to the distributed CHP systems utilizing bio-waste. Among the various kinds of fuel cells, Molten Carbonate Fuel Cells (MCFCs) are uniquely suited to use the anaerobic digester gas produced from opportunity fuels (by-products of food processing facilities, wastewater treatment plants etc.). Several demonstrations with the biogases generated by the food and beverage plants showed that the MCFCs operate as well on digester gas as they do on natural gas. Direct FuelCell® (DFC®) power plants developed by FuelCell Energy (FCE) also showed that these plants can be co-fired with natural gas (i.e., fuel blending). Thus, when the digester gas production volume is variable, blending provides feedstock flexibility, which means that the fuel can be fully utilized at all times (which is important in paying back the initial investment). The fuel cell power plants also harvest waste heat, which can be used to produce steam for hot water and other heating needs. The overall energy efficiency of the MCFC CHP installations is at least twice that of grid-supplied power, with the thermal efficiency often exceeding 80%.

Because most food and beverage processing plants require 5 MW or less of power, fuel cell power plants can meet most, if not all, of the power requirements at these facilities. In 2010, 19 DFC®-based CHP facilities are in place running on anaerobic digester gas (ADG) produced from food waste and wastewater (plant sizes varies from 300kW to 1.5MW), representing the largest installed fuel cell-based waste-to-energy capacity.

In addition to CO_2 and CH_4, the biogas generated in the digesters and fermentation units contains various contaminants that must be removed to prevent degradation of the plant performance. These gases contain relatively large concentrations of sulfur compounds (up to 1.5% vol.), which is a highly potent poison for the anode electro-catalyst and is known to corrode fuel cell components (e.g., interconnects) and all other process equipment. Several studies showed that as little as 0.4 ppmv of sulfur in the feed gas could reduce the fuel cell performance by more than 20% to 30%, and higher sulfur concentrations lead to permanent failure (Israelson, 2003). The most common sulfur species in the biogas is hydrogen sulfide (H_2S), but biogas also contains a variety of organic sulfur species as well, including dimethyl sulfide (Me_2S), dimethyl disulfide (Me_2S_2), methanethiol (MeSH), carbon disulfide (CS_2) and carbonyl sulfide (COS). In addition to these, test data and field measurements indicate the presence of traces of even higher sulfide compounds such as dipropyl disulfide (Me_6S_2) and diethyl disulfide (Me_4S_2). Depending on the biomass feedstock and digester design, the concentration of these higher sulfide species ranges from 0.1 ppmv to as high as 30 ppmv.

In the conventional approach, the biogas can be desulfurized by a number of physical, biological and chemical processes. Because it is difficult to reduce the sulfur content from the percent range to ppb range, a two-step cleaning process is usually followed (e.g., a biological or chemical process for rough gas cleaning and adsorption for sulfur polishing). It is important to note that all the existing bulk desulfurization process are designed to remove H_2S, and do very little to remove the organic sulfur compounds, particularly the disulfides.

In this project, TDA Research Inc. (TDA) has developed a low-cost, high-capacity expendable sorbent that can remove both H_2S and organic sulfur species in biogas to the ppb levels. This sorbent bed operates downstream of bulk desulfurization system (as a polishing bed) to provide an essentially sulfur-free gas to the fuel cell. Our sorbent uses a highly dispersed active phase with modifiers to remove the sulfur species. The active adsorptive phase is highly dispersed on a mesoporous support so that it can remove large organic sulfur compounds, including the diethyl and dipropyl sulfides.

3. Project Objectives

The overall objective of this project was to will develop a new, high capacity, expendable sorbent, and to test it in collaboration with FCE to remove sulfur species from ADG, thereby providing an essentially sulfur-free biogas that meets the cleanliness requirements of DFC® power plants. This sorbent bed will operate downstream of a bulk desulfurization system (as a polishing bed) and remove any residual H_2S and all other organic sulfur species from the biogas. This will be an enabling technology for the small-scale fuel cell-based CHP systems that allows them to operate on biogas feedstocks as an alternative to natural gas. A successful sorbent – one that achieves a high sulfur capacity and removal efficiency – reduces the operating costs associated with sorbent replacement and the labor burden required for the change outs. It will minimize waste and hence the disposal costs. These benefits will increase the cost effectiveness of the overall process, and enable the use of biogas produced from bio-waste to be utilized in the MCFC-based CHPs.

TDA had previously identified an effective sorbent for the intended application and showed the high performance of the sorbent in bench-scale experiments using simulated biogas. Our objective in this project was to demonstrate the technical and economic viability of the novel sorbent in field demonstrations integrated with the fuel cell using actual biogas in support of commercializing the new biogas desulfurization technology. To meet this goal the specific objectives of this project are:

- **Sorbent Optimization:** Optimize the key features of the sorbent, such as the concentration of the active material content, the source of the active material precursor, the amount and type of binders, calcination temperature and duration to enhance sorbent performance.

- **Scale-up of Sorbent Production:** Increase the batch size of the preparations from 100 mL to 1 ft^3. This enables us to provide the amounts of sorbent needed to support relatively large field demonstrations. We will manufacture the sorbent using high throughput equipment to ensure that future increases in production capacity are easily achievable.

- **Sorbent Performance Verification:** Bench-scale verification of TDA's sorbent performance using simulated biogas.

- **Slipstream Demonstrations:** Perform field demonstrations using a relatively small (1ft^3) sorbent bed using a slipstream of biogas from FCE's ADG-fed power plants.

- **Large-scale Demonstration:** Carry out a large-scale demonstration using enough sorbent to desulfurize all the biogas in a DFC® 300kW plant.

- **Cost Analysis:** Perform a detailed engineering analysis to assess the economic viability of the new sorbent technology based on the field demonstration results. The sorbent performance, cost and benefits will be compared to the commercially available and competing systems.

3.1 Work Plan

The proposed R&D effort was divided into six technical tasks (2 through 7) and Task 1, the project management task that ran the entire duration of the project, In Task 1, we provided quarterly progress reports, and project spending and schedule updates. In Task 2 TDA optimized the sorbent composition and production methodology and scaled-up the sorbent production using scalable production equipment to prepare a large batch of sorbent for evaluation in the field demonstrations. In Task 3, we evaluated the sorbent at bench-scale under representative operating conditions. In Task 4, we carried out an independent verification of TDA's sorbent performance at FCE facility using simulated biogas. In Task 5, we performed three field demonstrations using a relatively small (1ft^3) sorbent bed using a slipstream of biogas from one of FCE's ADG-fed power plants. In Task 6, we built and installed a prototype unit to carry out a large-scale demonstration using prototype desulfurizer with enough sorbent to desulfurize all the biogas in a 300kW plant. In Task 7, we carried out a detailed engineering and cost analysis to assess the economic viability of the new sorbent technology based on the field demonstration results and a Stage 4 plan will be developed commercialize the technology. A final report will be submitted that details the results from the project.

4. Results

4.1 Task 2. Sorbent Optimization and Scale-up

4.1.1 Task 2.1 Sorbent Optimization

We prepared various sorbent formulations using different active phases and supports and tested them under simulated biogas in the presence of H_2S, ethyl mercaptan (EM) and ethyl disulfide (EDS). These sorbent screening experiments were carried out in an automated test setup capable of running fixed bed adsorption breakthrough experiments. We identified the optimal support and active phase using the results from bench-scale evaluation for the various sulfur compounds. We also measured and characterized the physical properties for the sorbents prepared. Table 1 shows the summary of the physical properties for the supports used in this optimization work. The results from the sorbent optimization task are summarized under the Task 3. Sorbent Screening.

Table 1. Summary of the physical properties for the supports used.

Support	Surface Area (m^2/g)	Micropore volume (cc/g)	Total pore volume (cc/g)	Pore Size (Å)	Strength (lbf/mm)
I	1023	0.27	0.56	23	1.2
II	775	0.27	0.54	44	1.5

4.1.2 Task 2.2 Sorbent Production Scale-up

TDA's biogas desulfurization sorbents at the start of the project were being prepared and calcined in small batches (in lab equipment, beakers and flasks). During the course of the project we scaled up the production of our biogas desulfurization (polishing) sorbent SulfaTrap^{TM}-R8. We increased the preparation batch size to 4 L per batch for the step where we impregnate our sorbent support with active materials. This is done by using large mixers with just enough solution of the active material to fill up the sorbent pores. The support is dropped into the solution, and then the jars containing the sorbent and solution are capped and rolled in a roller cabinet (Figure 1). Then sorbent material is accumulated and dried in a rotary furnace at 35 L batch size (Figure 2). Following these procedures we prepared SulfaTrap^{TM}-R8 on two different supports, at this 1 cu ft. activation batch size, one having smaller pores and another having larger pores.

Figure 1. Roller cabinet (mixer).

Figure 2. Rotary furnace for 1 cu ft. batch size.

TDA has also installed a continuous rotary calciner (kiln) that enables us to prepare the biogas sorbent in 6 cubic feet batch size. The Bartlett and Snow continuous rotary kiln shown in Figure 6 is electrically heated and has a 7" Inconel tube that can be heated up to 1100°C. After the sorbent is impregnated with active phases it is fed into the kiln using a single screw feeder, as shown in Figure 7. It has a computer control system using Labview software. It has all the safety features needed to operate in safely and an afterburner to process the off gases in an environmentally sound manner.

Based on our prior experience in scaling up the production of our natural gas sorbent to multi ton per year scale and also the availability of rotary calciner for calcination of the sorbent, we decided on an optimized batch size of 6 cubic feet for the large scale sorbent preparation (large-scale demonstrations) and 1 cubic feet batch size for the intermediate batches for the slipstream demonstrations.

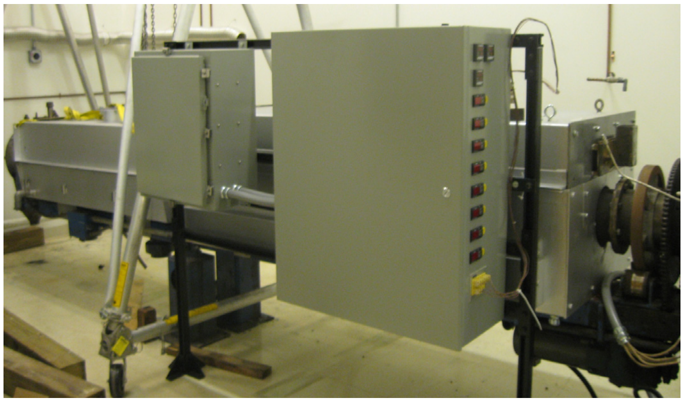

Figure 3. TDA's 7" continuous rotary kiln.

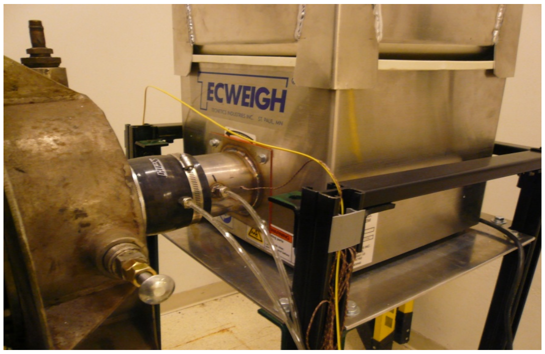

Figure 4. Screw feeder for rotary kiln.

4.2 Task 3. Sorbent Screening

We carried out bench-scale tests to screen the sorbent formulations prepared in the sorbent optimization and scale-up task (Task 2), measuring their sulfur removal capacity using simulated ADG streams.

__Sorbent Testing Apparatus:__ The removal efficiency of the refractory sulfur compounds were measured in an existing automated testing apparatus (Figure 5). The reactor cell consisted of a 2.5 cm Silico Steel tube (Restek Corporation) containing a frit at its mid-point to support pellets (1/8”-1/32” diameter pellets). A Mellen furnace surrounding the reactor is used to control the temperature. The gases were introduced into the system through electronic mass flow controllers. A sparger was used to introduce moisture into the gas stream. The sorbent regeneration were carried out using either methane or other reducing or inert gas stream such as nitrogen or steam; we will test air as well. After mixing in a manifold, the mixture passes through a sparger where the stream is humidified (if desired). A valve system allows the feed gases to bypass the reactor and flow directly to the analytical system for accurate measurement of the feed gas composition. The apparatus is fully automated and can run without an operator for long periods of time including overnight. We use Control EG software to monitor test conditions, log data and safely shut down the apparatus in case of a malfunction.

Analysis of the sulfur compounds was carried out using a gas chromatograph. This increases the sampling frequency and offers a better way of monitoring the breakthrough of the sulfur components, a process transient in nature. These GCs are equipped with a Flame Ionization Detector (FID), a Flame Photo Ionization Detector (FPD) and a 30-meter Alltech AT-1 column for sulfur and hydrocarbon analysis. The sulfur detection limit of the FPD detectors used for part of the testing is 0.1 ppmv. TDA has also has a chemiluminescence detector (Siever Instruments Model 900) with sulfur detection capability of 5 ppbv, was also used to ensure high removal efficiency over selected sorbents.

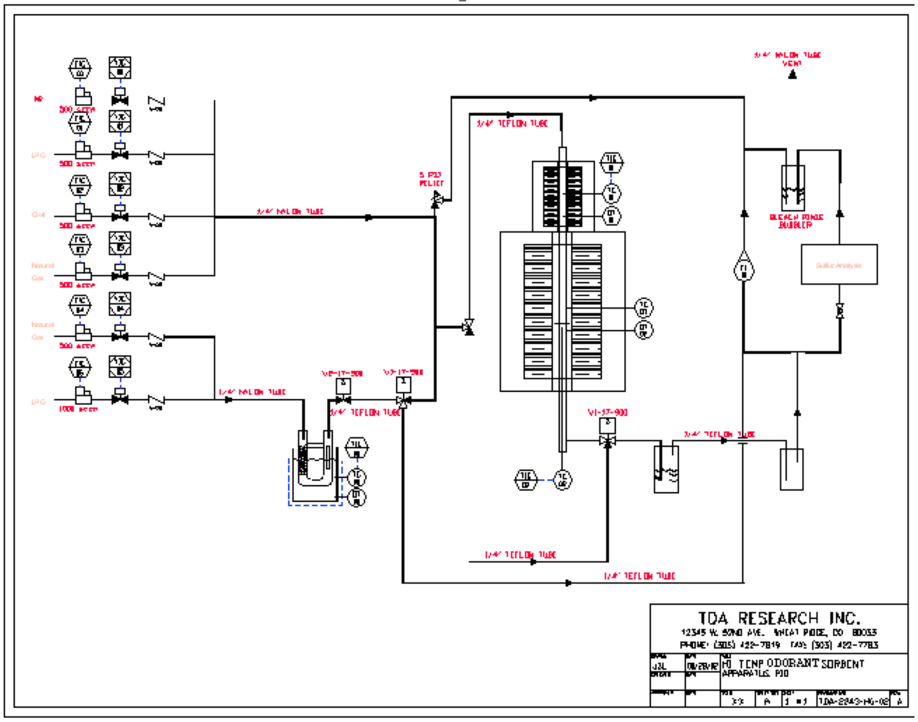

Figure 5. P&ID of the test unit.

After exiting the analytical system, the effluent gas stream was sparged into an absorber solution to prevent any release of sulfur into the environment.

Siloxane Removal: We modified an existing test apparatus so that it could carry out screening experiments for simultaneous siloxane removal from biogas so that the breakthrough of both sulfur and siloxane species in the biogas can be monitored. The description of the methods followed for Siloxane generation and detection are explained below:

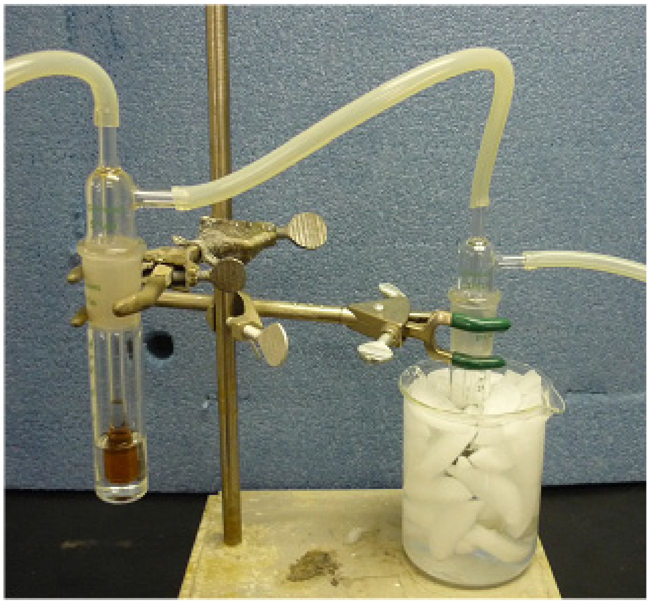
Figure 6. Impinger Apparatus.

Instrumentation: Siloxane and sulfur concentrations were determined by gas chromatography (GC). Initial siloxane generation analysis was determined via GC with a mass selective detector (MSD). Once the approximate generation rates were determined, the results were confirmed by GC with a flame ionization detector (FID). Proper compound elution was insured by installing a capillary GC column that would elute the siloxane species with the necessary separation for detection.

Sulfur detection was carried out with GC equipped with a flame photometric detector (FPD) instead of an FID. The FPD is a selective detector that will respond only to compounds containing sulfur atoms. However the FPD signal is subject to quenching in the presence of high concentration non-sulfur containing compounds. To minimize this effect, we ensured that the sulfur compounds and siloxanes elute at individual time by using a capillary column with a thicker retentive phase on each detector (a Restek RTX-1® (30m length, 0.53 mm ID) with a 7.0 micron film thickness was used). Compared to the same column with a 1.0 micron film thickness, the co-elution, quenching effect of CH_4, CO_2, and siloxane species on the FPD was minimized.

The GC we used to analyze the biogas stream composition contains both an FID and FPD. Each has a separate capillary column attached to a stream selecting valve that sends a 1.0 mL sample to the individual detectors. Each GC was calibrated with siloxane solutions prepared at varying concentrations in methanol (MeOH). A calibration curve was prepared for each siloxane species and used to determine the compound concentrations under various conditions.

Siloxane Generation: There are several methods for generating a gas stream containing siloxane species. The first technique is compressed gas bottle. The vapor pressure of hexamethyldisiloxane (MM) is high enough (42 torr@25ºC) to obtain a 300 ft^3 cylinder of 40% CO_2 with 100 ppm of the MM siloxane in methane (CH_4). However the vapor pressures of octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) are too low (1.05 torr and 0.2 torr @25ºC respectively) to be effective for use in a compressed gas cylinder. A cylinder containing hexamethyldisiloxane (MM) was ordered from Matheson-Linweld Gases Denver.

The second viable technique is permeation tube. Vici-Metronics produces a wide variety of compounds in various styles of permeation tubes. These tubes are placed in a u-tube vessel. Based upon temperature and flow, a particular generation rate can be obtained. This gas stream can be further diluted in a synthetic biogas mixture so that the desired concentrations of siloxanes can be tested. The drawback to this method is that the siloxane permeation tubes are not standard items and must therefore be custom manufactured, and therefore the tubes would not be certified and the generation rates need to be experimentally measured. TDA then would have to develop a method to calibrate the instrumentation for the siloxanes (see impinger generation of siloxanes below for this calibration method). This would allow the determination of the generation rates of the permeation tubes. Since these tubes are very useful in terms of design and ease of use in our apparatus, three tubes containing MM, D4, and D5 were ordered from Vici-Metronics.

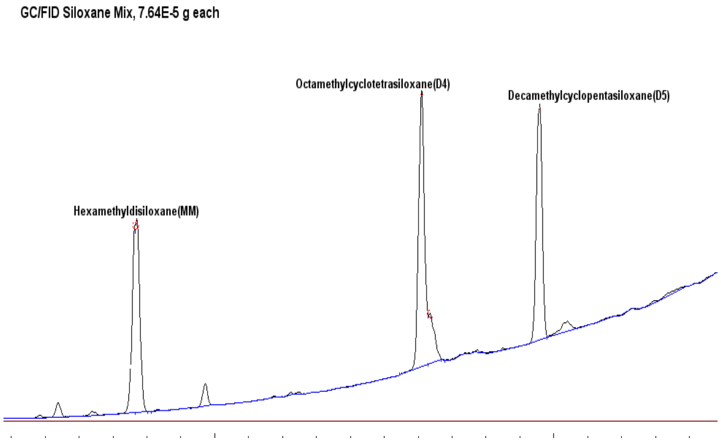

Figure 7. GC/FID Chromatogram of siloxane mixture in

The third method for siloxane gas stream generation is to flow gas through an impinger. Gas is flowed through an impinger into a volume of siloxane. The gas stream carries the siloxane vapor out of the impinger into the apparatus and into the adsorbent bed. The gas stream exiting the adsorbent bed is then analyzed for presence of remaining siloxane. The generation rate of this method is determined by the bubbling of gas vapor containing siloxane into a second impinger containing a solvent, usually methanol (MeOH). The solvent impinger is placed into an ice bath to minimize evaporation. At set time intervals, small aliquots of MeOH are withdrawn from the solvent impinger and analyzed via gas chromatograph (GC). The GC is calibrated with siloxane solutions of varying concentrations. The siloxane solution concentrations are calculated based upon these calibrations. Based upon these concentration results, a siloxane generation rate can be determined. This method was used to determine the rate of siloxane generation for the permeation tubes from Vici-Metronics. Variations in temperature and gas flow were tested to obtain optimum siloxane concentration.

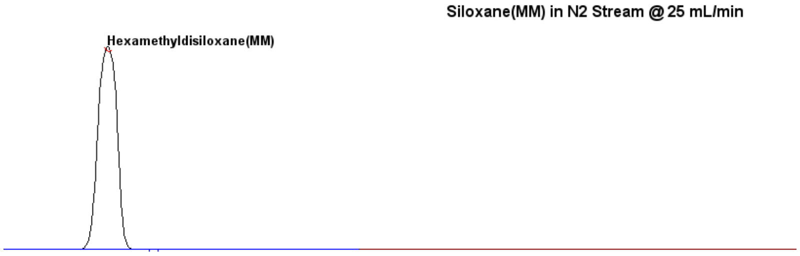

Figure 8. GC/FID Chromatogram of Hexamethyldisiloxane.

In the initial experiments TDA used the impinger method for siloxane generation. Hexamethyldisiloxane (MM), octamethylcyclotetrasiloxane (D4), and decamethylcyclopentasiloxane (D5) were individually placed into the impinger set-up (see Figure 6) and the respective generation rates were determined at varying conditions. These experiments were at ambient temperature (~22 ºC) and a nitrogen flow rate of 100 sccm. The analysis of the MeOH samples indicated that the siloxane concentration was too high (~12% in 10 mL MeOH) compared to the siloxane concentrations found in actual biogas samples. In order to deliver less siloxane in the simulated biogas stream, the nitrogen flow was decreased to 25 sccm. This resulted in a hexamethyldisiloxane (MM) concentration in the nitrogen stream of approximately 500 ppmv. This stream was further diluted in the adsorption experiments by 10-20 times to reach necessary siloxane concentration in the simulated biogas stream.

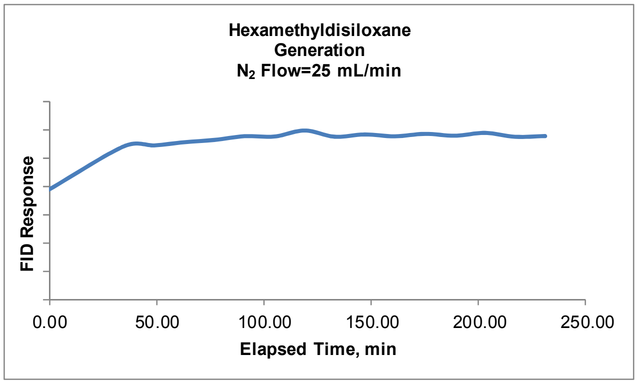

Figure 9. Siloxane concentration in N_2 with time.

Using the siloxane generation rate as the standard, the impinger was connected directly to the GC/FID/FPD in order to determine the response of the detector to the siloxane in the gas stream. Figure 9 shows the GC FID data over a run time of 4 hours with the N_2 flow at 25 sccm indicating that the siloxane concentration in the gas stream equilibrates within 45 minutes. This equilibration time is needed after the impinger is connected to the testing apparatus to allow the siloxane(s) to fill all gas lines and to ensure homogeneous gas mixing. We carried out similar experiments to determine the generation rate of octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5). Using the calibrated siloxane generation rate we carried out tests to characterize the siloxane removal rate for our SulfaTrap^{TM} sorbents.

4.2.1 Task 3.1 Sorbent Optimization Results

We evaluated the performance of the new sorbent materials in fixed bed adsorption breakthrough experiments. The results for various sorbent formulations prepared in Task 2.1 are provided in Table 2. We identified the optimal support and active phase using bench-scale tests for the various sulfur compounds. Support I (which has the higher surface area and smaller pores) achieved higher capacity for H_2S while the mercaptan capacity was higher for the larger pore support II.

Table 2. Results from sorbent evaluations under simulated biogas conditions. T = 22°C, CH_4 = 50%, CO_2 = 50% (dry basis), sat. H_2O, GHSV =4,000 h^{-1}.

			Breakthrough sulfur loading (% wt. sulfur)		
Sample #	Support Type	Active Phase	H_2S	EM	EDS
1	I	A	43.5%	2.9%	-
2	I	B	38.2%	-	-
3	I	C	34.7%	2.2%	-
4	II	A	-	-	1.6%
5	II	C	24.0%	3.4%	1.6%

4.2.2 Task 3.2 Sorbent Production Scale-up Results

The objectives of this task were to verify the performance of the sorbents prepared in Task 2.2. We tested the SulfaTrap^{TM}-R8 samples prepared at the 35 L batch size for sulfur removal at representative conditions. These tests are carried out at higher sulfur level and higher space velocities to accelerate the tests. The results obtained with SulfaTrap^{TM}-R8 at different batch sizes are provided in Figure 10. The results for SulfaTrap^{TM}-R8 samples at lower sulfur levels with supports having different pore sizes are provided in Figure 11. The SulfaTrap^{TM}-R8 sorbent sample achieved 2.12% wt. sulfur capacity (i.e., 10.2 mg sulfur adsorbed per mL sorbent) with support A and 2.73% wt. sulfur capacity (i.e., 9.6 mg sulfur adsorbed per mL sorbent) with support B when the inlet sulfur level was 75 ppmv H_2S.

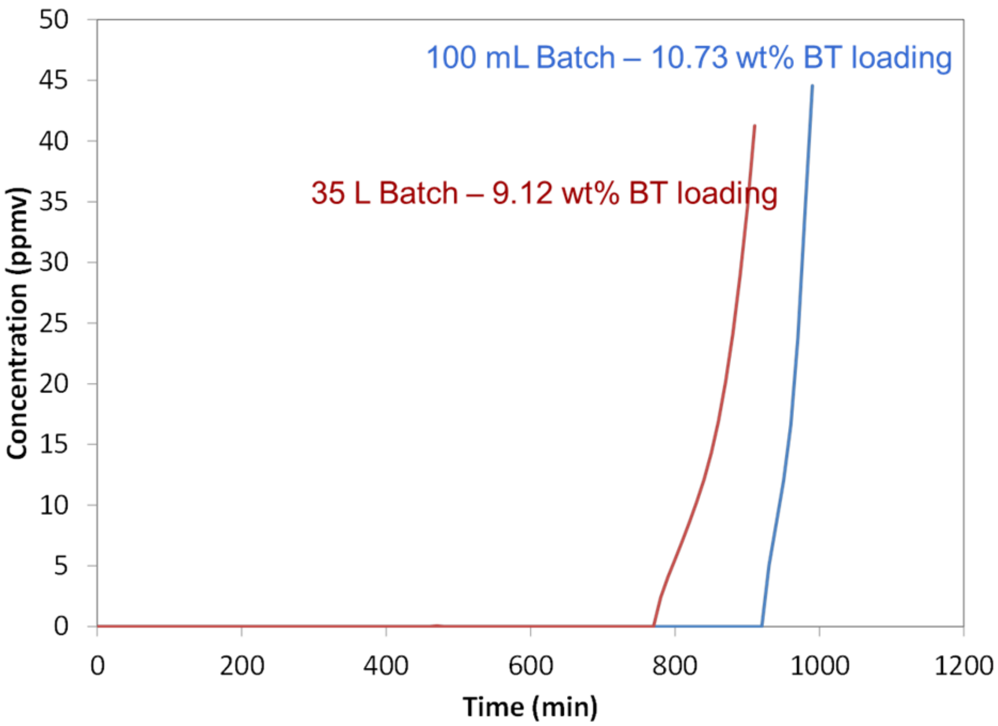

Figure 10. H_2S breakthrough at room temperature on SulfaTrap^{TM}-R8 (prepared using two different batch sizes using Support B) at GHSV=4,000 h^{-1}, H_2S=400 ppmv in simulated biogas (54.2% CH_4, 36.1% CO_2, 7.5% N_2, 2.2% H_2O).

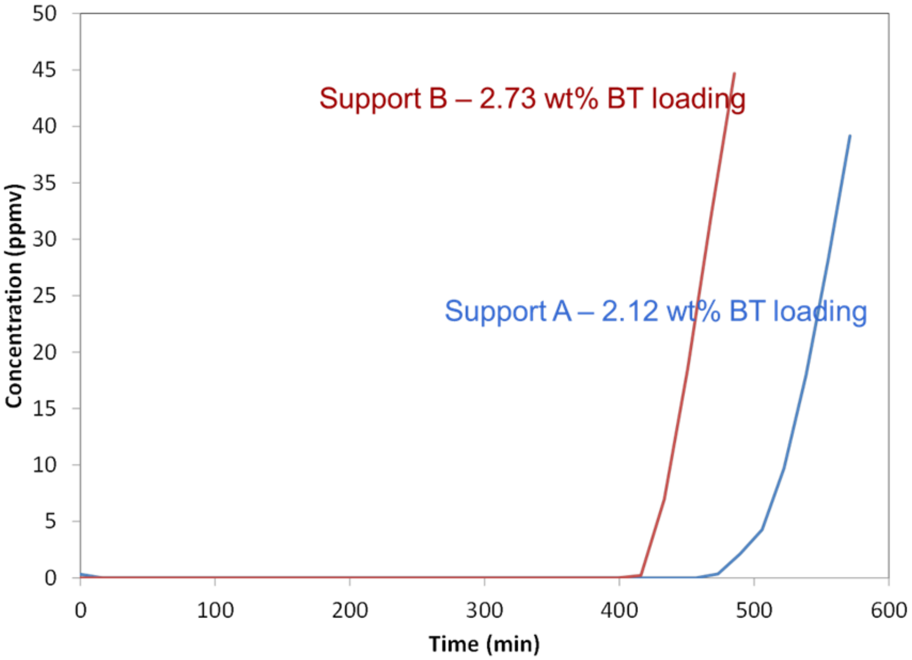

Figure 11. H_2S breakthrough at room temperature on SulfaTrap^{TM}-R8 (prepared using two different supports at 35 L batch Size) at GHSV=12,000 h^{-1}, H_2S=75 ppmv in simulated biogas (54.2% CH_4, 36.1% CO_2, 7.5% N_2, 2.2% H_2O).

4.3 Task 4. Verification Testing

The objectives of this task for FCE were to verify the performance of TDA's sorbent through extensive bench-scale tests and carry out comparisons against baseline ADG desulfurization sorbents. The initial verification testing was carried out at TDA. FCE's in-house team, consisting of the applications group, field service representatives and gas desulfurization experts reviewed TDA's test results for sulfur capacity of our R8 material, compared it against the breakthrough capacities for the commercial sorbents. The results for the SulfaTrap™-R8 material were much better than those for the commercial sorbents.

4.3.1 Sulfur and Siloxane Capture Determination

SulfaTrap™-R8 was evaluated in an accelerated flow rate test at an L/D of 4 with baseline component concentrations of 500 ppmv MM siloxane, and 75 ppmv H_2S. The results indicate MM breakthrough in 1.5 hours, with a calculated siloxane loading of 15.6 wt%, and H_2S breakthrough in 8 hours, at a 2.15 wt% loading (Support B). The SulfaTrap™-R8 sample mass was recorded before and after testing. The sample exhibited a 22% increase in mass, consistent with the loadings determined by GC results, with the rest of loading accounted for by the adsorption of water. A second experiment was performed with H_2S only (no siloxane) in order to determine the effect of MM siloxane on the H_2S loading. These experimental results indicated a similar breakthrough, as shown in Figure 12. As we see, MM siloxane had little effect on the H_2S capacity of the sorbent.

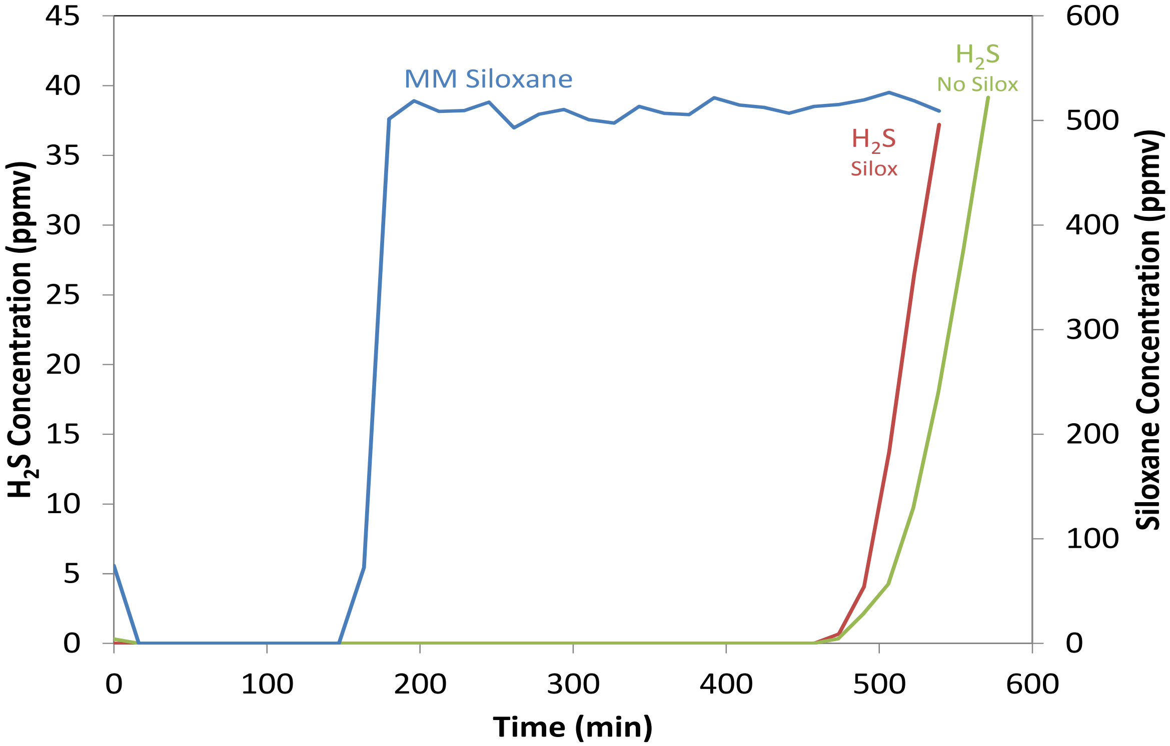

Figure 12. Siloxane and H_2S breakthrough at room temperature on SulfaTrap™-R8 at GHSV=6,000 h^{-1}, MM siloxane = 500 ppmv and H_2S=75 ppmv in simulated biogas.

4.3.2 Effect of Space Velocity on Sulfur Capture

Adsorption experiments with sorbent (SulfaTrap^{TM}-R8) prepared using Support A (V) were performed under standard (but accelerated) conditions of 12,000 h^{-1} GHSV and ambient temperature (~22ºC) with 75 ppmv H_2S. No siloxanes were included in these experiments in order to establish a baseline sorbent performance for H_2S removal. Results indicated their sulfur capacity was similar to the initial R8 sample, with a 2.73 wt% sulfur loading as H_2S. A second experiment was performed at 4,000 h^{-1} GHSV, and 225 ppmv H2S (same total amount of sulfur contacting the sorbent per unit time) to simulate previous TDA H_2S experiments. The lower space velocity conditions yielded an improved sulfur loading of 6.5 wt%. In actual usage, the GHSV will be on the order of 50 h^{-1}, and we expect even better sulfur capacity at this condition.

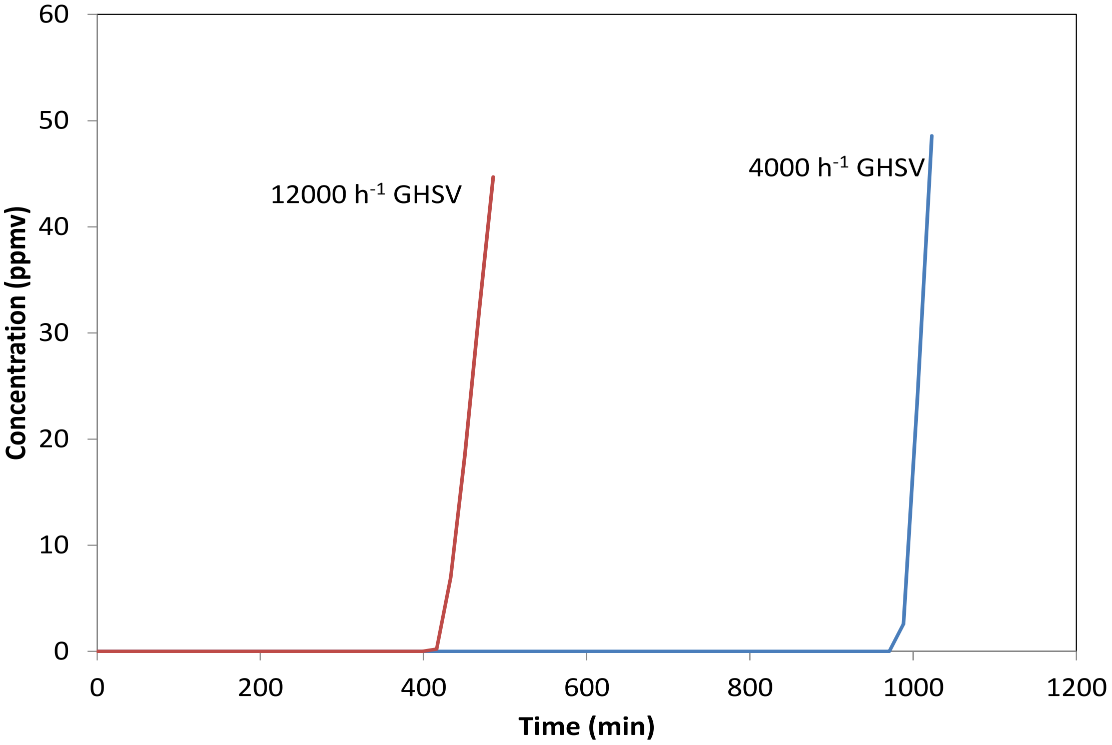

Figure 13. Impact of space velocity: H_2S breakthrough profile comparison.

4.3.3 Sorbent Performance Verification Tests at FCE

FCE performed laboratory testing on three of TDA's sorbents. The sorbents tested were Sulfatrap-R8, Sulfatrap-R2B and Sulfatrap-R5D. All testing and gas analyses were performed at FCE's facility. The SulfaTrap^{TM}-R8 media was designed for general sulfur removal including H_2S and mercaptans. The SulfaTrap^{TM}-R2B sorbent was designed for removal of dimethyl sulfide (DMS) but is also effective for other sulfur species, with the exception of carbonyl sulfide (COS). However, this sorbent, which was initially developed for natural gas desulfurization is generally not recommended for general sulfur removal from biogas due higher sulfur levels in the biogas and it is also much more expensive than the SulfaTrap^{TM}-R8 sorbent. The final sorbent tested, Sulfatrap-R5D was designed to remove COS and is a low temperature hydrolysis catalyst and sorbent. All three sorbents were included in the sorbent performance verification testing in order to evaluate the complete polishing bed that removes all the sulfur and siloxanes in the biogas to the ppb levels needed for fuel cell operation.

Experimental Methods: Table 3 shows the test the parameters for laboratory testing of the SulfaTrap™ sorbents. Two separate vessels were used for the test and were connected in series. The first vessel contained Sulfatrap™-R8 and the second vessel contained Sulfatrap™-R2B and Sulfatrap™-R5D. Sample ports were located on the inlet and exit of the first vessel, and on the exit of the last vessel. All samples were collected in tedlar bags and analyzed at FCE using GC equipped with a sulfur chemiluminescence detector to allow for low ppb level detection. A schematic of the test setup is shown in Figure 14.

Test Results: Samples were taken at various points during the test to monitor the performance of the media and determine when sulfur breakthrough occurred. Figure 15 through Figure 18

Table 3. Sulfatrap™ laboratory testing parameters.

<table>
<tr><th colspan="5">Sorbent Bed Properties</th></tr>
<tr><th>Sorbent</th><th>Media Volume (mL)</th><th>GHSV (h⁻¹)</th><th>Residence Time (s)</th><th>Sorbent Bed L/D</th></tr>
<tr><td>R2B</td><td>100</td><td>2740</td><td>1.3</td><td>2.6</td></tr>
<tr><td>R5D</td><td>50</td><td>5480</td><td>0.66</td><td>1.3</td></tr>
<tr><td>R8</td><td>100</td><td>2740</td><td>1.3</td><td>2.6</td></tr>
<tr><td colspan="5"></td></tr>
<tr><th colspan="2">Gas Composition</th><th colspan="3">Inlet Concentration</th></tr>
<tr><td colspan="2">Isopropyl Mercaptan</td><td colspan="3">150 ppb</td></tr>
<tr><td colspan="2">Tert-Butyl Mercaptan</td><td colspan="3">1600 ppb</td></tr>
<tr><td colspan="2">Methyl Ethyl Sulfide</td><td colspan="3">200 ppb</td></tr>
<tr><td colspan="2">DMS</td><td colspan="3">1500 ppb</td></tr>
<tr><td colspan="2">COS</td><td colspan="3">500 ppb</td></tr>
<tr><td colspan="2">Moisture</td><td colspan="3">3000 ppm</td></tr>
<tr><td colspan="2">Natural Gas</td><td colspan="3">Balance</td></tr>
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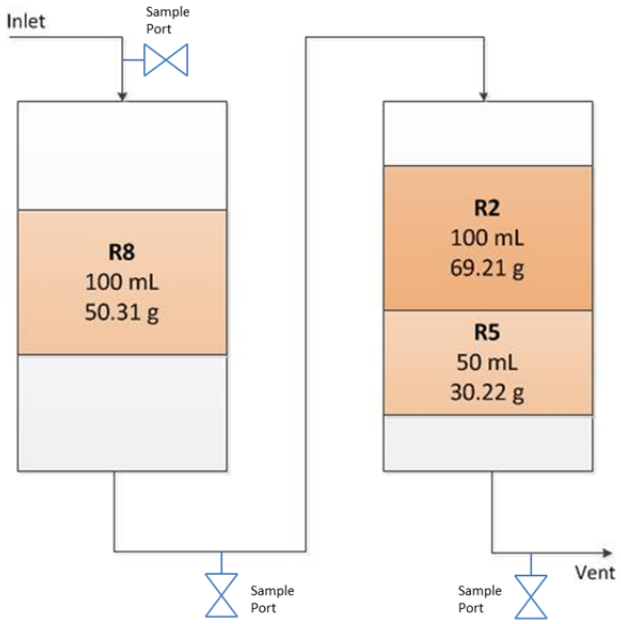


Figure 14. Schematic of test setup.

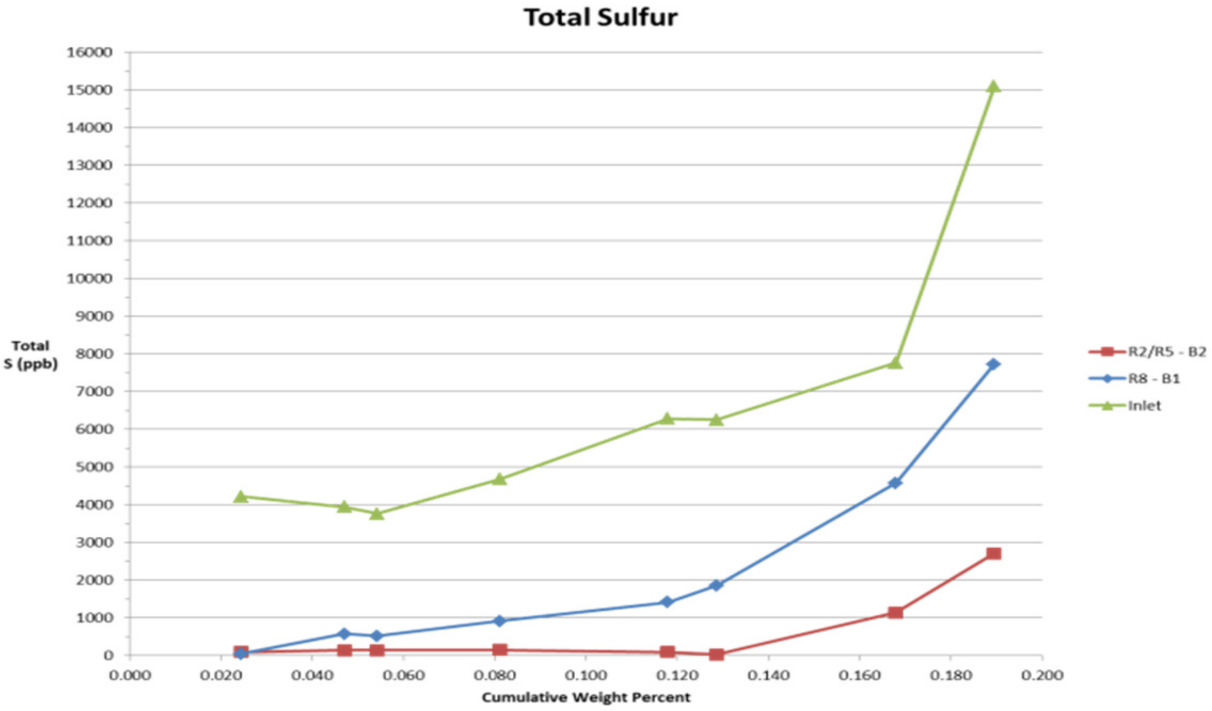


Figure 15. SulfaTrap™ test tesults from FCE - performance of all three media. The tests were accelerated by increasing the inlet sulfur concentration as shown by the green curve.

shows the performance of the Sulfatrap™ sorbents as measured by FCE for the conditions given in the experimental methods section above.

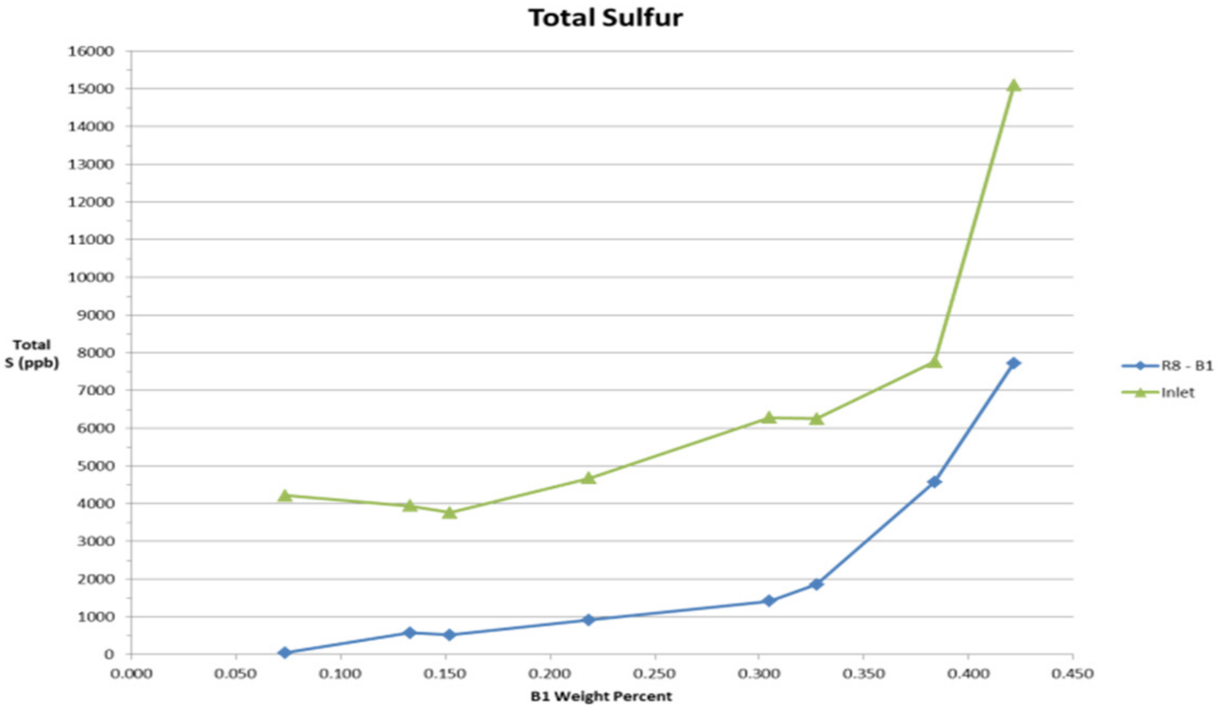


Figure 16. SulfaTrap™ Test results from FCE - performance of SulfaTrap^{TM}-R8 media only. The tests were accelerated by increasing the inlet sulfur concentration as shown by the green curve.

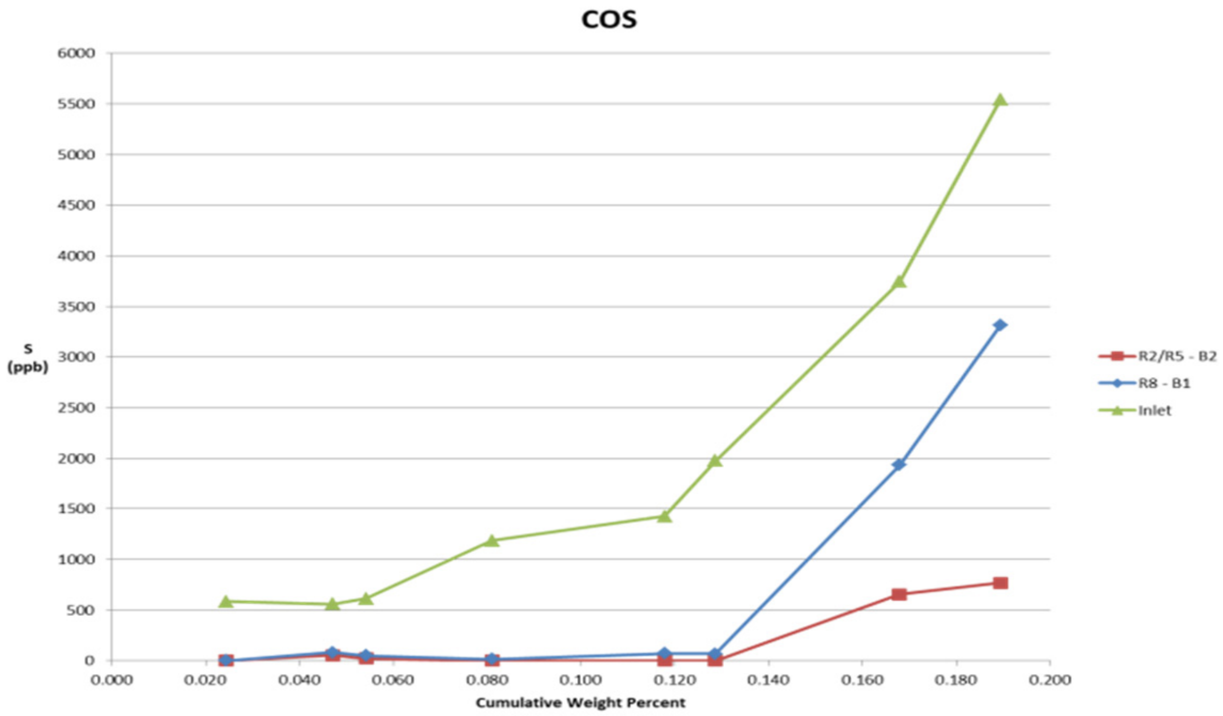


Figure 17. SulfaTrap™ test results from FCE - performance for COS. The tests were accelerated by increasing the inlet sulfur concentration as shown by the green curve.

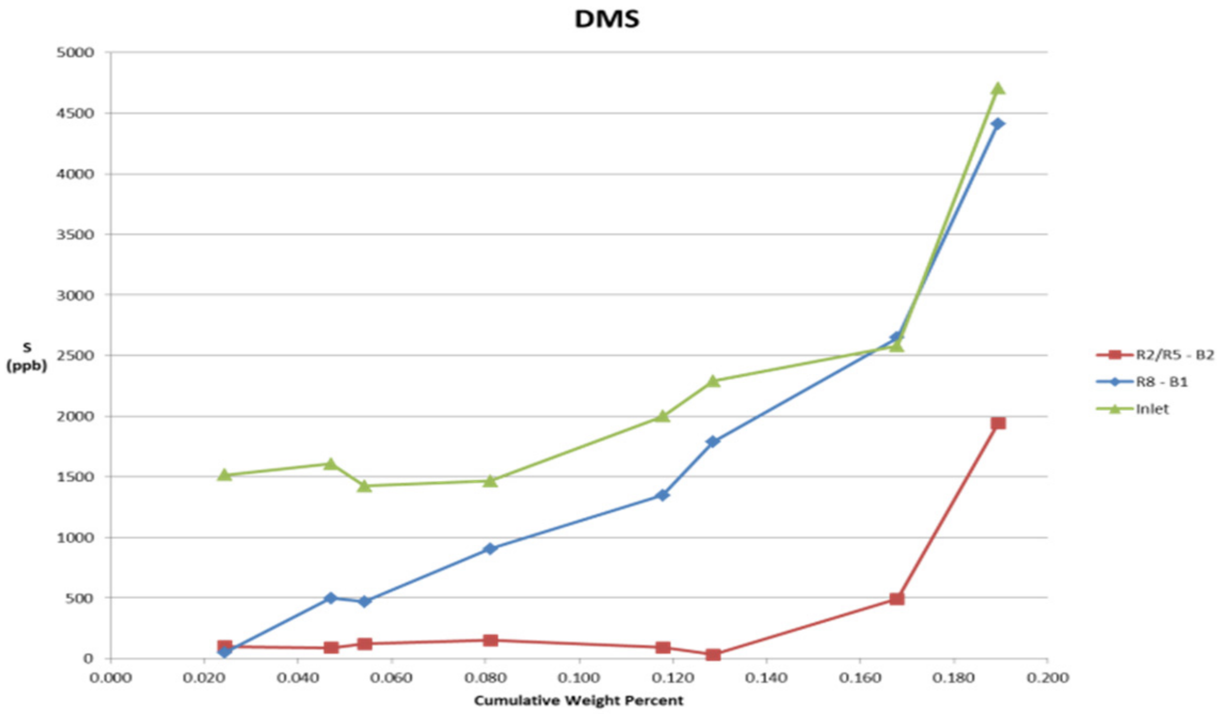


Figure 18. SulfaTrap™ test results from FCE - performance for DMS. The tests were accelerated by increasing the inlet sulfur concentration as shown by the green curve.

The results from FCE show that the SulfaTrap™ sorbents have a breakthrough capacity of about 0.15 wt%, which is lower than the capacity measured at TDA. FCE defined breakthrough to be when the outlet reaches 7% of the inlet sulfur concentration. TDA reported the breakthrough capacities to be as follows:

- Sulfatrap-R2B – 0.8%
- Sulfatrap-R5D – 0.5%
- Sulfatrap-R8 – 1.1%

Interestingly, the SulfaTrap^{TM}-R8 media appears to have some capacity for COS, as shown in Figure 16(c). This is somewhat unexpected since SulfaTrap-R8 is a general sorbent and not designed to remove COS. Removal of COS generally requires hydrolysis, where it breaks down to form CO_2 and H_2S (which is readily adsorbed).

TDA recommended the L/D ratios for the vessels be kept relatively large, and suggested a minimum value of 4.0 since ratios lower than this recommendation can lead to incomplete sorbent utilization. FCE in their reactor design for the bench-scale sorbent performance evaluation kept the individual sorbent bed/layer L/D to be between 1.3 and 2.6. This might be the reason for the discrepancy between FCE's results and the TDA reported values.

4.4 Task 5. Slipstream Testing on ADG

The objectives of this task were to design, fabricate and test the SulfaTrap polishing sorbents under real biogas in a slipstream test unit at different ADG sites. We ran three different slip-stream tests, two at the Eastern Municipal Water District (EMWD) in Moreno Valley, CA, and one at the City of Tulare (CA) water treatment facility.

4.4.1 Description of the Slipstream Test Unit

Figure 19 shows a process and instrumentation diagram of the slipstream demonstration test unit. The test unit consists of multiple vessels to house the sulfur and siloxane sorbents, as well as a gas conditioning system to increase the gas pressure, reduce moisture content and adjust the temperature to achieve the optimum conditions for the siloxane sorbent. The slipstream flowrate is 1 SCFM (1.7 m^3/hr) per bed, which is about 1% of the total flow at FCE's DFC unit equipped ADG sites. The relatively large-scale evaluation is expected to be useful for further process design and implementation. The test setup consists of two main sections: low pressure removal of bulk sulfur and siloxane (from raw ADG tie point), and high pressure sulfur and siloxane polishing (post-bulk desulfurizer tie point at the test sites).

This unit was designed to house 3 reactors (two 1.3 L reactor for polishing sorbents and one 10L vessel for the bulk desulfurization sorbent) that ran in parallel so that different sorbents could be tested at the same time. Initially, we used the same reactor design to house both the bulk and polishing sorbents. All reactors have a plumbing design which allows sorbent change out without disconnecting plumbing. The main reactor body for the bulk desulfurizer consists of a 10" pipe and a class 150 flange to house the sorbent. A smaller (4" class 150) top flange is also used to provide the capability of easy sorbent change-out in the field (primarily useful for filling in the new sorbent). There is a drain plug at the bottom of vessel that allows sorbent replacement without disassembly. The bottom housing can be easily converted to a larger vessel; this provides easy adjustment of the sorbent inventory to achieve desired operating duration, as well as the capability of evaluating sorbents at different bed aspect ratios (L/D).

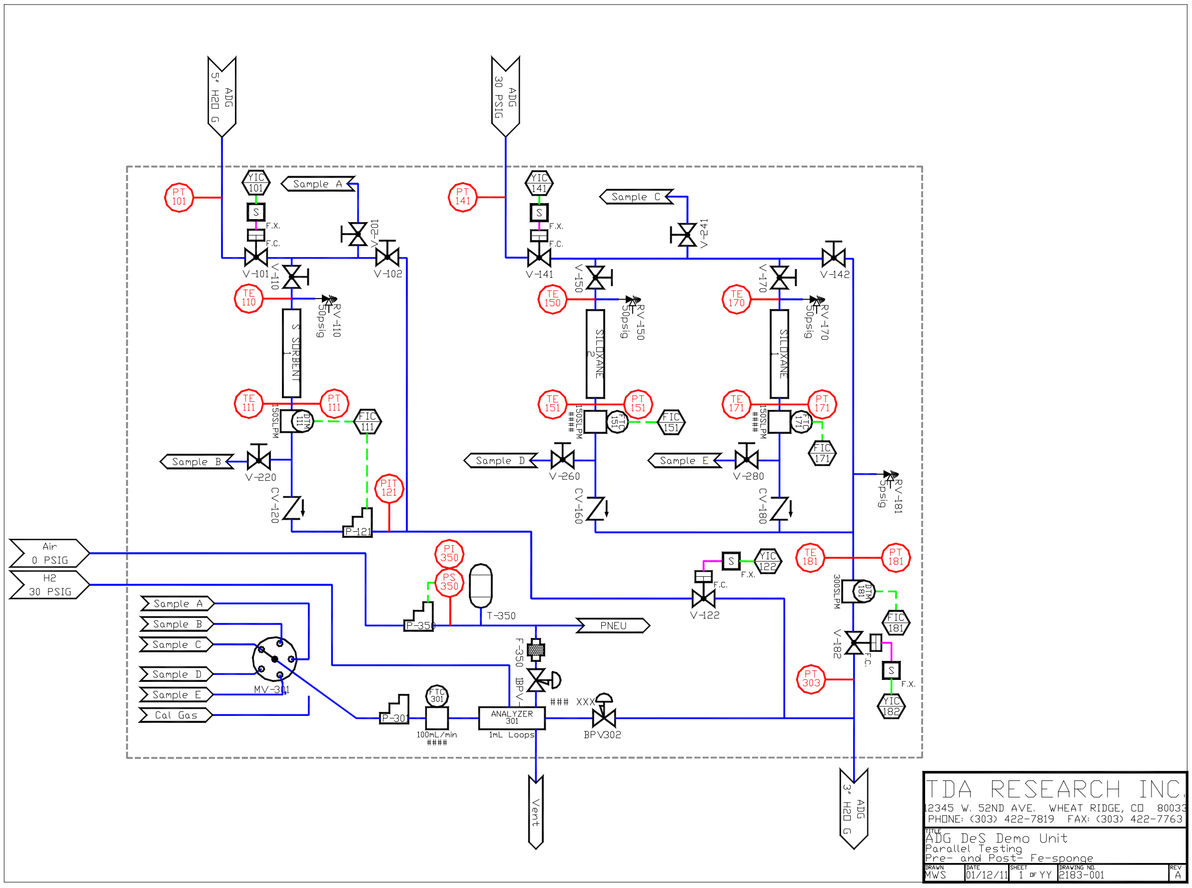


Figure 19. Process and instrumentation diagram (P&ID) of the test system.

The system is capable of evaluating two polishing sorbents concurrently for a direct comparison on the same gas stream. Flow is measured and controlled through all three beds, while an automated sampling system and built-in analyzer monitors sulfur and siloxane concentrations at multiple points in the system, with occasional verification of sensitivity by calibration gas sample. The control system monitors and logs all data points and gas chromatograph results. The entire test system is fully automated, and fully enclosed for outdoor installation.

Figure 20. Slip-stream vessels.

4.4.2 Slipstream Test System Fabrication

Figure 20 shows the three sorbent vessels during fabrication, Figure 21 is a close-up of some of the components, and Figure 22 shows the outer and inside view of our slipstream demonstration unit. The test unit consists of multiple vessels to house the sulfur and siloxane sorbents, as well as a gas conditioning system to increase the gas pressure, reduce moisture content and adjust the temperature to achieve the optimum conditions for the siloxane sorbent. The system also includes a SRI gas chromatograph equipped with a flame ionization detector and a flame photometric detector. The slipstream unit is sized to handle 1 SCFM (1.7 m^3/hr) per bed, which is about 1% of the total flow at the EMWD test site. This relatively large-scale evaluation is expected to be useful for further process design and implementation at full-scale.

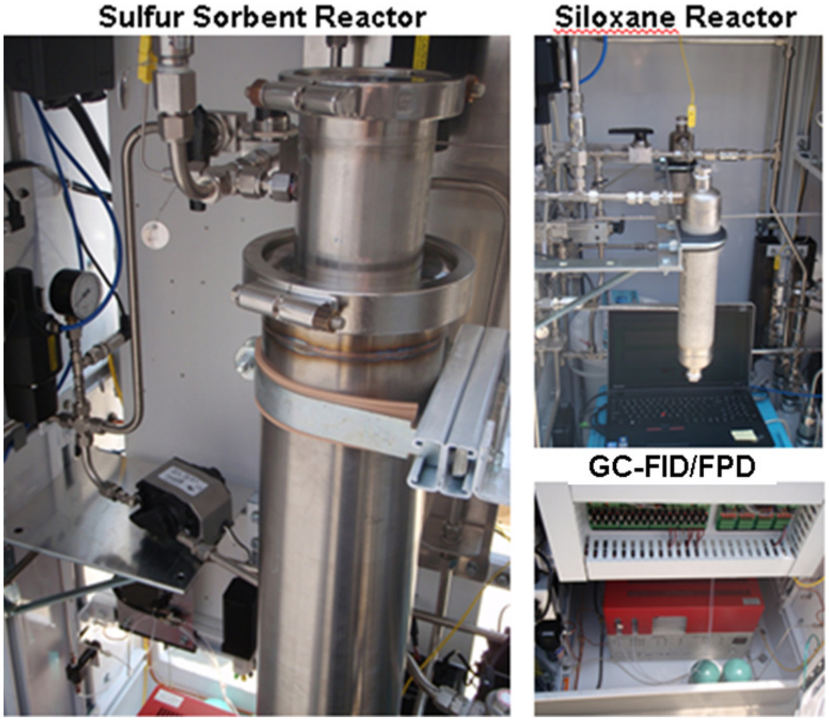


Figure 21. Slipstream system components.

Figure 22. TDA's Slipstream demonstration unit. Left: Outer view. Right: Inside view.

4.4.3 Slipstream Demonstration Tests at Moreno Waste Water Treatment Facility

The slipstream demonstration test was carried out in the Eastern Municipal Water District (EMWD) at their Moreno Waste Water Treatment Facility (WWTF). A site visit was conducted with personnel from host site, TDA and FCE to determine tie in points and available site utilities. Three tie in points were identified: one at the plant inlet (raw ADG) and two after the bulk desulfurization unit, one to use as feed and the second to use as a return line.

Figure 23. FCE’s MCFC (DFC® units) installed at the Moreno Waste Water Treatment Facility (WWTF).

Figure 24. Tie-in point for the slipstream demonstration system at Moreno WWTF.

<u>Integration On-site:</u> In the summer of 2011 we completed the installation and integration of the slipstream demonstration unit at the Moreno WWTF. The test setup was installed on-site at the tie-in point located downstream of the bulk desulfurization system on June 13, 2011. The demonstration unit uses a slipstream of gas after bulk desulfurization to use as feed and will return the gas in a return line after analysis of the sulfur removal capability of our SulfaTrap^{TM} sorbents. Figure 25 shows TDA’s slipstream demonstration unit installed on-site at Moreno

WWTF. The tank containing the bulk iron-sponge desulfurization sorbent can be seen in the background of Figure 25.

Figure 25. TDA's slipstream demo unit installed at Moreno WWTF.

4.4.4 Slipstream Testing

The Eastern Municipal Water District (EMWD) in Moreno Valley California was selected as one of the sites for the slipstream testing. The site is home to three FuelCell Energy DFC 300 power plants. The major sulfur species found in the EMWD digester gas are H_2S, COS, DMS and various mercaptans and thiophenes. Figure 26 shows the tie-in points and the configuration of the slipstream unit. The slipstream unit allowed for sampling upstream and downstream of the iron sponge system. Samples taken upstream were sent through a 8 L desulfurizer where we carry out the bulk desulfurization testing. Samples taken downstream of the iron sponge system

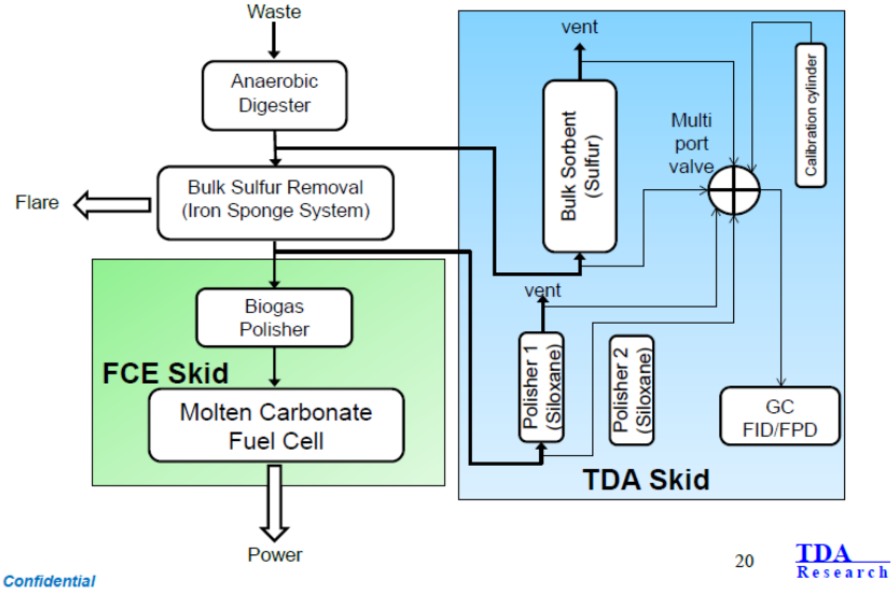


Figure 26. TDA Slipstream unit schematic.

were sent through the polishing desulfurizers. All samples were vented or diverted to a GC for analysis.

The slipstream test unit was first installed at EMWD and the slipstream testing successfully processed over 60,000,000 SCF of ADG through FCE skid and over 200,000 SCF of ADG through TDA's slipstream test skid in two campaigns during the test period. All data collection and analysis was performed by TDA during the demonstration.

Demonstration Test#1 at EMWD Wasterwater Plant: TDA's test rig was installed at EMWD July 7th-July 13th. FCE monitors cumulative flow through the ADG skid after bed replacement. Figure 27 shows the cumulative ADG flow through the FCE skid. The TDA rig installation is indicated on the chart. Over 3.7 MMSCF of ADG was processed through the FCE skid before power was shut off at the site on August 8th for electrical grid repair work. Power was restored September 19th and an additional 8.465 MMSCF of ADG was processed through the FCE skid before the units were shut down for fuel cell stack replacement on December 12th. The total slipstream flow through the TDA's desulfurizer was more than 80,000 SCF at the time of shut down.

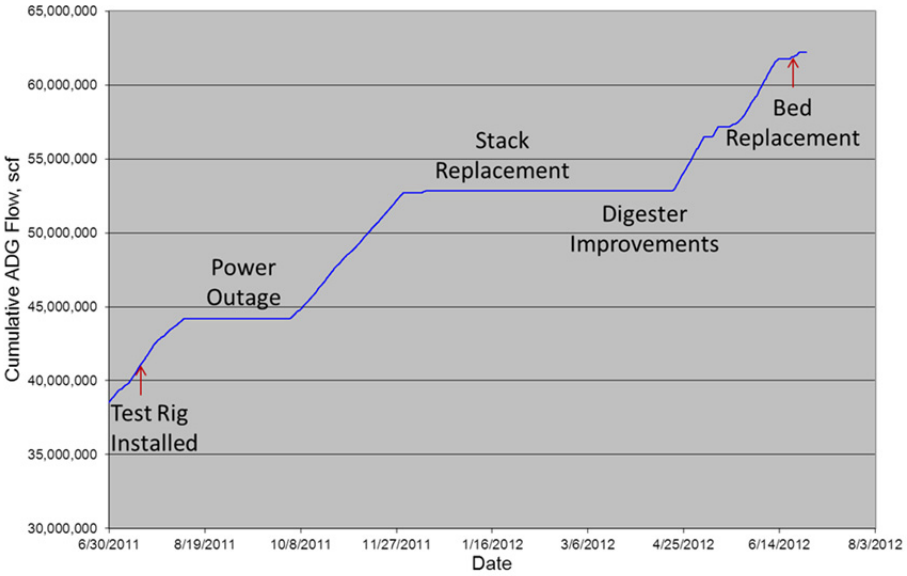


Figure 27. Cumulative ADG flow through FCE's EMWD skid.

TDA's skid has two beds a bulk desulfurizer that takes a slipstream of raw biogas before the iron sponge system and a polisher that takes a slipstream of desulfurized biogas from the biogas exiting the iron sponge system. In our first slipstream demonstration at EMDWP, we used SulfaTrap^{TM}-R8 sorbent for both the bulk desulfurizer (volume = 8 L) and the polisher (volume = 1 L).

We processed 88,460 cubic foot of raw biogas through the bulk desulfurizer, which has a volume of 8 L at a space velocity of 380 h^{-1}. We took inlet and exit measurement of the sulfur compounds present in the biogas from the bulk desulfurizer. The biogas contained only H_2S and the inlet measurements saturated the FPD signal at the retention time for H_2S indicating the sulfur concentration in the inlet biogas exceeds the range for our GC-FPD and the sulfur concentration is significantly more than 100 ppmv. Figure 28 shows the GC-FPD measurements for the bulk desulfurizer. The bulk desulfurizer filled with TDA's SulfaTrap^{TM}-R8 removed all of the sulfur compounds, in this case H_2S, down to < 0.1 ppmv.

In order to measure the sulfur capacity of the sorbent we sent the spent sorbent to Hazen Research, Inc. (Golden, CO) for independent sulfur measurement. The sulfur capacity of the

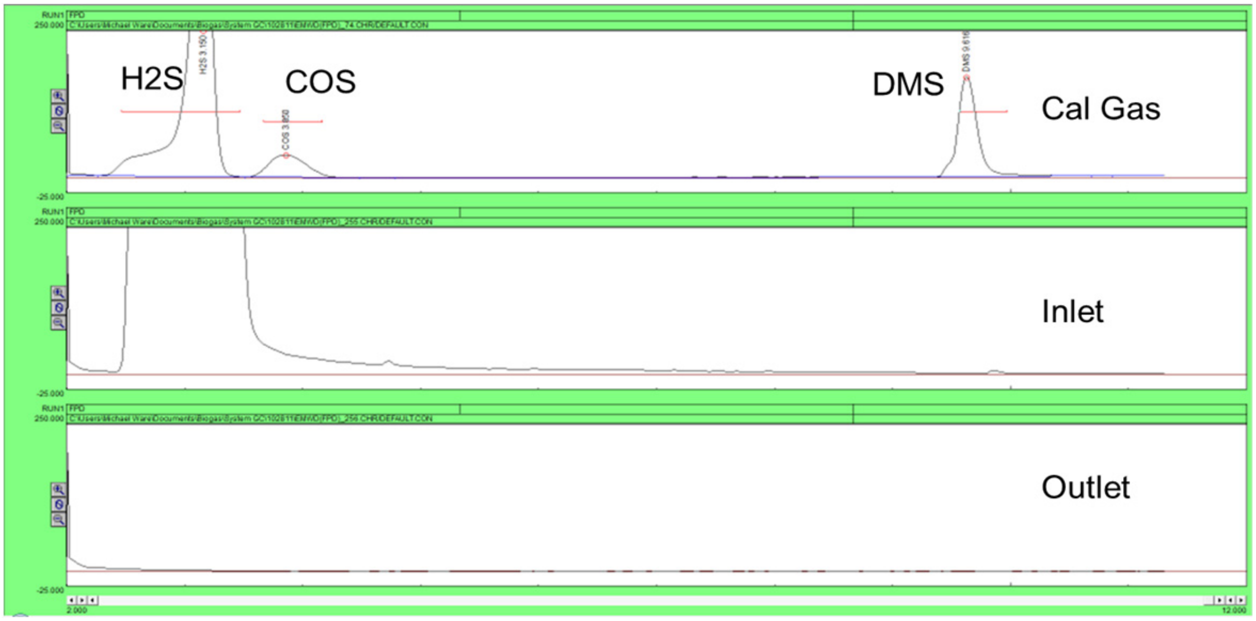


Figure 28. FPD chromatograms showing the complete removal of sulfur from biogas taken before the iron sponge system in the slipstream demonstration tests with SulfaTrap^{TM}-R8 (bulk desulfurizer).

bulk sorbent (SulfaTrap^{TM}-R8) was 8.04% wt. sulfur in the post characterization and the average sulfur concentration in the inlet raw biogas was estimated to be 179.1 ppmv.

We processed 47,510 cubic foot of biogas from the exit of the iron sponge (bulk desulfurization) system through the polisher, which has a volume of 1 L at a space velocity of 1,650 h^{-1}. We took inlet and exit measurements of the siloxanes and sulfur present in the biogas from the polisher. The biogas at the inlet of the polisher contained very little siloxanes or sulfur. Figure 29 shows the GC-FID measurements for the polisher showing the complete removal of the siloxanes

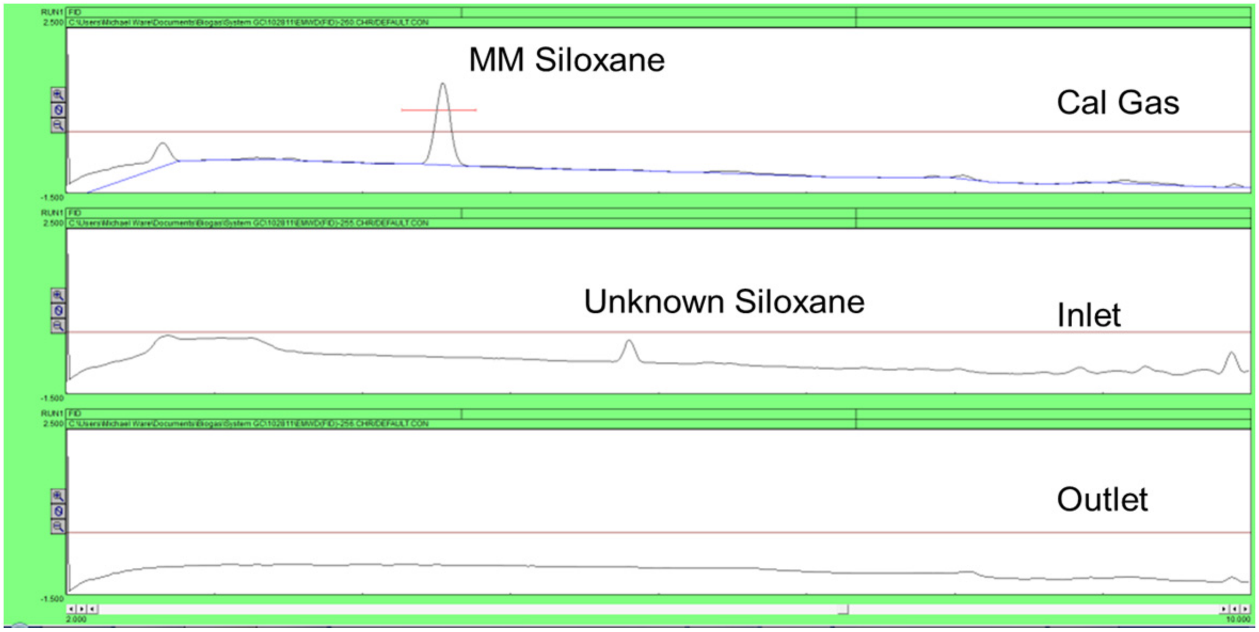


Figure 29. FID chromatograms showing the complete removal of siloxanes from biogas in the slipstream demonstration tests with SulfaTrap^{TM}-R8 (polisher).

present in the biogas. The polisher filled with TDA's SulfaTrap^{TM}-R8 removed all of the sulfur compounds and the siloxanes present in the biogas from the iron sponge system to < 0.1 ppmv.

We did not observe sulfur or siloxane breakthrough from the polisher during this slipstream demonstration. In order to measure the sulfur capacity of the sorbent we sent the spent sorbent to Hazen Research, Inc (Golden, CO) for independent sulfur measurement. The sulfur adsorbed on to the polisher (SulfaTrap^{TM}-R8) was 0.52% wt. sulfur in the post characterization and the average sulfur concentration in the inlet biogas to the polisher is estimated to be 1.31 ppmv. The siloxane present in the biogas is very small and hence the loading achieved at the end of demonstration test is below detection limits for post characterization measurement of siloxane loading.

Demonstration Test #2 at EMWD Wastewater Plant: We had previously successfully completed a slipstream demonstration test at the Eastern Municipality Water District Wastewater Plant, Moreno Valley, CA and our sorbent (SulfaTrap^{TM}-R8) removed the sulfur compounds in the bulk biogas and partially desulfurized biogas from the iron sponge system to sub ppm levels. The next test was planned for the Wastewater treatment Plant at Tulare, CA. However, there was a delay in getting the tests scheduled at Tulare Waste Water Treatment Plant, and in early April 2012 the EMWD wastewater plant was back online. Therefore, we carried out a second demonstration test at EMWD wastewater plant using SulfaTrap^{TM}-R7 (another higher capacity bulk desulfurizer) until the Tulare Plant become available for slipstream tests.

In the second demonstration test at EMWD wastewater plant we loaded the bulk desulfurizer and the polisher with SulfaTrap^{TM}-R7 and SulfaTrap^{TM}-R8 respectively. We processed 140,000 cubic foot of raw biogas through the bulk desulfurizer in total, which has a volume of 8 L at a space velocity of 380 h^{-1}. We took inlet and exit measurement of the sulfur compounds present in the biogas from the bulk desulfurizer. The biogas contained only H_2S and the inlet measurements saturated the FPD signal at the retention time for H_2S, indicating the sulfur concentration in the inlet biogas is out of range for our GC-FPD; the sulfur concentration significantly exceeded 100 ppmv. Figure 30 shows the GC-FPD chromatograms for the bulk desulfurizer up to 112,500 cubic foot of biogas processed, after this the flame in the online GC-FPD analyzer went down. The bulk desulfurizer filled with TDA's SulfaTrap^{TM}-R7 removed all of the sulfur compounds in this case H_2S down to < 0.1 ppmv. The sorbent capacity based on the average H_2S concentration of 180 ppmv is estimated to be above 9.8% wt. sulfur when the demonstration was stopped.

In the polisher bed loaded with fresh SulfaTrap^{TM}-R8, we have so far processed 60,400 cubic foot of biogas from the exit of the iron sponge (bulk desulfurization) system through the polisher, which has a volume of 1 L at a space velocity of 1,650 h^{-1}.

After completion of the demonstration at EMWD, the unit was moved to the city of Tulare wastewater treatment plant (WWTP). The unit was installed and TDA skid was operational for a shoirt duration while the FCE skid was not operational due to extended-duration problems with the digester.

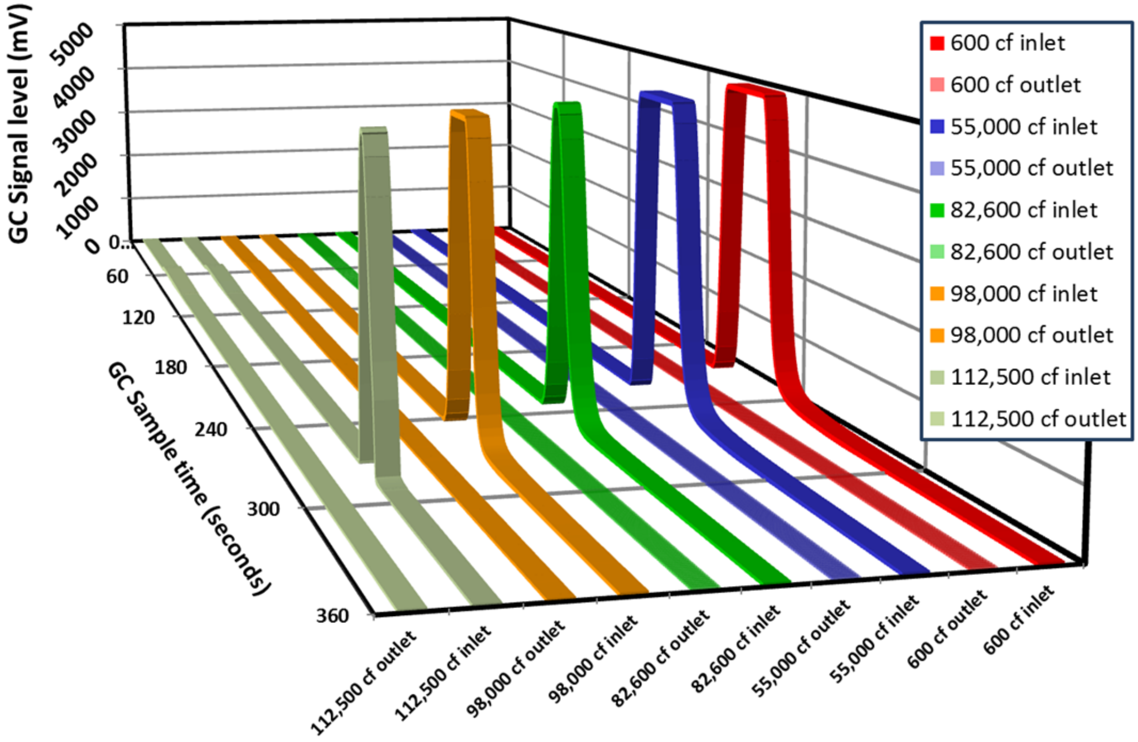


Figure 30. GC-FPD chromatograms showing sulfur peak at inlet and outlet of the bulk desulfurizer loaded with SulfaTrap^{TM}-R7.

Demonstration Test #3 at City of Tulare Wastewater Treatment Plant: TDA's test rig was moved from the EMWD site to the Tulare Wastewater Treatment Plant in the last quarter of 2012. Figure 31 shows the unit located at the Tulare site. Due to the agriculture and dairy processing in Tulare, the ADG gas has a substantially different contaminant mix than the ADG at the EMWD site. Additionally, the raw ADG at Tulare has a much higher hydrogen sulfide concentration: 670 ppmv versus ~150ppmv calculated for EMWD. This raw gas was available for sampling and testing in addition to the ADG post-H_2S scrubber (21 ppmv H_2S) gas.

Figure 31. Test skid at Tulare Wastewater Treatment Plant.

The system could not be completely installed at the Tulare site in December 2013 because an iron sponge change-out was scheduled for January 2013. TDA personnel returned to Tulare in mid-February and completed the installation. During that time, the Gas Chromatograph was completely cleaned and reassembled due to minor damage during the move. Due to sporadic use of the ADG gas by the fuel cells due to high oxygen levels – and subsequent cycling off-line of the site's clean- up skid – the initial test was connected to the raw ADG gas. While the raw gas has a high hydrogen sulfide level (680ppmv), it's flow and sulfur level are independent of the operation of the clean-up skid. The clean-up skid is only maintained and operated while supplying the fuel cells, leaving potential for large swings in the ADG sulfur level as the compressors cycled, changing the flow through the iron sponge columns.

Raw ADG flow was started on 2/14/13 through an 8L bed of SulfaTrap™-R8 in the bulk desulfurization side of the TDA test rig (380h^{-1} GHSV). The flow is set by a pump in the system, running approximately 1.8scfm against the backpressure in the return line to the second iron sponge column. Figure 32 shows the inlet, outlet, and calibration gas chromatographs from 2/23/13. At this snapshot no sulfur is detectable in the outlet (~250ppbv detection limit), and total flow through the bed is 24,000 CF. The chromatographs shown have been truncated on the time scale to eight minute length. However, the full GC cycle runs 20 minutes to detect larger sulfur compounds if any present.

The system's sample program runs through all five sample points (plus a calibration gas sample) approximately every 16 hours. The next sample point on February 24th is shown in Figure 33. The outlet shows a breakthrough level of about 20ppmv H_2S at the exit of the sorbent bed. Total flow at this snapshot is 25,600 CF.

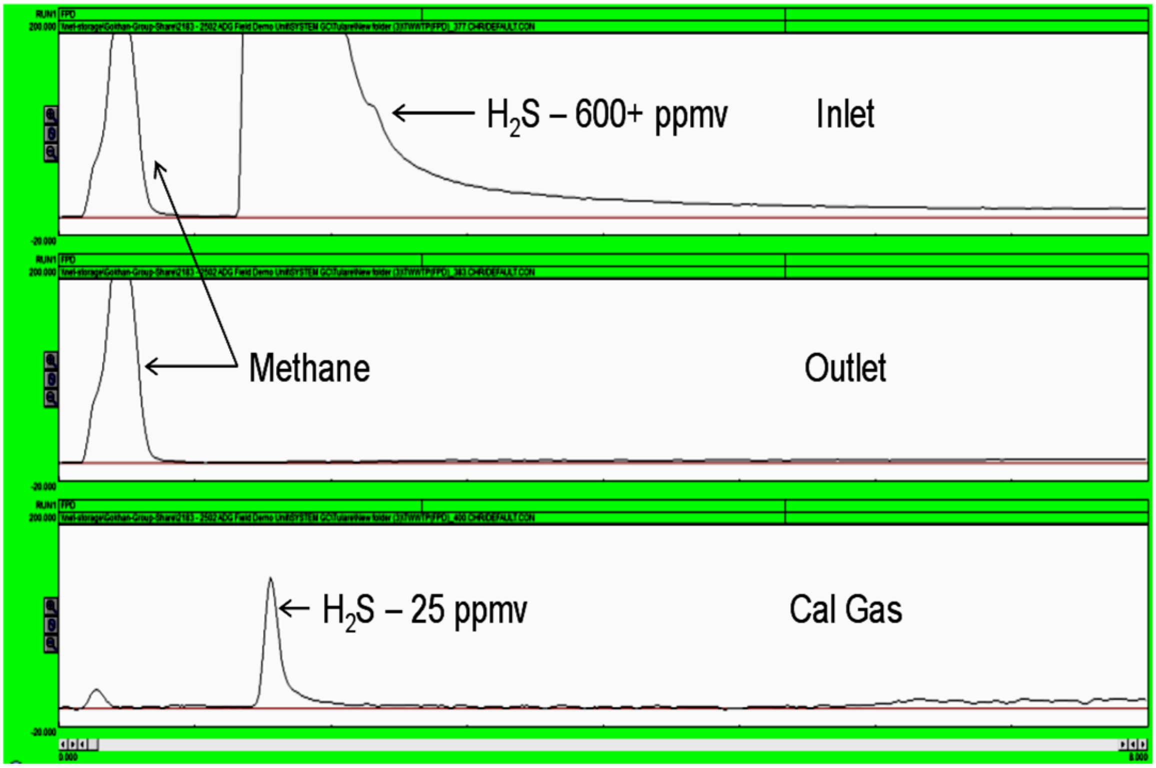


Figure 32. Gas chromatographs at 24,000 CF of raw ADG flow.

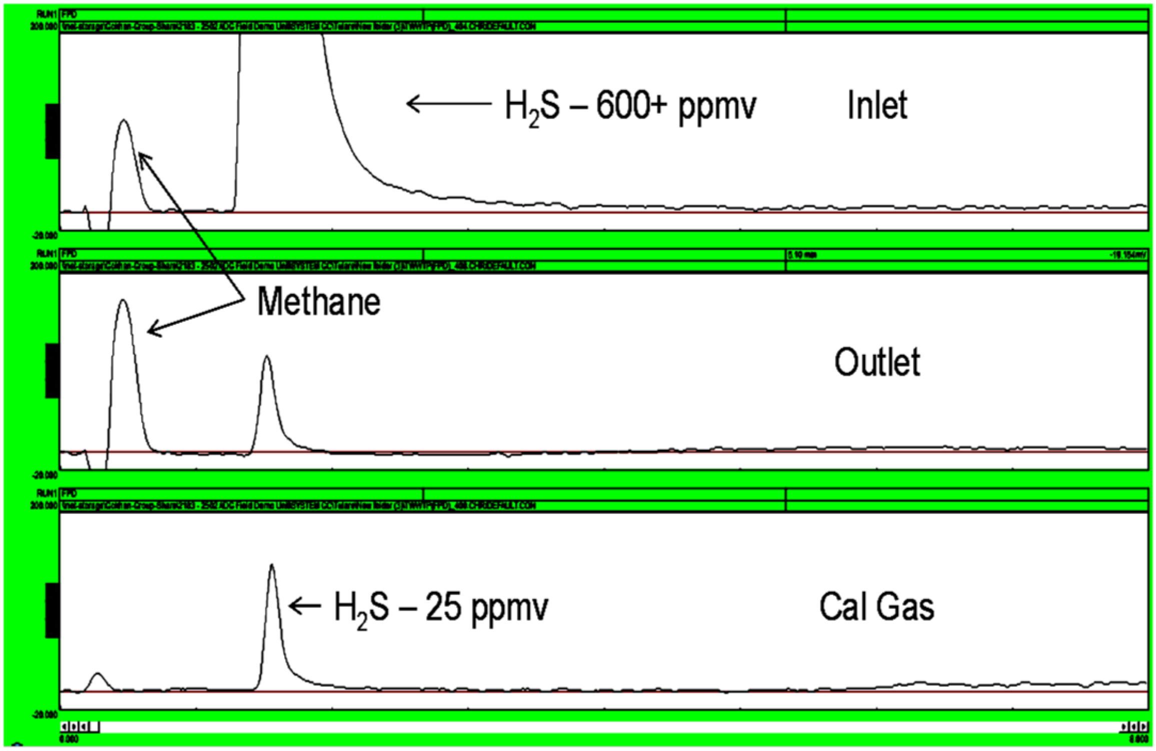


Figure 33. Gas Chromatographs at 25,600 CF of raw ADG flow.

At the high inlet sulfur levels of the raw ADG the GC-FPD detector is fully saturated, preventing the calibration from providing an inlet concentration. This trade-off in GC sensitivity was made to better evaluate the removal efficiency of the sorbent (higher sensitivity to detect low-level leakage at the exit of the bed). The Tulare gas clean-up skid for the FCE fuel cells was shut down on March 18, 2013. Hence, we used the baseline raw ADG sulfur measurements to estimate the pre-breakthrough capacity (i.e., after 24,000 SCF of ADG was processed by TDA's SulfaTrap^{TM}-R8). Based on the inlet H_2S concentration of 670 ppmv the breakthrough capacity for SulfaTrap^{TM}-R8 is estimated to be 16.8% wt. sulfur.

4.5 Task 6. Prototype Testing on ADG

Table 4. Sorbents used in prototype skid.

Sorbent	Required Volume (L) (6 Month Life)	Primary Use/Comments
R2B	99.0	Used primarily for DMS removal. Will remove all sulfur compounds but cost prohibitive for general sulfur removal.
R5D	31.1	Used primarily for COS removal. Hydrolysis catalyst and sorbent.
R8	212.1	General sorbent used for removal of H_2S and organic sulfur compounds. Not intended for DMS and COS removal.

4.5.1 Prototype Sorbent Skid Design

FCE designed and procured a full scale prototype sulfur polishing system sized for a DFC300 MCFC (300 kW). TDA provided guidance for the design of the sorbent vessels and for determining the sorbent loading requirements. The skid was manufactured by American Design and Manufacturing in South Windsor, CT.

Design Parameters: The skid design incorporated a lead/lag configuration to allow for sorbent replacement during operation. Each stage was sized for six months of operation. **Error! Reference source not found.** gives the parameters used in the design of the sorbent skid.

Sorbent Vessel Design: Based on the species present in the ADG, three different sorbents were selected for use in the skid. The sorbents selected were: SulfaTrap^{TM}-R2B, SulfaTrap^{TM}-R5D and SulfaTrap^{TM}-R8. The custom design allows for the TDA recommended L/D ratio to be met, which is important as it allows for more complete utilization of the sorbent. Preventing sulfur breakthrough is of the highest importance as sulfur is a stack poison and the cost of replacing a stack is very high. Therefore, the lead/lag design was selected, as it provided the best compromise between cost and operational requirements.

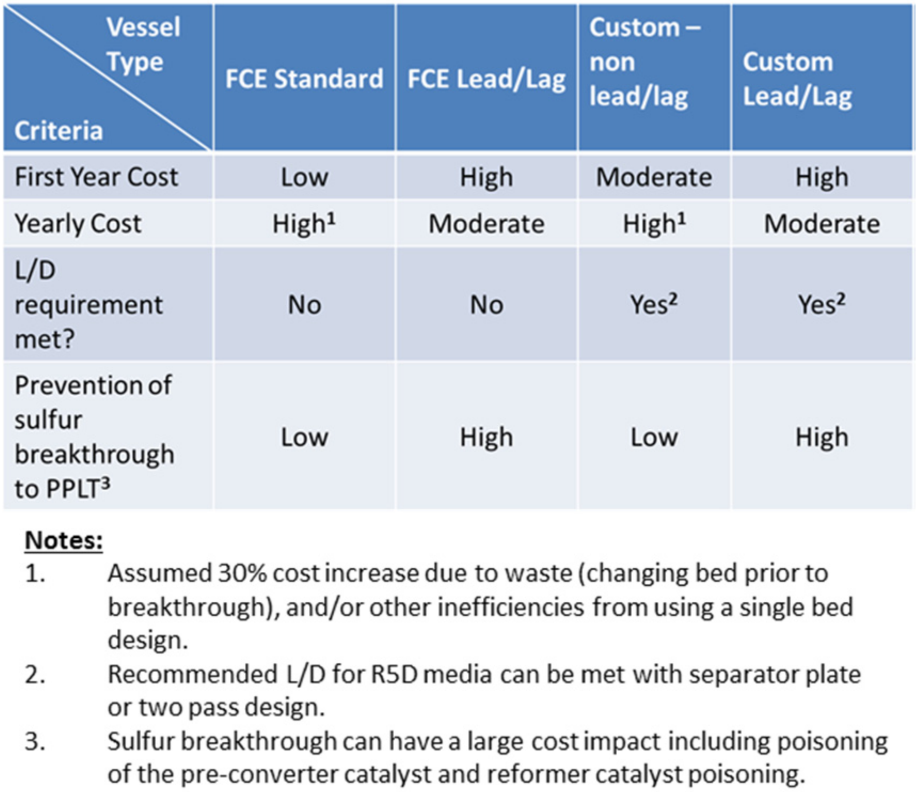
Table 4 lists the required sorbent volumes and information about each sorbent.

Two different vessel designs were evaluated, each in both single and lead/lag configurations. One of the designs evaluated was the FCE standard vessel design and the other was a custom design fabricated from commercially available piping components. Figure 34 gives a side-by-side comparison of the designs considered.

The custom design allows for the TDA recommended L/D ratio to be met, which is important as it allows for more complete utilization of the sorbent. Preventing sulfur breakthrough is of the highest importance as sulfur is a stack poison and the cost of replacing a stack is very high. Therefore, the lead/lag design was selected, as it provided the best compromise between cost and operational requirements.

To achieve the recommended L/D ratios, two separate vessels in series were selected for each stage. The first vessel was designed to contain the SulfaTrap^{TM}-R8 sorbent and the second vessel was designed to contain both the SulfaTrap^{TM}-R2B and SulfaTrap^{TM}-R5D sorbents. In order to maintain the recommended L/D ratio for the SulfaTrap^{TM}-R2B and SulfaTrap^{TM}-R5D sorbents a vessel with a center tube and annular area was used. Figure 35 shows the R8 and R2/R5 vessel designs.

The vessels were designed and manufactured from standard piping components and have a MAWP of 150 psig. The only custom component on either of the vessels is the top flange on the R2/R5 vessel. To allow for loading sorbent into both the annular area and the center tube, a blank flange was machined as shown in Figure 35 (b). Isolation between the annular area and center tube was achieved by incorporating an o-ring seal. Another o-ring grove was machined into the flange to seal between the annular area and ambient environment. In the R8 vessel, the gas stream enters from the top and exits through the bottom of the vessel. The vessel was designed to include free space above the top surface of the sorbent to allow for dispersion of the gas as it enters the vessel. In the R2/R5 vessel, the gas stream enters from the side, flows down through the annular area, and up through the center tube before exiting through the top of the vessel.

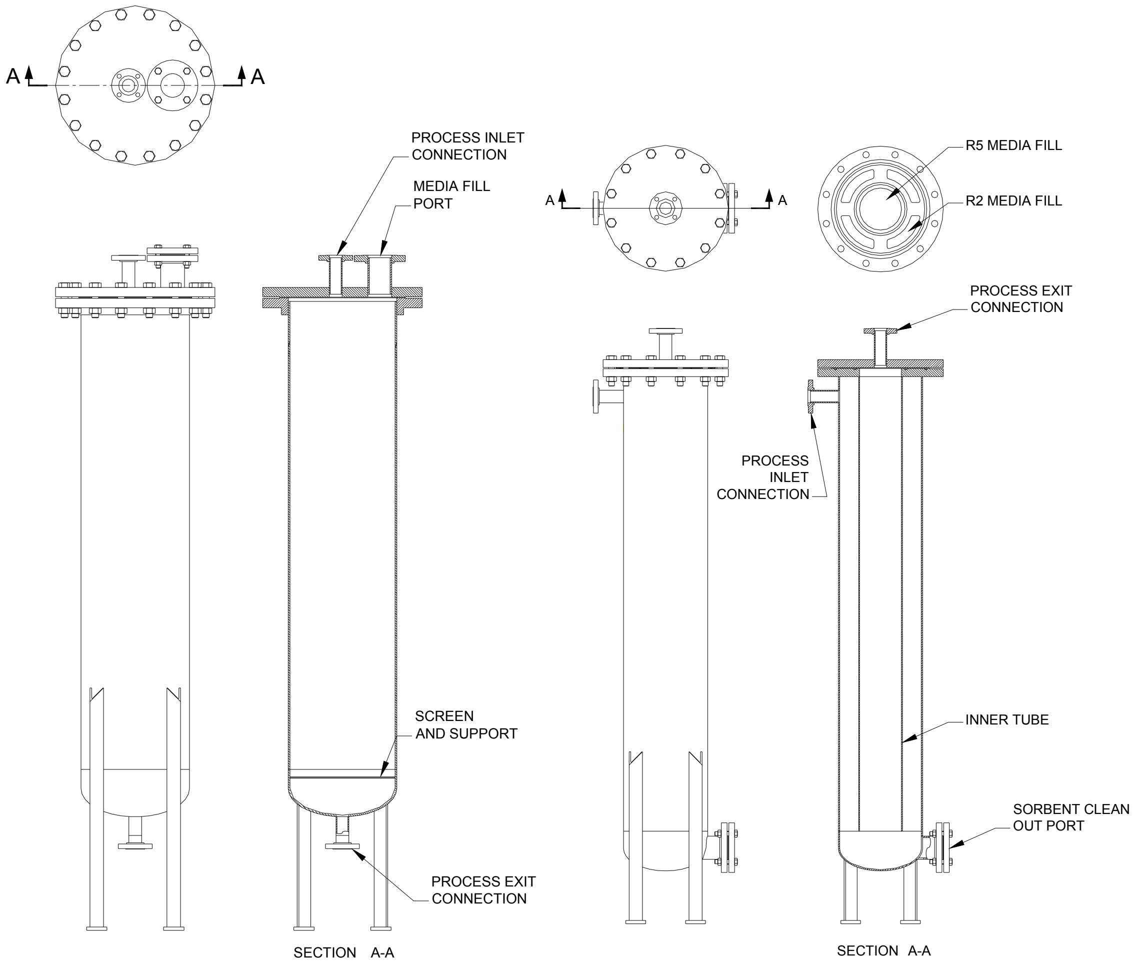


Vessel Type Criteria	FCE Standard	FCE Lead/Lag	Custom – non lead/lag	Custom Lead/Lag
First Year Cost	Low	High	Moderate	High
Yearly Cost	High[1]	Moderate	High[1]	Moderate
L/D requirement met?	No	No	Yes[2]	Yes[2]
Prevention of sulfur breakthrough to PPLT[3]	Low	High	Low	High

Notes:

1. Assumed 30% cost increase due to waste (changing bed prior to breakthrough), and/or other inefficiencies from using a single bed design.
2. Recommended L/D for R5D media can be met with separator plate or two pass design.
3. Sulfur breakthrough can have a large cost impact including poisoning of the pre-converter catalyst and reformer catalyst poisoning.

Figure 34. Comparison of sorbent vessels considered for the prototype system.



(a) (b)

Figure 35. Sorbent vessel designs. (a) R8 vessel, (b) R2/R5 vessel.

The sorbent is loaded into and removed from each vessel in a different manner. The R8 vessel was designed for sorbent loading and removal through the media port on the vessel cover. Removal of the media requires the use of a vacuum.

The R2/R5 vessel requires that the top cover be removed to load the sorbent. The top flange has a center hole through which the SulfaTrap^{TM}-R5 media is loaded, and slots to load the SulfaTrap^{TM}-R2 media in the annular area. Removal of the media is accomplished through the clean-out flange located on the side of the vessel at the bottom.

The vessels were designed to be installed outdoors and will most likely be subjected to direct sunlight. Therefore, the effect of solar loading on the sorbent performance was analyzed. Since the sorbents work primarily through physical adsorption, temperature has a large effect on the performance. Figure 36 shows that as the temperature rises above 40^{0}C, the capacity of the sorbent drops off dramatically. Based on this, we modified the system so that the maximum operating temperature was below 40^{0}C.

In warmer locations, the internal operating temperature of the vessel can easily exceed 40^{0}C as shown in Figure 37. This correlates strongly with the color (solar absorptivity) and properties of the external tank surface. The best option to maintain a low operating temperature is to use a reflective surface. For this application Reflectix duct insulation was selected. Reflectix is outdoor rated and is secured to the tank surface using aluminum tape.

Table 5. Sorbent vessel information.

Parameter	**R8 Vessel**	**R2/R5 Vessel**
Material of Construction	Schedule 10 304 Stainless Steel Piping Components, 150lb Flanges	
Diameter	16 in (Nom)	12 in (Nom)
Overall vessel Length	76.5 in	76 in
Sorbent Bed Length	69.5 in	R2 = 69 in, R5 = 60 in
Sorbent Bed L/D	4.5	R2 = 6.6, R5 = 9.0
Inner Tube Diameter	-	6 in
Inlet Outlet Connections	1-1/2" Flange	
MAWP (psig)	150	150

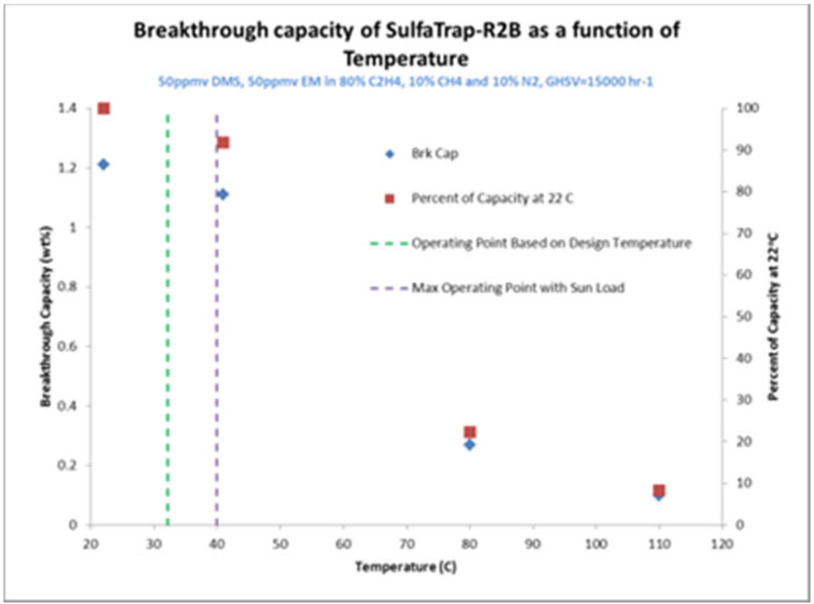


Figure 36. SulfaTrap^{TM}-R2B: Breakthrough capacity vs temperature.

System Configuration: The prototype system was designed to accept ADG at a flow rate of 82 SCFM and an inlet pressure of 30 – 40 psig. The pressure in a digester is typically very low and must be increased to a useable pressure. To maintain a constant operating pressure, a pressure regulator was incorporated into the design.

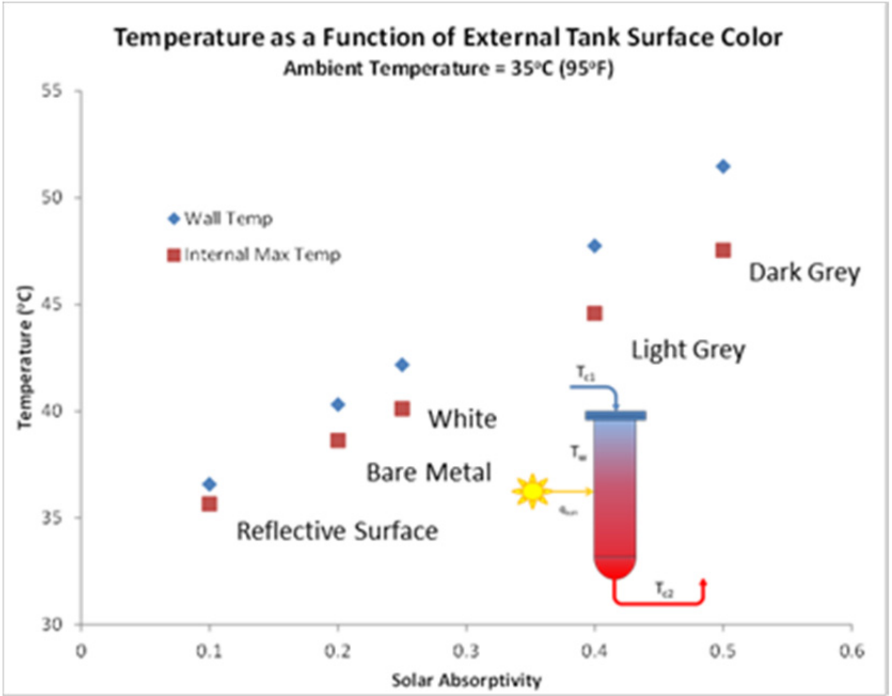


Figure 37. Internal operating temperature as a function of solar absorptivity.

The process piping was selected was 1-1/2" schedule 40. The total pressure drop through the pipe and sorbent beds was estimated to be ~10 psig at 82 SCFM. The inlet pressure requirement to FCE's DFC power plants is 15 psig which sets the inlet regulator (PCV200) set point requirement to 25 psig.

Each vessel is protected with pressure relief valves which will relieve pressure in the event of a fire, or other over-pressurization. The pressure relief valves were designed to have set-points of 35 psig which is well below the MAWP of the vessels. Each of the relief valve outlets is plumbed to a common header diverting flow during an over-pressurization to the center of the skid.

A hazard analysis was performed on the system to determine and mitigate the potential safety risks. The hazard analysis uncovered the need for on skid gas detection and automatic shutoff in the event of a gas leak. A methane sensor was incorporated into the design and interlocked to the main shutoff valve, CV200. CV200 was designed to be a fail close valve and on the loss of power will shut off gas flow to the skid. Additional safety features on the skid include three status lights and an estop button. The e-stop button allows for shutting off gas flow to the skid in the event of an emergency. The three status lights provide indication of normal operation (green), warning of gas detection above 25% LEL (amber) and shutdown due to a gas concentration above 50% LEL (red). All electrical components are rated for hazardous area operation.

The system includes valves for isolation of individual stages allowing sorbent change-out to take place during operation. Once the sorbent has been replaced, the vessels and associated piping can be purged to remove air by connecting to the hand valves (210A/B) just upstream of the R8 vessels and appropriately positioning the other valves to allow the flow to exit through the vent. Purge flow control is accomplished by an orifice located in the line that connects to the vent. The stage can then be put back into operation and becomes the lag stage.

The skid design and P&ID are shown in Figure 38 and Figure 39. The skid base is fabricated from carbon steel and painted with an epoxy paint suitable for outdoor applications. All support structures are fabricated from stainless steel. The skid is equipped with fork truck slots and four mounting brackets.

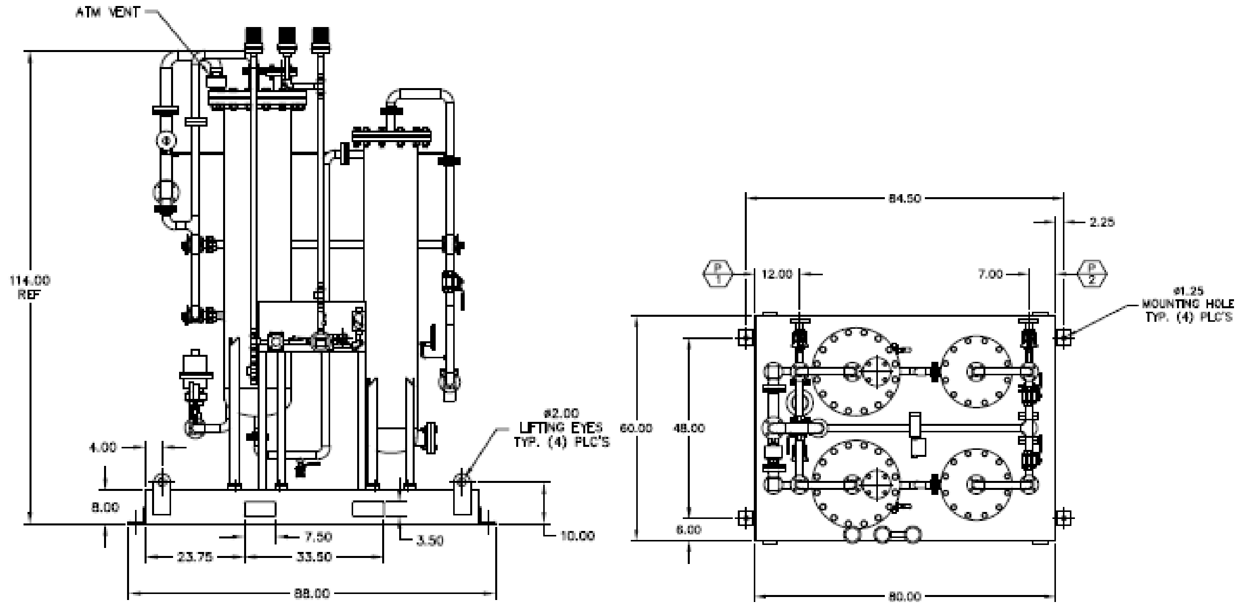


Figure 38. Prototype system general arrangement sketch.

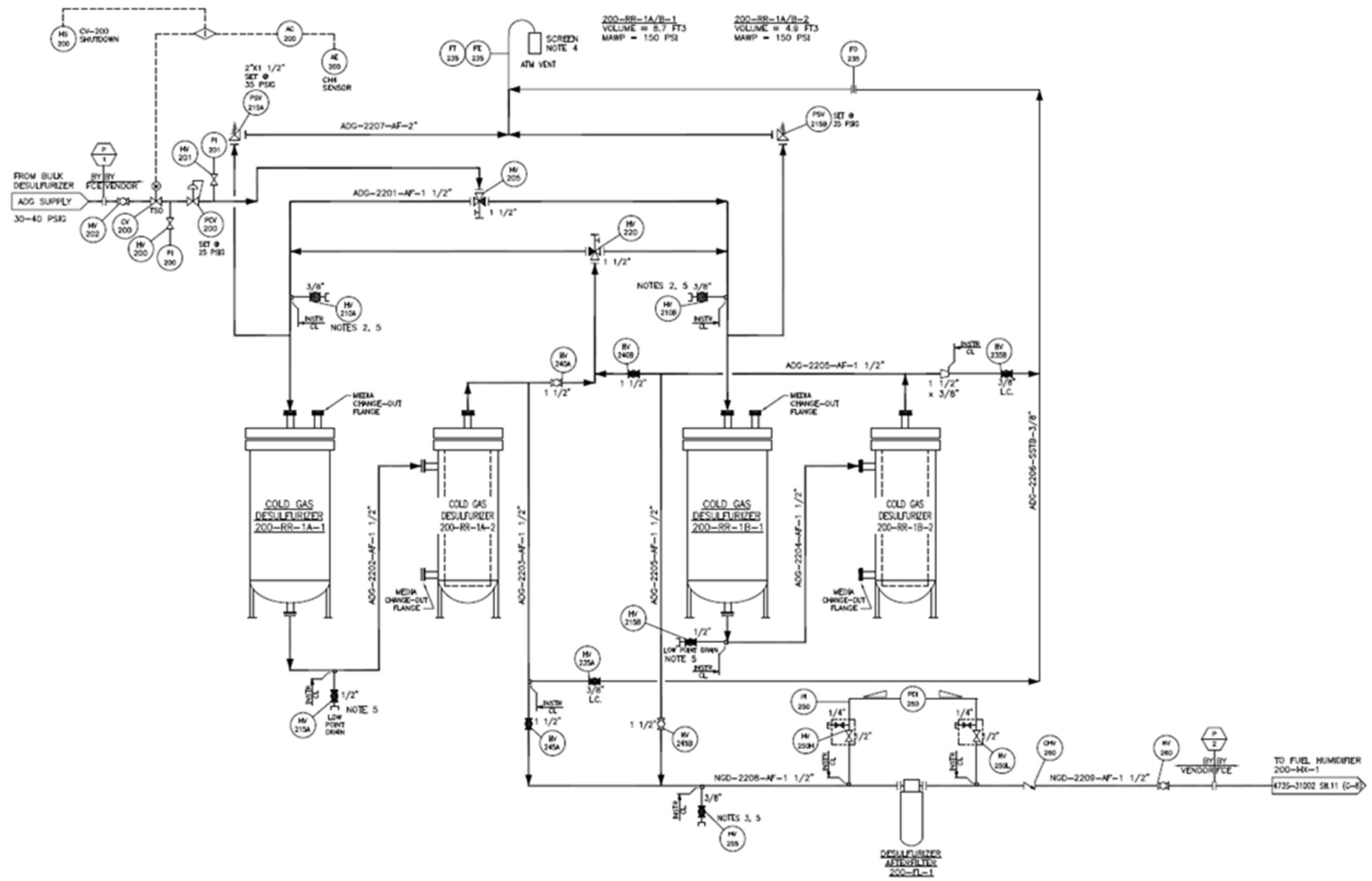


Figure 39. Prototype system P&ID.

4.5.2 Prototype Skid Fabrication

The prototype unit consists of two sets of sorbent vessels to provide lead-lag operation of the paired beds. Valving permits the redirection of flow so that a set of vessels offline and the lead-lag order can be switched. All process flow valves are full-flow ball valves with flanged connections. Process piping consists of 1.5" Schedule 40 304L pipe and butt weld fittings. A 3-D SolidWorks layout is shown in Figure 40, and a photograph of the unit is shown in Figure 41.

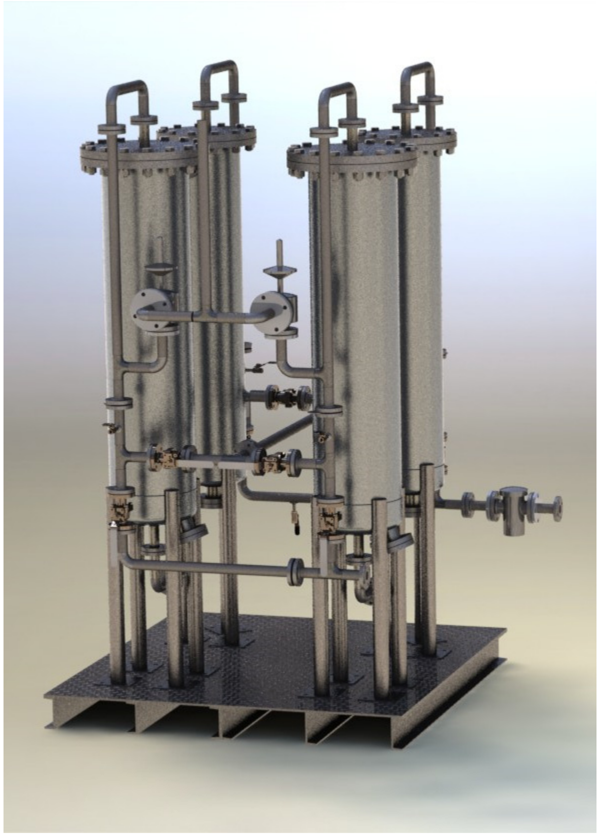


Figure 40. 3-D layout of the lead-lag prototype desulfurizer skid

Figure 41. Picture of lead-lag full-scale prototype skid.

Drain connections on each vessels are provided as 3" Class 150 flanges. To facilitate vacuum truck evacuation of the sorbent, blind flanges can be replaced with a 3" flanged ball valve and 3" cam lock fitting – all stainless. Prior to filling the vessels with sorbent, polypropylene felt was loosely packed against the face of the valve ball. During initial operation of the valve is opened for draining the ball will only contact the polypropylene, preventing premature wear or gouging of the sealing surface due to contact with the hard ceramic desulfurization media.

After the completion of the fabrication, FCE carried out shakedown testing of the prototype unit (Figure 41), which included evaluation of the flow valves, butt-welded fittings and leak testing.

4.5.3 Sorbent Production for Prototype Test Unit

We designed the sorbent loading configuration for the polishing desulfurizer beds for the conditions of a wastewater treatment plant. Biogas has high moisture content and we investigated different configurations. If there are heavy sulfur compounds such as disulfides in the gas to be cleaned, we used R2F to remove DMS and mercaptans, R5C to remove COS and R8F to remove large mercaptans and disulfides. Figure 42 shows the two configurations for biogas polishing. We decided to use the 3-sorbent configuration with R8F, R2F and R5C, all of which were produced for use in the test campaign. TDA produced and qualified the desulfurization sorbents needed for the full-scale prototype unit demonstration: 230L of SulfaTrap-R8 for bulk sulfur removal, 90L of SulfaTrap-R2B for general polishing and 30L of SulfaTrap-R5 for COS polishing and verified their performance at the bench-scale.

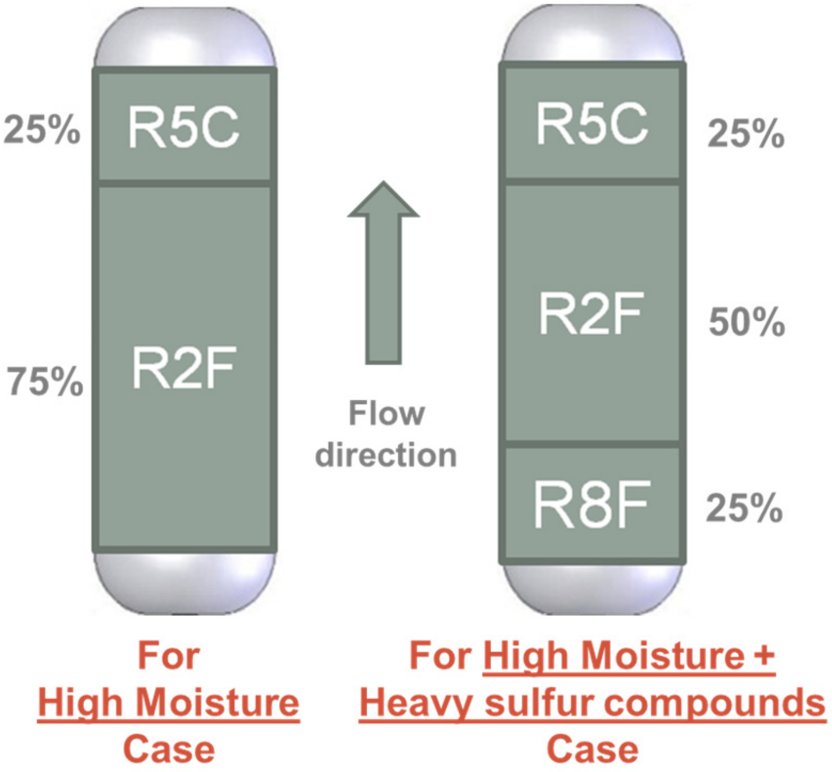


Figure 42. Suggested configurations for sorbents in desulfurizer beds.

TDA shipped the 12.1 CF of sorbents for prototype unit demonstration on September 14, 2014. This included 3.5 CF of R2F sorbent to remove DMS and mercaptans, 1.1 CF of R5C to remove COS and 7.5 CF of R8F to remove large mercaptans and disulfides.

4.5.4 Installation of Prototype Desulfurization Skid at Demonstration Site

Figure 43. Sacramento South Area Transfer Station anaerobic digester operated by Clean World.

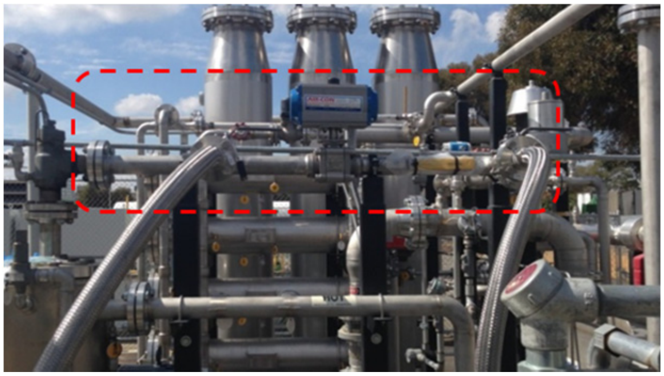


Figure 44. New Spool Piece and Tie-In Location on Gas Conditioning Skid.

A biogas site located at the South Area Transfer Station (SATS) in Sacramento, CA was selected for the demonstration (Figure 43). The site is operated by Clean World Partners and produces 50 to 100 SCFM of gas from food waste for use in waste hauling trucks. Before being compressed, the gas is passed through a bulk desulfurizer (Sulfatreat) and then through a gas conditioning skid. A location between the compressor and membranes on the gas conditioning skid was chosen as a tie-in location for the polishing skid The tie-in was accomplished by replacing an existing spool piece with a new spool piece which included a bypass valve to divert flow to and from the polishing skid (Figure 44).

The gas conditioning skid purifies methane using membrane separation and therefore operates at elevated pressure (in the range of 90 - 100psig). To minimize pressure drop, only a single stage consisting of one SulfaTrap^{TM}-R8 vessel and one SulfaTrap^{TM}-R2/R5 vessel was being used for this demonstration. In addition, the regulator on the polishing skid was removed, and the pressure relief valve on the stage being used was raised to 150 psig.

FCE shipped the polishing skid to SATS and was on-site to oversee and assist with the installation. TDA's sorbents (3.5 CF of SulfaTrap^{TM}-R2F sorbent to remove DMS and mercaptans, 1.1 CF of SulfaTrap^{TM}-R5C to remove COS and 7.5 CF of R8F to remove large mercaptans and disulfides) were loaded into the two desulfurizer beds. The system was successfully installed and was ready to process gas towards the end of September, 2014 (Figure 45). FCE commenced the field tests, which had to be halted due to leak from a hole in one of the digester tanks that prevented the plant from running. Several attempts were made at applying a patch to the tank but were unsuccessful. Because there was no biogas available to run our unit, no operating data was collected for the prototype system and the prototype unit testing on biogas (ADG) was halted and the project was completed on December 15, 2014. Since only a very small fraction of the raw biogas entered our prototype desulfurizers, we did not carry out the post characterization of the spent sorbent from our prototype tests. However, we did complete the characterization of the spent sorbent from our slipstream tests, this data was provided in Section 254.4.4.

Figure 45. Picture of Sulfur Polishing Skid Installed at SATS.

4.6 Task 7. Cost Analysis

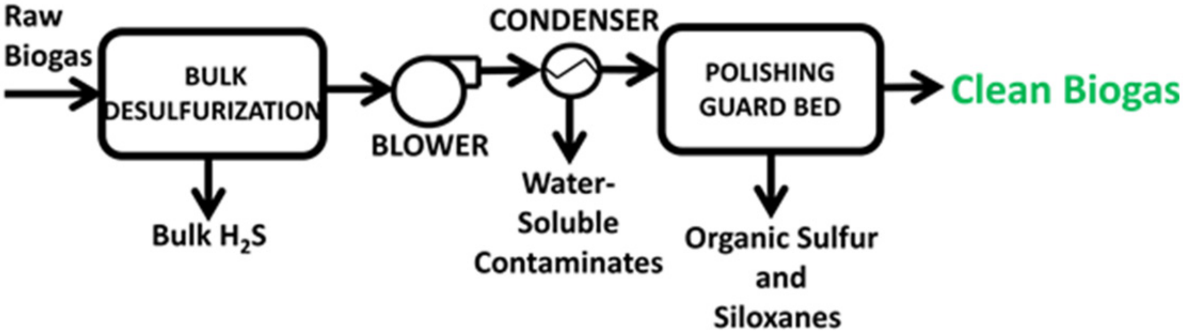


Figure 46. Biogas desulfurization process flow diagram.

Table 6. Biogas moisture level as a function of temperature and pressure.

Pressure	torr	1034	1810	2327
Pressure	atm	1.36	2.38	3.06
		P= 20 psia	P=35 psia	P=45 psia
Temp	P H2O	H2O ppmv	H2O ppmv	H2O ppmv
20	17.5	16924	9671	7522
25	23.8	23017	13153	10230
30	31.8	30754	17574	13668
35	42.2	40812	23321	18139
40	55.3	53481	30561	23769
45	71.9	69535	39734	30904

We carried out a detailed cost analysis for biogas deep desulfurization system (polisher) that removes both sulfur and siloxanes. TDA's polisher operates downstream of a bulk desulfurization system (this unit could use biological, liquid redox or solid scavengers) as shown in Figure 43. The polisher has high moisture and oxygen tolerance and has no cooling/pressurization requirements (i.e., no chillers are needed). Table 6 shows the moisture content of the biogas as a function of pressure and temperature; we see that moisture level is always high. We used this as a design basis and carried out the detailed cost analysis for both complete sulfur/siloxane control (including the bulk desulfurization) and just the sulfur/siloxane polishing. The design basis was processing 130 scfm of biogas to produce 300 kW power.

We calculated the annual sorbent replacement cost for total sulfur/siloxane control using TDA's SulfaTrap^{TM} sorbents to be $36,470, which is about 12.2% of the value of electricity generated from the biogas (300 kW at $0.12/kWh and 95% time on stream). When using TDA's SulfaTrap^{TM} sorbents for just polishing sulfur/siloxane, we calculated the annual sorbent replacement cost to be $9,960 which is about 3.3% of the value of electricity generated from the biogas (300 kW at $0.12/kWh and 95% time on stream). The details of the cost analysis are provided in Table 7.

The final task in project was to complete the cost analysis on the SulfaTrap^{TM} sorbents and compare them to sorbents currently used, and to develop a Stage 4 (next step) Plan. The current cost for sorbent used in ADG sulfur polishing systems is $48 per cubic foot of media, and on this basis TDA's sorbents are more expensive. A more useful cost to work with is on a per volume of gas treated basis, which works out to be $886/MMSCF of ADG processed for the current polishing sorbents.

Sulfatrap™ sorbents are much more expensive than the sorbents currently used for sulfur polishing per volume of gas treated (because of our sorbent's very high sulfur capacity). For the least expensive TDA sorbent, SulfaTrap^{TM}-R8, the cost on per lb basis is about an order per folume or pound of sorbent, but are far less expensive of magnitude greater than the currently used sorbent, and the SulfaTrap^{TM}-R2 and SulfaTrap^{TM}-R5 sorbents are about 2 and 5 times more expensive than the R8 sorbent, respectively. However, the SulfaTrap™ sorbents outperform the sorbents currently used. A cost analysis on unit volume of gas treated basis shows that TDA's sorbent cost $145.7/MMSCF, which is less than 1/6th the cost of polishing the ADG with the current sorbent media. For complete desulfurization (including bulk sulfur removal) the cost of desulfurization using SulfaTrap^{TM} media as both bulk desulfurization and polishing sorbent is $533.6/MMSCF. Thus, the cost of carrying out both bulk and polishing using TDA's sorbents is only 60% of the cost of polishing only using current products. In order to further validate the cost and performance of the SulfaTrap^{TM} polishing sorbents a full-scale demonstration is needed.

Table 7. Cost Analysis for Biogas desulfurization.

Flow Rate	130	SCFM									
	3705	SLPM									
	165.4	mol/min									
SulfaTrap-R7E			**SulfaTrap-R8**			**SulfaTrap-R2F**			**SulfaTrap-R5C**		
H_2S	200	ppmv	H_2S	0.200	ppmv	DMS	0.500	ppmv	COS	0.100	ppmv
			MM	0.219	ppmv						
			EM	0.714	ppmv						
			NPM	0.241	ppmv						
Total	200	ppmv	Total	1.374	ppmv	Total	0.500	ppmv	Total	0.100	ppmv
Sulfur Removal	1524.3	g/day	Sulfur Removal	10.5	g/day	Sulfur Removal	3.8	g/day	Sulfur Removal	0.8	g/day
Capacity	27.0%	wt.	Capacity	4.5%	wt.	Capacity	1.2%	wt.	Capacity	1.1%	wt.
	5645.7	g/day		232.7	g/day		317.6	g/day		69.3	g/day
Change Duration	180	days	Change Duration	180	days	Change Duration	180	days	Change Duration	180	days
Sorbent Need	1016.2	kg	Sorbent Need	41.9	kg	Sorbent Need	57.2	kg	Sorbent Need	12.5	kg
Density	0.92	kg/L	Density	0.52	kg/L	Density	0.74	kg/L	Density	0.74	kg/L
	1105	L		81	L		77	L		17	L
GHSV	201	h^{-1}	GHSV	2760	h^{-1}	GHSV		h^{-1}	GHSV	13190	h^{-1}
SulfaTrap-R7E			SulfaTrap-R8			SulfaTrap-R2F			SulfaTrap-R5C		
Sorbent Cost	$ 12.00	/L	Sorbent Cost	$ 17.50	/L	Sorbent Cost	$ 25.25	/L	Sorbent Cost	$ 96.00	/L
Cost	$ 13,255.16			$ 1,409.72			$ 1,950.49			$ 1,617.98	
Annual Sorbent Cost		$/year	% COE	300	kW						
Total Sulfur/Siloxane Control		$ 36,467	12.17%	0.12	$/kWh						
Sulfur/Siloxane Polishing		$ 9,956	3.32%	95%	Time On Stream						
				$ 299,592	Revenue from Electricity						

Stage 4 Plan:

While positive results were obtained from the slipstream testing, operating data from the full scale prototype demonstration was not obtained. Hence, in the next phase of the project, the plan is to carry out a prototype demonstration at another site and then move forward with a full-scale demonstration with TDA's SulfaTrap^{TM} polishing sorbents, which are expected to provide a cost savings of more than 80% compared with the use of conventional sorbents.

5. Summary

In this project, TDA Research Inc. (TDA) developed several low-cost (per unit volume of gas processed), high-capacity expendable sorbents that can remove both the H_2S and organic sulfur species in biogas to the ppb levels. This sorbent bed operates downstream of a bulk desulfurization system (as a polishing bed) to provide an essentially sulfur-free gas to a fuel cell (or any other application that needs a completely sulfur free feed).

The novel sulfur sorbents developed by TDA have been tested in the laboratory at both TDA and FuelCell Energy (FCE), and at the pilot scale to demonstrate their performance for anaerobic digester gas (ADG) fueled fuel cell applications. The tests at FCE were conducted in a vessel with lower L/Ds (1.3 and 2.6) than the recommended L/D of 4: as a result the loadings before breakthrough in the tests at FCE were lower than the tests at TDA with a L/D of 4 or higher.

Once the sorbent development and bench-top testing was complete, TDA built a fully automated test skid to support the slipstream tests. Both SulfaTrap^{TM}-R8 and SulfaTrap^{TM}-R7 were tested successfully, and they provided complete removal of the sulfur compounds. The sorbents achieved high capacities. SulfaTrap^{TM}-R8 adsorbed over 18% sulfur by during the slipstream tests while the SulfaTrap^{TM}-R7 never reached breakthrough (the loading had reached 9.8% sulfur by wt. before the test was stopped). We carried out two slipstream demonstrations at EMWD and one at Tulare waste water treatment plant. In these tests, we have demonstrated the ability of the sorbents to remove the sulfur compounds and siloxanes with very high capacity and removal efficiency.

After the slipstream tests were complete TDA and FCE designed, and manufactured a full scale prototype desulfurization skid capcble of treating 82 scfm biogas, suitable for a DFC300 (300 kW) power plant, and then shipped the unit to the Sacramento South Area Transfer Station (SATS) for testing. The system was designed in a lead/lag configuration, allowing sorbent change-outs to occur while in operation. Each of the beds 12 cu ft. in volume and was designed for three months of operation.

Three Sulfatrap™ sorbents, R2B, R5D and R8 were selected for the prototype system, based on an FCE-generated ADG specification. Each lead/lag stage consisted of an R8 vessel and an R2/R5 vessel. The R8 vessel was positioned upstream of the R2/R5 vessel for removal of H_2S and mercaptans, allowing the R2 and R5 sorbents to be conserved for DMS and COS, respectively.

The prototype system was installed at the Sacramento South Area Transfer Station (SATS) in Sacramento, California. Unfortunately, the prototype system was never tested because leaks were discovered in the digester tanks at the site, and there was therefore no gas available to run our unit. Several attempts were made to repair the tanks but were unsuccessful, and the SATS was never able to supply us with gas.

We also assessed the feasibility of using SulfaTrap™ sorbents in the commercial DFC power plants and calculated the annual sorbent replacement cost for total sulfur/siloxane control using TDA's SulfaTrap^{TM} sorbents to be $36,470, which is about 12.2% of the value of the electricity generated from biogas (300 kW at $0.12/kWh and 95% time on stream). When using TDA's SulfaTrap^{TM} sorbents for just polishing sulfur/siloxane, we calculated the annual sorbent replacement cost to be $9,960 which is only about 3.3% of the value of electricity generated from biogas (300 kW at $0.12/kWh and 95% time on stream).

The cost for sorbent currently used in ADG sulfur polishing systems is $48 per cubic foot of media, but a more useful comparison is on a per volume of gas treated basis (before the sulfur breaks through the bed). In this case, the cost of sulfur removal is $886/MMSCF of ADG processed with the current sorbent, while the cost of using SulfaTrap™ sorbents as a polishing sorbent is $145.7/MMSCF, thus the cost of using our sorbent is less than 1/6th of the cost of using the current sorbent media used for polishing. For complete desulfurization (including bulk sulfur removal) the cost of desulfurization using SulfaTrap™ media as both bulk desulfurization and polishing sorbent is $533.6/MMSCF. Thus, we can provide both bulk and polishing sulfur removal at only 60% of the cost of doing only polishing with the current media.

While we successfully completed the slipstream testing and demonstrated the technical viability of the technology, the operating data from the full scale prototype demonstration was not complete. Hence, in the future work, we recommend to carry out the full-scale prototype demonstration at another site.