

Bio-Fueled Solid Oxide Fuel Cells

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Overview

Timeline

- SBIR Phase III Project start: 10/1/2010
- Transferred to FCTO Q3 FY2011
- Project end: 9/30/2014

Budget

- Total Funding Spent*: \$1,324,680
- Total Project Value: \$1,617,970
- Cost Share Percentage: None

* as of 3/31/2014

Barriers

- **Barriers addressed**
 - Biogas contains harmful trace contaminants (such as organic sulfur species and siloxanes) that must be removed to less 10 ppbv
 - Impurities present in biogas poison the catalysts and SOFC stacks reducing their efficiency and lifetime

Partners

- Interactions/ collaborations
 - FuelCell Energy - SOFC Skid, Field Tests
 - SMUD⁺ - Demonstration Site
 - Infilco Degremont - Demonstration Site
- Project lead
 - TDA - Biogas Cleanup Sorbent & System; Field tests; Cost Analysis

⁺ SMUD – Sacramento Municipal Utility District

Project Objectives – Relevance

- **Overall Objective**
 - **Demonstrate the operation of a bio-fueled SOFC in a waste-to-energy application**
- **Specific Objectives**
 - **Develop and demonstrate the efficacy of a sorbent-based gas clean-up system to remove harmful impurities from biogas that will meet the cleanliness requirements of SOFC stacks**
 - **Demonstrate operation of a 2 kW_e biogas fueled SOFC stack integrated with a biogas cleanup system in a waste-to-energy application**
 - **Demonstrate the economic viability of our biogas cleanup technology**

FY 2014

- **Our partner FCE has completed the fabrication of the 2 kW_e SOFC module, which is being tested at their facility using simulated gases**
- **TDA has completed the design of the interface skid between the SOFC and biogas cleanup skid**

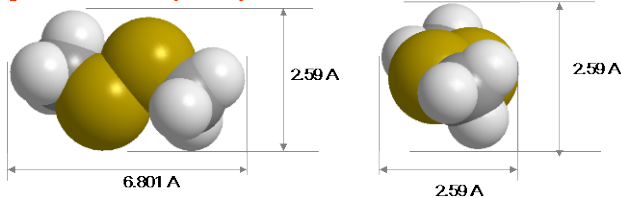
Work Plan – Relevance

Task	Objectives
1. Sorbent Production and Scale-up	Optimize the sorbent formulations to remove all of the harmful contaminants in biogas and scale-up the production of the sorbent
2. Gas Cleanup Demonstration System	Design and build a gas cleanup demonstration system for a 2 kW _e SOFC demonstration system that operates on biogas from wastes
3. SOFC Test Module	Build a 2 kW _e SOFC test system for the slip stream demonstrations with biogas
4. Shakedown Tests	Test the integrated 2 kW _e SOFC system (both the cleanup system and the SOFC) in-house prior to biogas site deployment
5. Slipstream Demonstrations	TDA and FCE to jointly perform one field demonstration (revised from two due to funding reduction) of the integrated system, each 6 months using a different slipstream of biogas generated from wastes
6. Engineering Analysis	Carry out a detailed engineering and cost analysis to assess the economic viability of the new sorbent technology for biogas fed fuel cell power plants
7. Business Development	Develop a marketing and commercialization strategy to advance the technology and to turn the concept into a practical product
8. Reporting	Submit quarterly and annual progress reports and a comprehensive final report at the end of the project

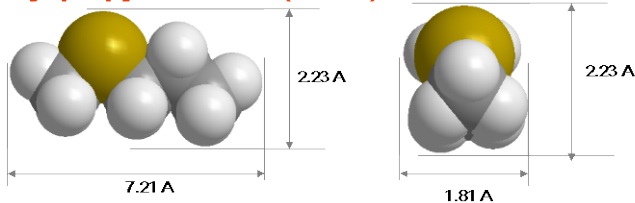
Approach – Contaminants in Biogas

- ADG contains high concentrations of sulfur and other contaminants (e.g., siloxanes and halides) that are detrimental for the fuel cell

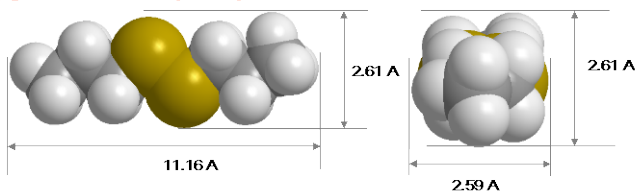
Methyl di-sulfide (MDS)



Methyl propyl di-sulfide (MPDS)



Propyl di-sulfide (PDS)



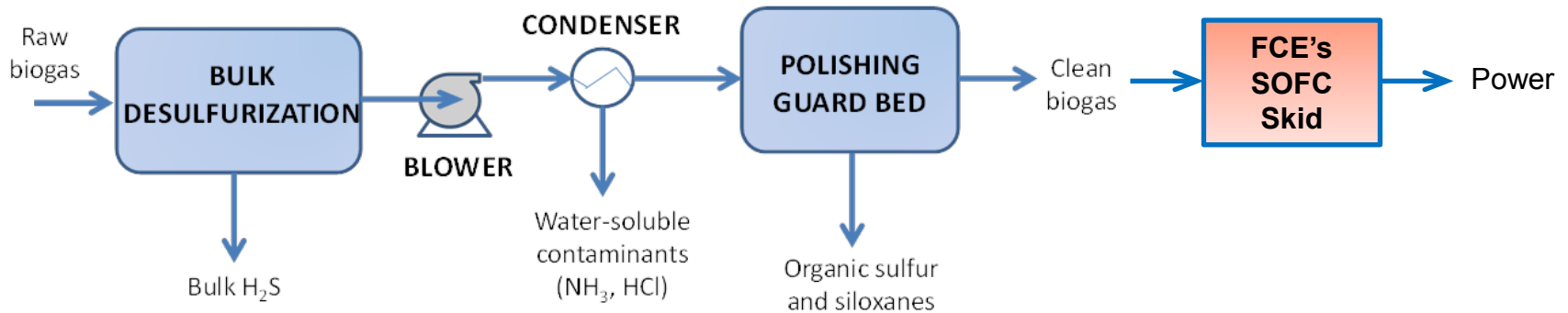
- Current technologies lack the capability to remove complex biogas sulfur species such as organic di- and tri-sulfides

Typical ADG gas composition after bulk sulfur removal

Gas Pressure	5-20 iwc, positive
Gas Temperature	110°F (max)
Gas Composition, by volume	60% CH ₄ , 30% CO ₂ 8% N ₂ and 2% O ₂
Moisture Content	Saturated
Siloxanes	
Total	4.5 ppmv
D4	0.4 ppmv
D5	4.1 ppmv
Halogens	1 ppmv
Sulfur	
Hydrogen sulfide	200 ppmv
Carbonyl sulfide	5 ppmv
Carbon disulfide	1 ppmv
Dimethyl sulfide	5 ppmv
Dimethyl disulfide	5 ppmv
Other disulfides	2 ppmv
Methyl mercaptan	5 ppmv
Ethyl mercaptan	1 ppmv
BTX	less than 1 ppmv

Approach - Biogas Clean-up System

TDA's Biogas Clean-up System Integrated with a SOFC



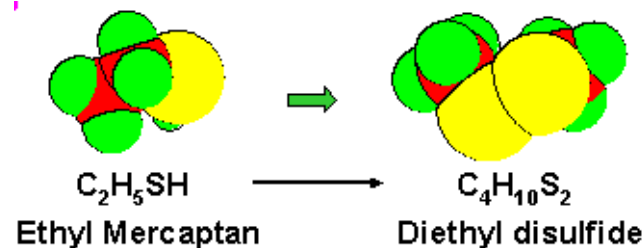
Clean-up System

Fuel Cell

- TDA's approach is to use an ambient temperature gas clean-up system to remove all contaminants to ppbv levels
- The purification system includes a bulk desulfurization system (regenerable) followed by a polisher
- Key requirement for the sorbent is tolerance to high levels of moisture (biogas is expected to have at least 4,000 ppmv moisture) to eliminate the energy penalty for:
 - Biogas compression
 - Chilling

Biogas Cleanup – Approach

- **TDA’s biogas cleanup system uses TDA proprietary bulk desulfurizer and an additional polishing bed**
 - We decided to use our own bulk desulfurizer as commercial systems are shown to contribute to the formation of very complex sulfur species that are difficult to remove, such as the di- and tri-sulfides



- **Polishing bed is designed to remove siloxanes and the organic sulfur species**

Field Test Plans

- **Field Tests will carried out with our biogas desulfurization sorbents**
 - Cal-DeNier Dairy, Grand Valley, CA
 - 2 CFM – Demonstration of complete gas clean-up skid with 2 kW_e SOFC

Accomplishments & Progress

Task 1: Sorbent Production and Scale-up – Completed 09/30/2011

- Optimized sorbent to remove COS in addition to other sulfur species
- Increased production batch size from 20 mL to 35 L

Task 2: Gas Cleanup Demonstration System – Completed 02/29/2012

- Fabricated a skid-mounted field deployable prototype clean-up system

Task 3: SOFC Test Module – on-going

- FCE completed the fabrication of the 2 kW_e SOFC test skid
- Shakedown tests using simulated gas are under progress

Task 4: Shakedown Tests – Completed 12/31/2012

- Completed the shakedown testing of the biogas cleanup system

Task 5: Slipstream Demonstrations

- Interface requirements between the biogas cleanup skid and SOFC skid has been identified and the design of the interface skid was completed
- TDA in collaboration with SMUD completed an assessment of site modifications needed at Cal DeNier Dairy

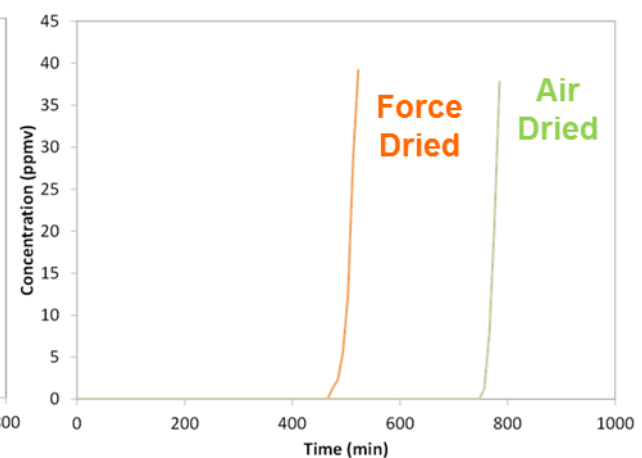
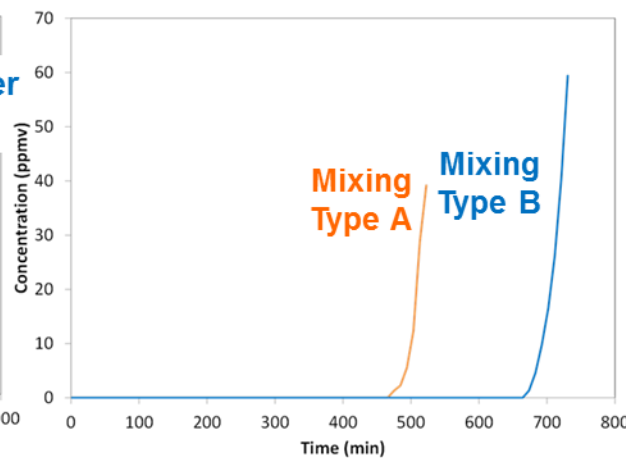
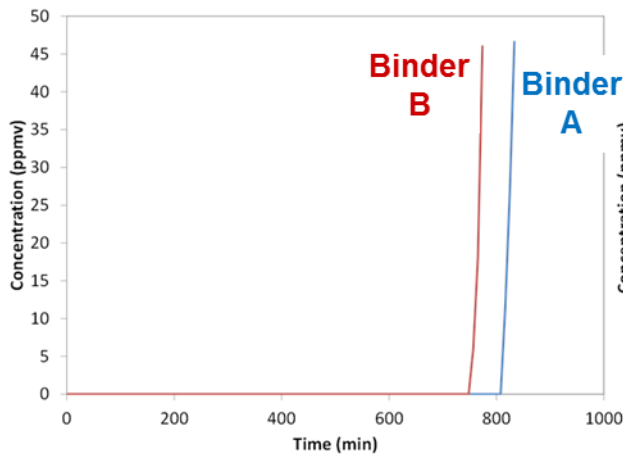
Sorbent Optimization – Accomplishments & Progress

Impact of Binder Type

Impact of Mixing Technique

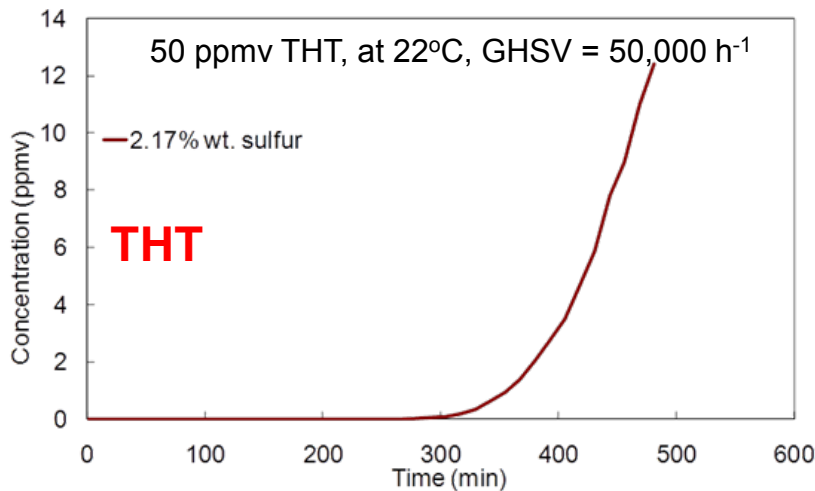
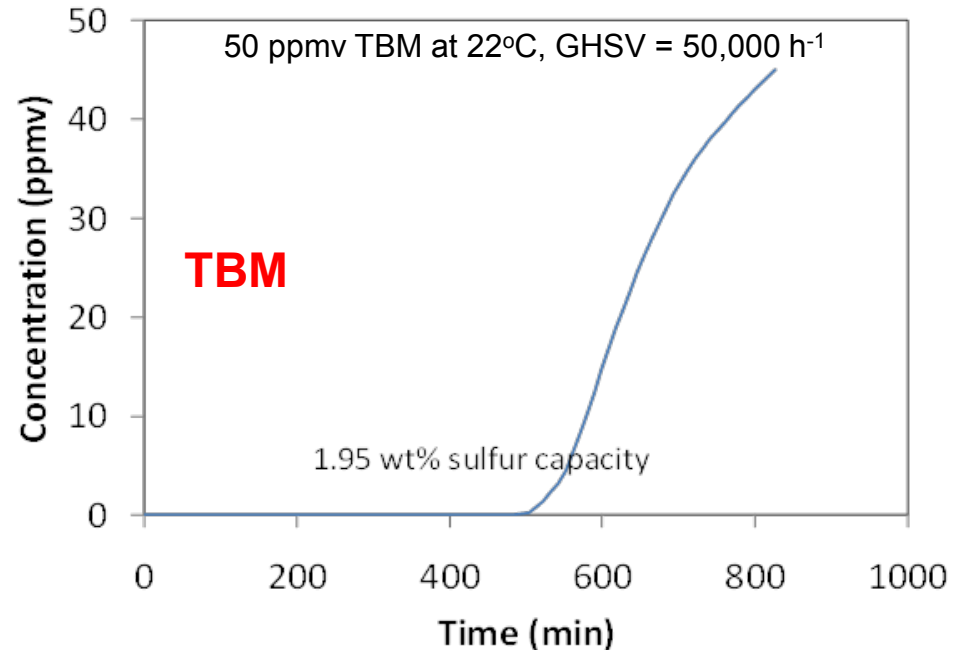
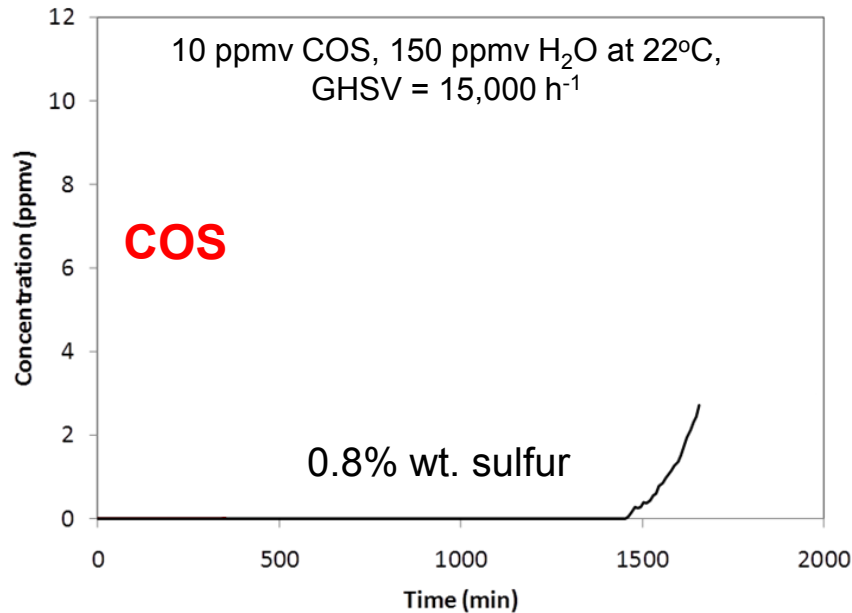
Impact of Drying Condition

T=21°C, 2,000 ppmv H₂S, 2.2% H₂O, 57.8% CH₄, 40% CO₂, GHSV = 4000 h⁻¹



- Optimized our sorbent formulations to remove all the organic and inorganic sulfur species including mercaptans, thiophenes, COS and H₂S from ADG
- Optimized the binder composition, mixing technique and drying conditions for our biogas desulfurization sorbent
- Optimized the physical properties of the sorbent such as surface area, density, and mechanical strength

Removal of Other Sulfur Compounds – Accomplishments & Progress



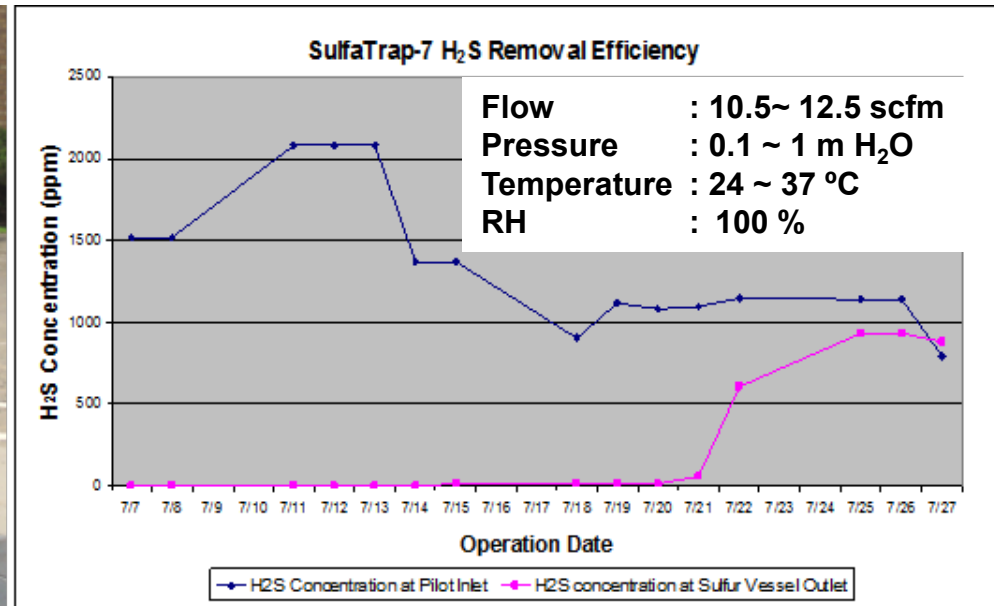
- **We optimized our sorbent formulations to remove all the organic and inorganic sulfur species such as H₂S, COS, mercaptans (TBM) and thiophenes (THT) from the ADG**

Expendable Bulk Sorbent Field Test – Accomplishments & Progress

12 CFM gas clean-up skid built
by TDA for Degremont



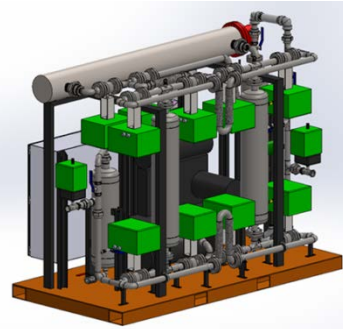
Field Test Results for our Expendable Bulk
Desulfurization Sorbent SulfaTrap™-R7



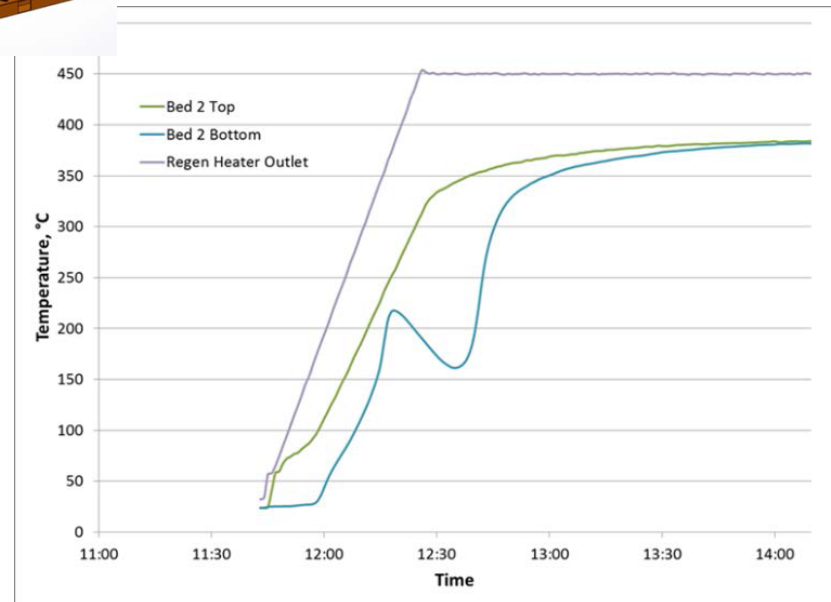
- Infilco Degremont carried out field tests with our expendable sorbent at Nasedmond Wastewater Treatment Plant, Suffolk, VA at no-cost to DOE project
- TDA sorbent achieved 17.5% wt. sulfur capacity (lb of sulfur per lb sorbent)

Biogas Cleanup Skid – Accomplishments & Progress

TDA's Biogas Cleanup Skid



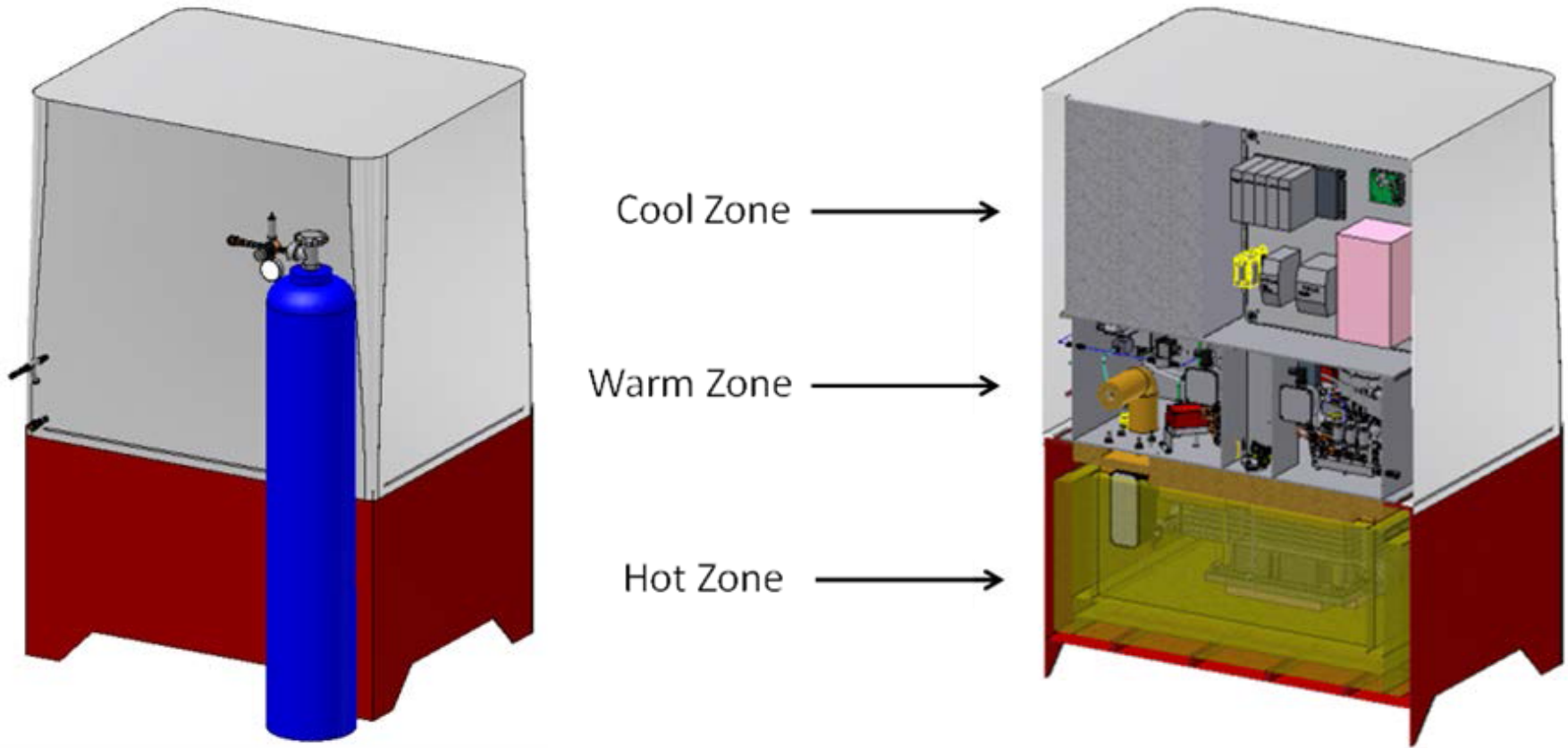
Shakedown Test with Sorbent



- Completed the fabrication and shakedown testing of our skid-mounted field-deployable prototype biogas clean-up system

SOFC Test Module – Accomplishments & Progress

3-D layout of FCE's SOFC Test Skid



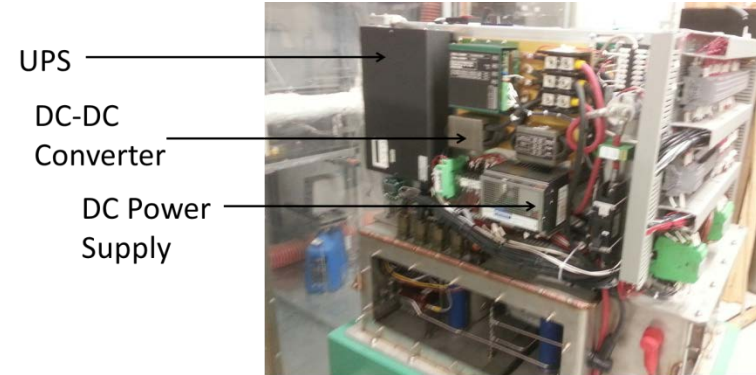
- 3-D layout of FCE's 2 kW_e SOFC test skid for biogas

SOFC Test Module – Accomplishments & Progress

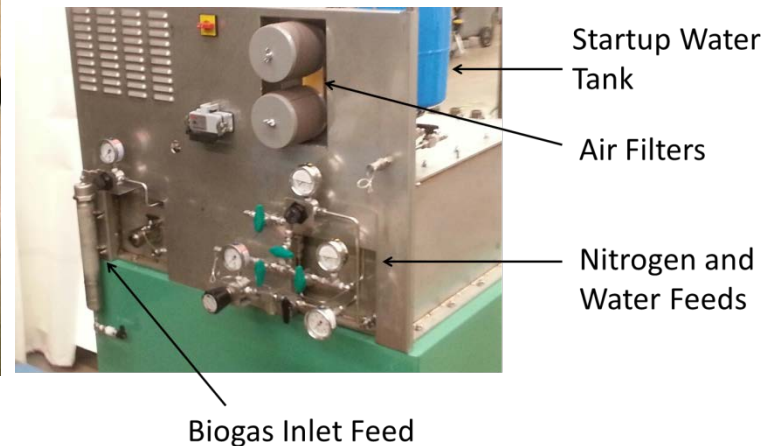
Integrated SOFC System



Electrical BOP

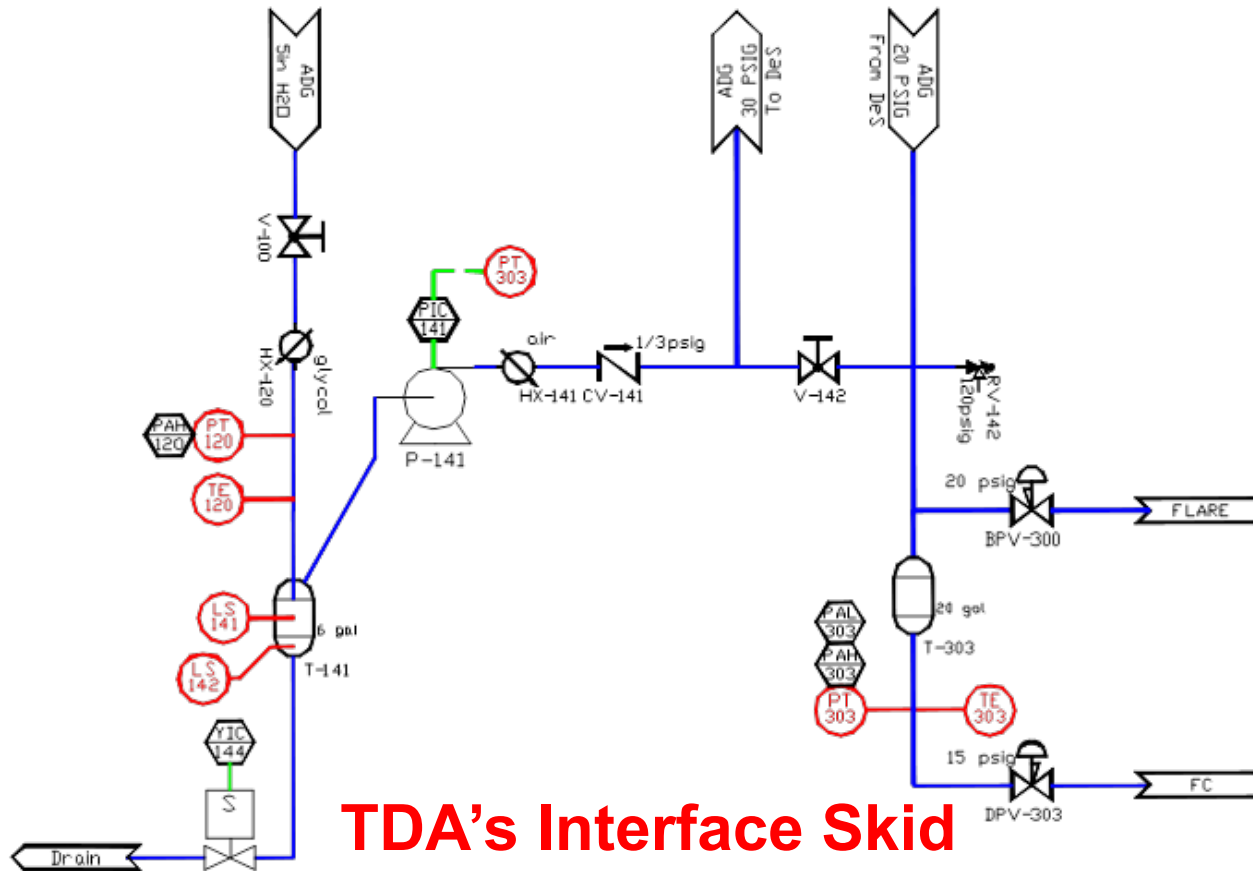


Mechanical Interconnections



- FCE completed fabrication of the integrated 2 kW_e SOFC test skid

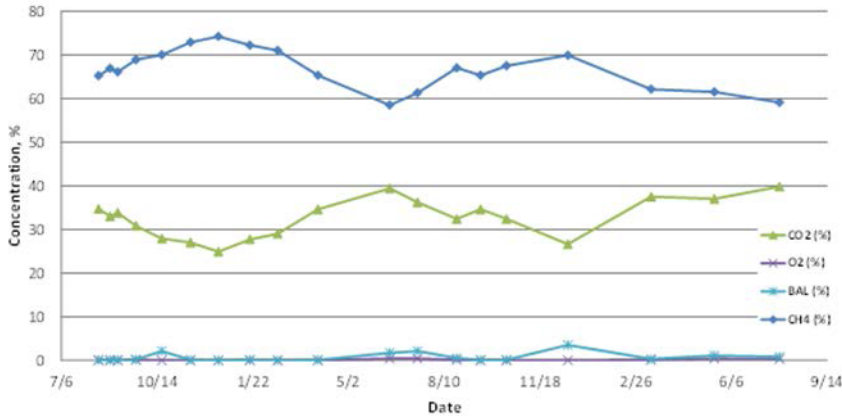
Biogas Cleanup Skid – Accomplishments & Progress



- Completed the design of the interface skid that connects the biogas cleanup skid to the SOFC skid

Field Test Site - Cal-DeNier Dairy Farm – Accomplishments & Progress

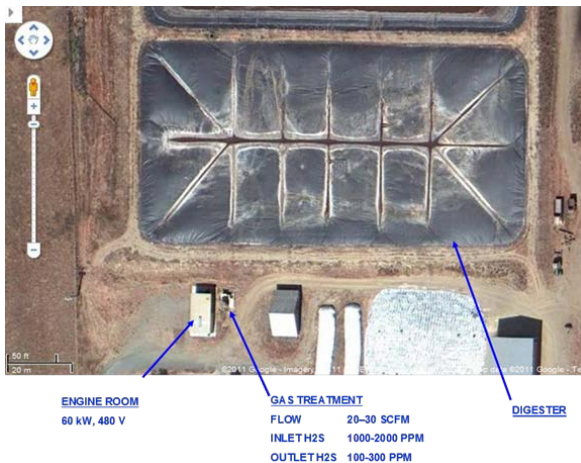
Biogas Composition



H₂S Concentration before and after existing microbial sulfur cleanup system



Cal DeNier Dairy Farm Layout



Demonstration Site Area



- Site modifications are identified and being implemented

Commercialization – Accomplishments

- **At the end of SBIR Phase 2 project, TDA developed the SulfaTrap™ line of sorbents initially for desulfurization of natural gas for fuel cell applications**
- **Since 2008 sorbent has been supplied in increased quantities, 42 tons in 2012, 65 tons expected in 2013 and expected to be 100 tons in 2014 for natural gas-fired fuel cells**
- **In this project these sorbents are applied for biogas applications and will be demonstrated integrated with a SOFC**
- **In 2012, TDA spun-off a separate business, SulfaTrap, LLC to supply these sorbents for the fuel cell market**
- **The spin-off was fully funded in February 2013 and began operations**

Response to Previous Year Reviewer's Comments

- **The project was not reviewed in FY 2013; responses to FY2012 comments included:**

Biogas fueled SOFCs are not common

- SOFC are known to provide the highest possible net efficiency for Combined Heat and Power (CHP) applications. Hence there is a need to demonstrate successful operation of SOFC on biogas and this project will serve the need.
- As this will be one of the first demonstrations of SOFC in biogas there are challenges that will be encountered; we have FCE as our partner who is capable of handling them
- FCE is the current market leader in using fuel cells (MFCs) for biogas application.

Comparison Against existing off-the-shelf- Cleanup Solutions

- TDA's Sorbent both bulk desulfurization and polishing sorbents achieve significantly higher capacity for H₂S and complex organic sulfur species respectively. The results are included in this Year's review.
- TDA's sorbents remove the complex sulfur compounds such as disulfides and siloxanes down to less than 10 ppbv needed for fuel cells compared to less than 100 ppbv for commercial sorbents
- Infilco Degremont carried out field tests with our expendable bulk desulfurization sorbent and achieved better capacities than commercial sorbents

Collaborations

LPG Desulfurizers



Packaged Desulfurizers



Lead/Lag Desulfurizer



- TDA provided various desulfurization systems and sorbent materials for different applications
- Received several enquiries about our sorbents for desulfurization of biogas
- Attended various trade shows including FC Expo 2014 and GasTech 2014



Remaining Challenges and Barriers

FY 2014

- **Successful demonstration is key for wide spread utilization of the SulfaTrap™ sorbents in biogas applications**
 - Integration of the biogas cleanup skid and the SOFC skid
 - Successful field demonstration with biogas at Cal DeNier Dairy Farm
 - Detailed Cost Analysis and Economic Assessment of the Biogas fueled SOFC system

Future Work

FY 2014

- **Carry out field installations of the biogas cleanup and SOFC test skids at Cal DeNier Dairy farm**
- **Carry out a 3 month long field test with the integrated biogas fueled SOFC system at Cal DeNier Dairy Farm; possible 2nd demonstration at food packaging plant.**
- **Carry out a detailed engineering and cost analysis to assess the economic viability of the new sorbent technology for biogas fed fuel cell power plants**
- **Develop marketing and commercialization strategy to advance the technology and to turn the concept into a practical product**

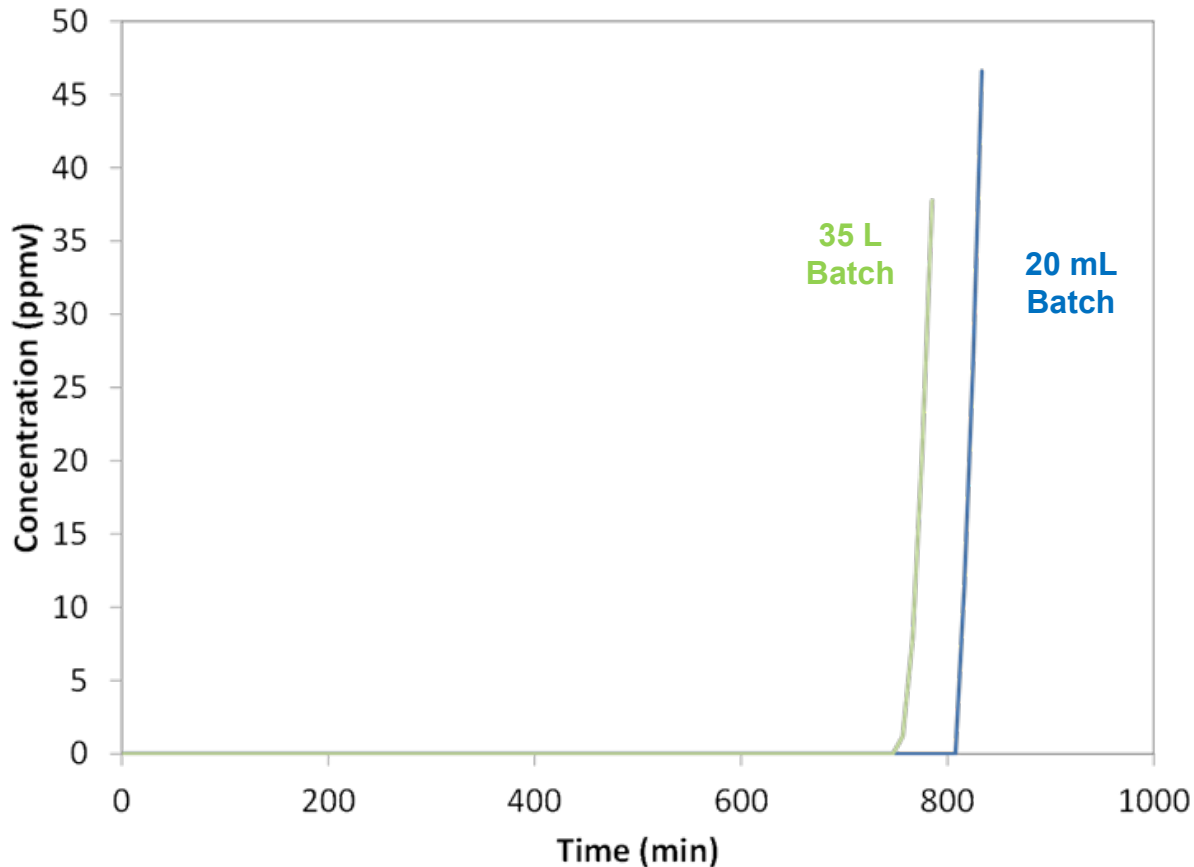
Project Summary

- **Relevance** - Promotes use of fuel cells in waste-to-energy applications by eliminating one of the greatest barrier; the contaminants in biogas that are harmful to the fuel cell
- **Approach** -
 - TDA leverage its experience with sulfur removal for natural gas to systematically develop an universal gas cleanup system for biogas
 - FCE will leverage their experience in operating MCFCs using biogas to develop a robust and efficient biogas-fired SOFC
 - TDA, FCE and SMUD will carry out field tests using actual biogas to assess the operation of the integrated system
- **Accomplishments**
 - Spun-off a separate business SulfaTrap LLC to supply these sorbents to the fuel cell market for natural gas and LPG desulfurization
 - Completed sorbent scaleup, built the gas cleanup skid, completed fabrication of the SOFC skid, Site identified and modifications needed are being carried out, an initial demo at WWTF is successfully carried out
- **Collaboration** –Partnerships with FCE, SMUD, Degremont; contacts established and providing sorbent samples for evaluations to other fuel cell developers
- **Future Work** - Complete field test and economic analysis

Technical Back-Up Slides

Sorbent Production Scale-up – Accomplishments & Progress

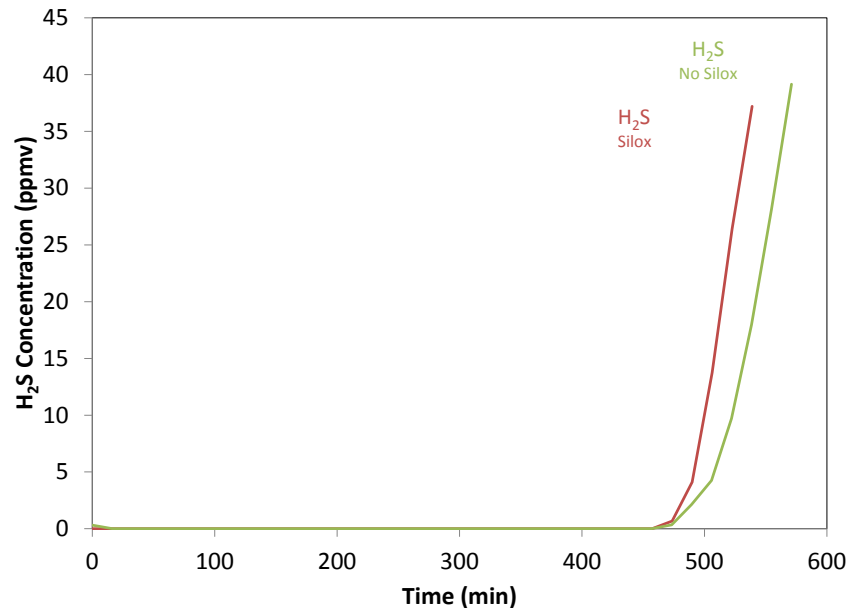
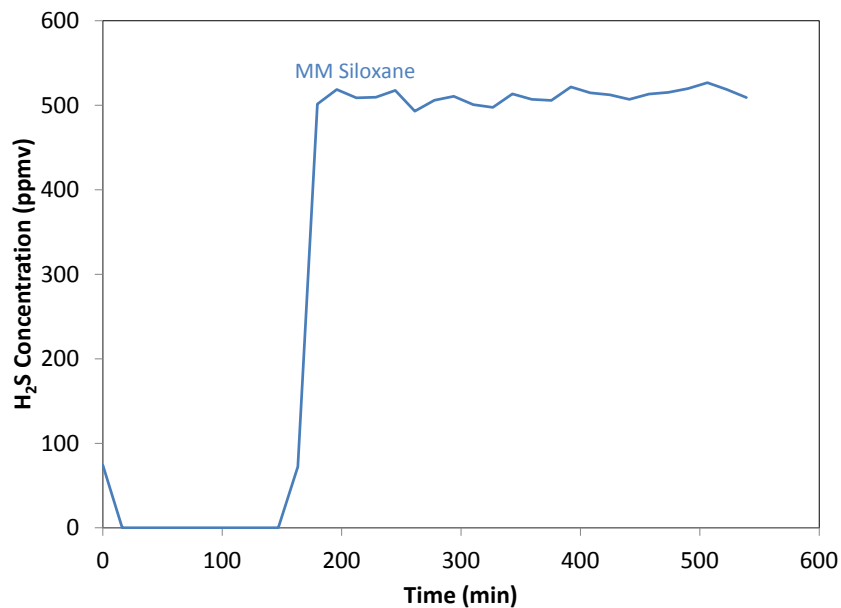
T=21°C, 2,000 ppmv H₂S, 2.2% H₂O, 57.8% CH₄, 40% CO₂, GHSV = 4000 h⁻¹



- We increased production batch size for our sorbent from 20 mL to 35 L with virtually no change in performance

Multi-contaminant Removal – Accomplishments & Progress

**SulfaTrap™-R8 Sorbent, T = 20°C, 2.2% H₂O, 7.5% N₂, 36.1% CO₂, 54.2% CH₄,
MM siloxane = 500 ppmv, H₂S = 75 ppmv, GHSV = 12,000 h⁻¹**



- **SulfaTrap™-R8 sulfur sorbent achieves a high siloxane capacity of greater than 21.5% wt. siloxane capacity and a sulfur loading of 2.15% wt.sulfur**

