

# Bio-Fueled Solid Oxide Fuel Cells

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**Project ID**  
**PD091**

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# Overview

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## Timeline

- Start date: 10/1/2010
- End date: 9/30/2013
- Percent complete: **45%**

## Budget

- Total project funding
  - DOE share: \$ 1,944,516
  - Contractor share: \$ 0
- Funding received in FY11
  - \$ 684,781
- Planned funding for FY12
  - \$706,764

## Barriers

- Barriers addressed
  - Anaerobic digester biogas generated from wastes has harmful trace poisons (such as organic sulfur species and siloxanes) that must be removed
  - Impurities present in biogas poison the catalysts and stacks of SOFCs reducing their efficiency and lifetime
- Targets
  - Provide ultraclean biogas to fuel cells
  - Increase reliability and efficiency of electricity generation using biogas generated from wastes

## Partners

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

\* SMUD – Sacramento Municipal Utility District

# Relevance - Objectives

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- **Overall Objective**
  - Provide ultraclean biogas to demonstrate the operation of a high efficiency SOFC stack in a waste-to-energy application
- **Specific Objectives**
  - Develop and demonstrate a high capacity sorbent to remove sulfur species from biogas, thereby providing an essentially sulfur-free biogas that meets the cleanliness requirements of SOFC fuel cells
  - Demonstrate operation of a 2 kW<sub>e</sub> biogas fueled SOFC stack integrated with a biogas cleanup system, in two different waste-to-energy applications
  - Demonstrate the economic viability of our sorbents to cleanup biogas

# Relevance – Work Plan

Task	Objectives
1. Sorbent Production and Scale-up	Optimize the sorbent formulations to remove all of the harmful contaminants in biogas (to ppb levels) 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 <sub>e</sub> SOFC demonstration system that operates on biogas from wastes
3. SOFC Test Module	Build a 2 kW <sub>e</sub> SOFC test system for the slip stream demonstrations with biogas
4. Shakedown Tests	Test the integrated 2 kW <sub>e</sub> 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 two field demonstrations 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 – Biogas Composition

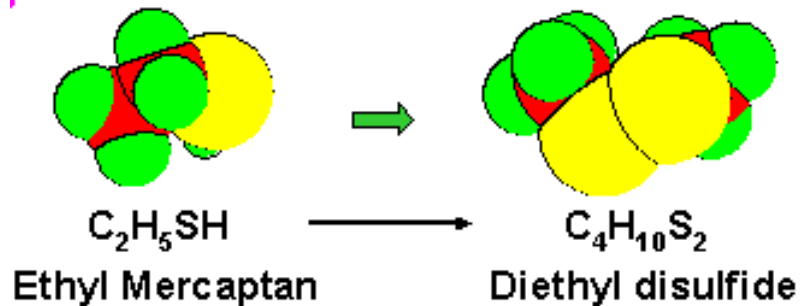
- **Typical ADG gas composition after bulk sulfur removal**

Gas Pressure	5-20 iwc, positive
Gas Temperature	110°F (max)
Gas Composition, by volume	60% CH <sub>4</sub> , 30% CO <sub>2</sub> 8% N <sub>2</sub> and 2% O <sub>2</sub>
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

- **ADG contains high concentrations of sulfur and other contaminants (e.g., siloxanes and halides) that are detrimental for the fuel cell**
  - The main source of the volatile sulfur compounds in bio-solids is the degradation of proteins such as the amino acid methionine and cysteine, forming H<sub>2</sub>S and MeSH
- **Sulfur is a well-known poison for fuel cell electrocatalysts**
- **Hence, sulfur and siloxanes need to be removed to ppb levels so that biogas can be used in fuel cells**

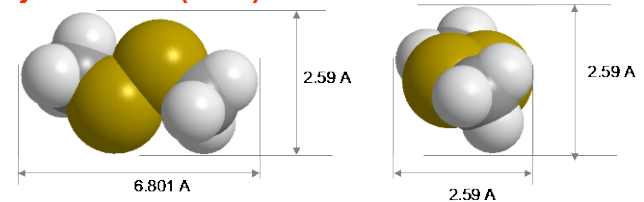
# Approach – Contaminants in Biogas

- Several desulfurization technologies are available to remove  $H_2S$ , but these are not very effective for organic sulfur compounds
  - Mercaptans constitutes up to 500 ppmv sulfur in wastewater plants
- Iron sponge and iron-oxide based adsorbents are used to remove  $H_2S$
- Not only these are ineffective for mercaptan removal, but iron oxides in the presence of high concentrations of water catalyzes the formation of complex sulfur compounds

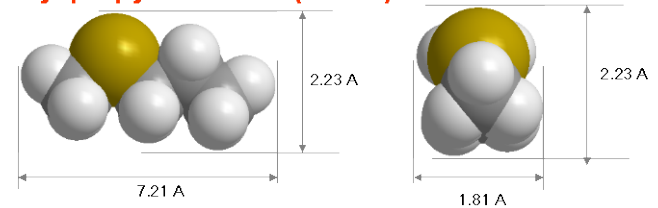


- These sulfur species may then be methylated to form higher sulfides (e.g.,  $Me_2S$ ) or can be oxidized to form higher sulfides ( $Me_2Se_2$ ), all of which are harmful

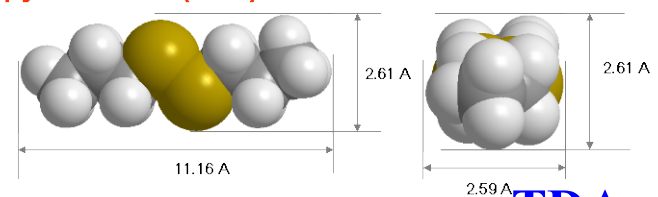
Methyl di-sulfide (MDS)



Methyl propyl di-sulfide (MPDS)

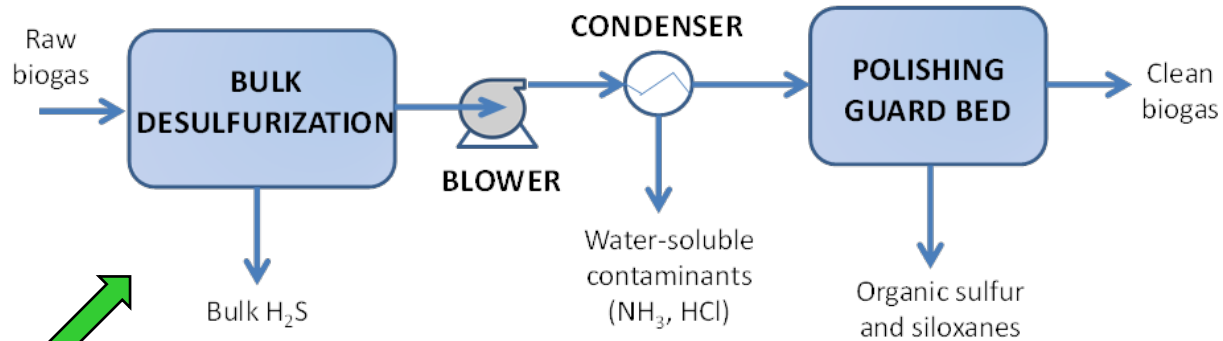


Propyl di-sulfide (PDS)



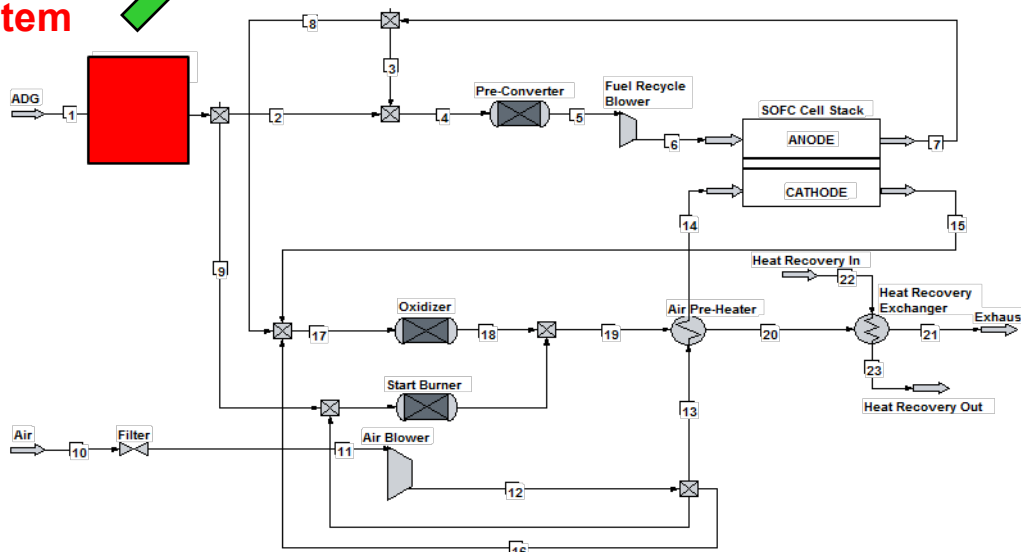
# Approach – Biogas Cleanup

## TDA's Biogas Clean-up System



Clean-up System

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



# Approach – Biogas Cleanup

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- **TDA's biogas cleanup system uses our own bulk desulfurizer and an additional polishing bed**
  - We decided to use our own bulk desulfurization system because we have found that some of the commercially available bulk sulfur removal systems are contributing to the formation of very complex sulfur species that are difficult to remove, such as the di- and tri-sulfides
- **Bulk desulfurization field tests will evaluate two different types of sorbents**
  - Expendable and Regenerable Sorbent
- **Polishing bed is designed to remove siloxanes and the organic sulfur species**
- **FCE is developing a 2 kW<sub>e</sub> SOFC test module to demonstrate the operation of the higher efficiency SOFC using biogas from wastes**

## Field Test Plans

- **The Field Tests are being 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<sub>e</sub> SOFC
  - Sacramento Wastewater Treatment Plant – 2 CFM – Demonstration of complete gas clean-up skid with 2 kW<sub>e</sub> SOFC



# Accomplishments & Progress

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

- **Optimized our sorbent formulation to remove all the organic and inorganic sulfur species including mercaptans, thiophenes, COS and H<sub>2</sub>S from the ADG down to ppb levels**
- **Increased the production batch size from 20 mL to 35 L**
- **Optimized the binder composition and drying conditions for our biogas desulfurization sorbent**

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

- **Completed the fabrication of our skid-mounted field-deployable prototype biogas clean-up system**

## **Task 3: SOFC Test Module**

- **FuelCell Energy (FCE) has completed the design of the SOFC Test Skid and begun the integration of the 2 kW<sub>e</sub> SOFC stack on a test skid**

## **Task 4: Shakedown Tests – In Progress**

- **In the next period, TDA will begin shakedown testing of the biogas cleanup system**

## **Task 5: Slipstream Demonstrations**

- **FCE has initiated the subcontract with SMUD and SMUD has provided the historical ADG gas analysis data for the Cal-DeNier Dairy Farm**

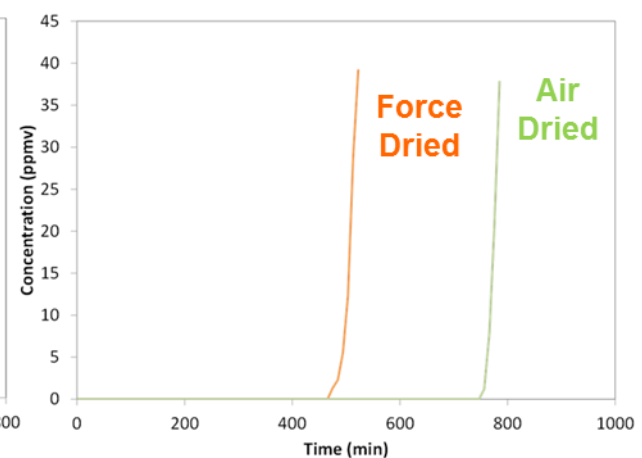
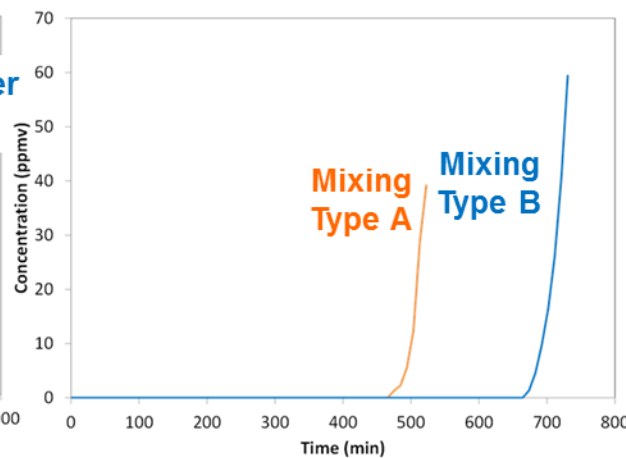
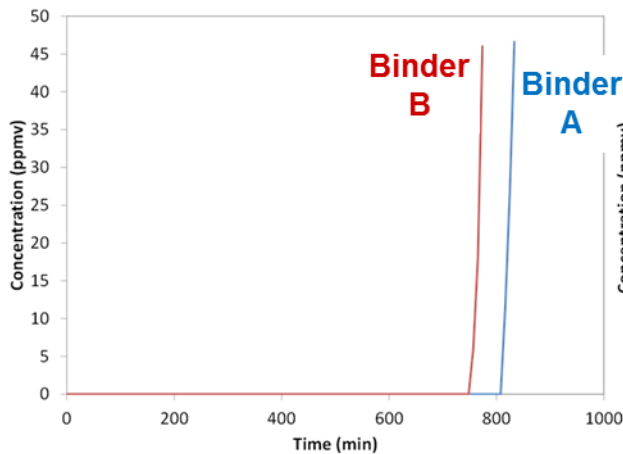
# Sorbent Optimization

## Impact of Binder Type

## Impact of Mixing Technique

## Impact of Drying Condition

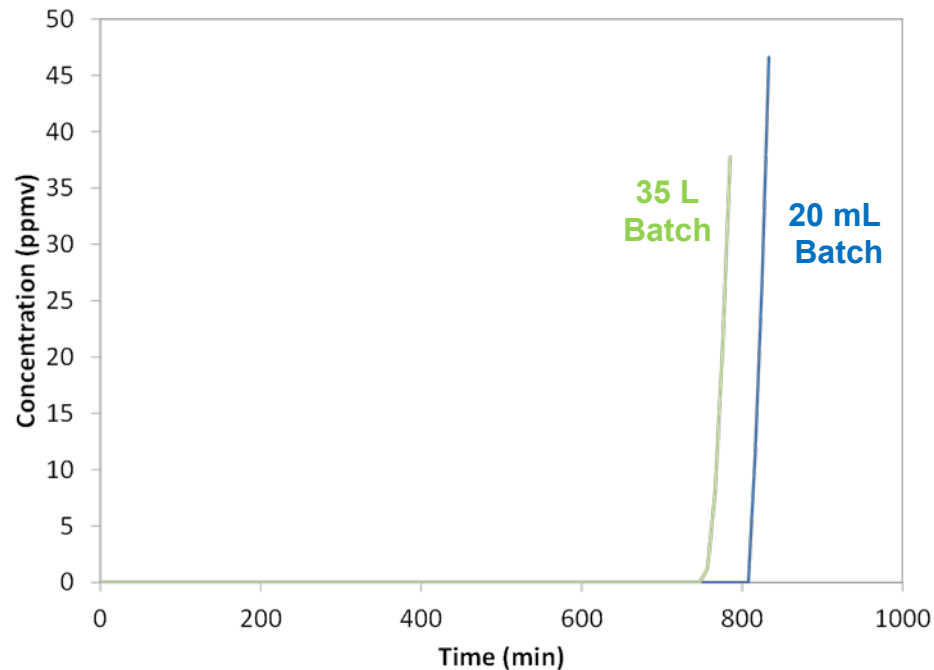
T=21°C, 2,000 ppmv H<sub>2</sub>S, 2.2% H<sub>2</sub>O, 57.8% CH<sub>4</sub>, 40% CO<sub>2</sub>, GHSV = 4000 h<sup>-1</sup>



- Optimized our sorbent formulations to remove all the organic and inorganic sulfur species including mercaptans, thiophenes, COS and H<sub>2</sub>S from the 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

# Sorbent Production Scaleup

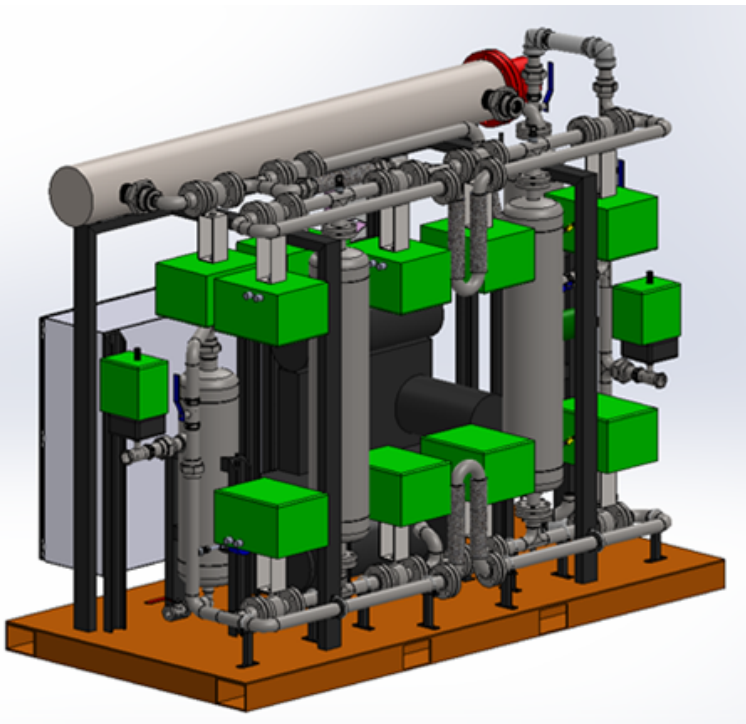
T=21°C, 2,000 ppmv H<sub>2</sub>S, 2.2% H<sub>2</sub>O, 57.8% CH<sub>4</sub>, 40% CO<sub>2</sub>, GHSV = 4000 h<sup>-1</sup>



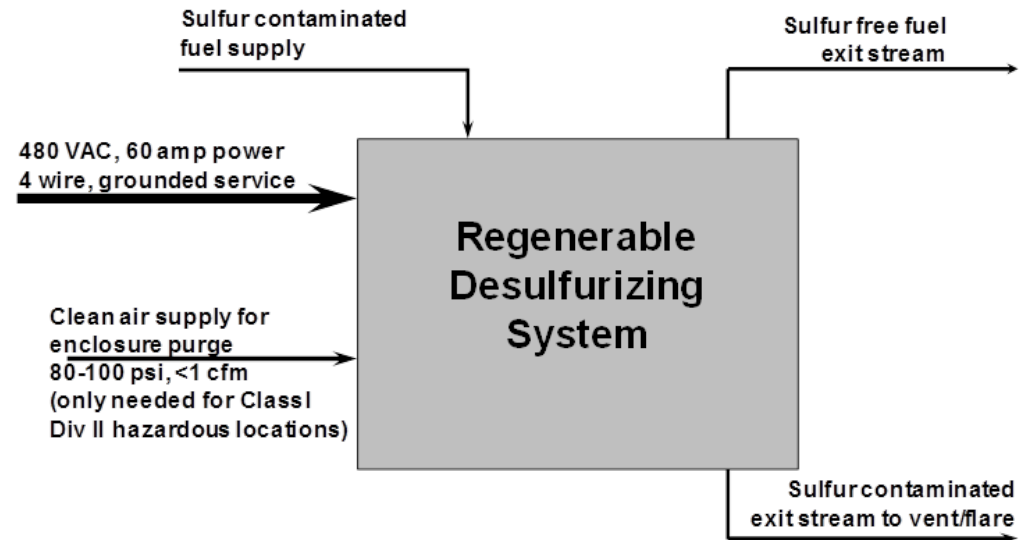
- We increased the production batch size for our biogas desulfurization sorbent from 20 mL to 35 L with virtually no change in the sorbent performance

# Design of Biogas Cleanup Skid

## 3-D layout of TDA's Biogas Cleanup Skid



## Utilities Requirement under Regenerable Operation



# Fabrication of Biogas Cleanup Skid

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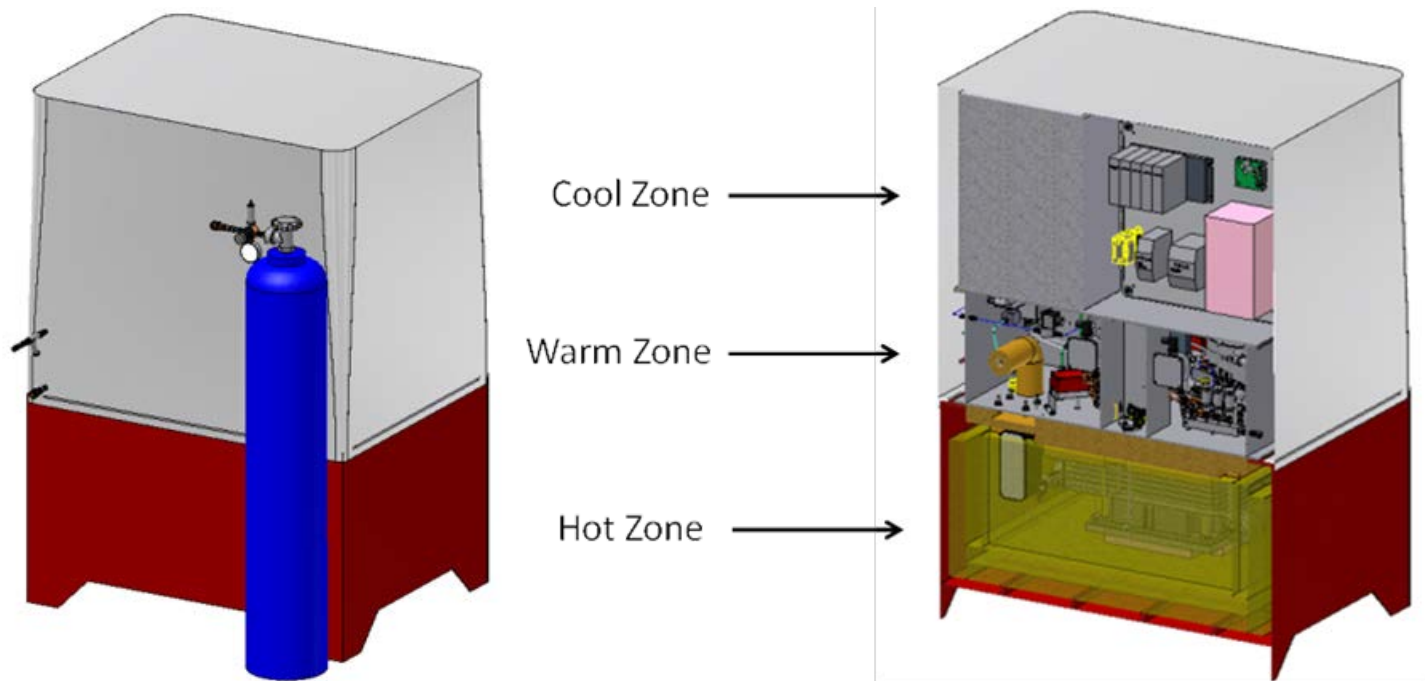
## TDA's Biogas Cleanup Skid



- Completed the fabrication of our skid-mounted field-deployable prototype biogas clean-up system
- In the next period, TDA will begin shakedown testing of the biogas cleanup system

# SOFC Test Module

## 3-D layout of FCE's SOFC Test Skid



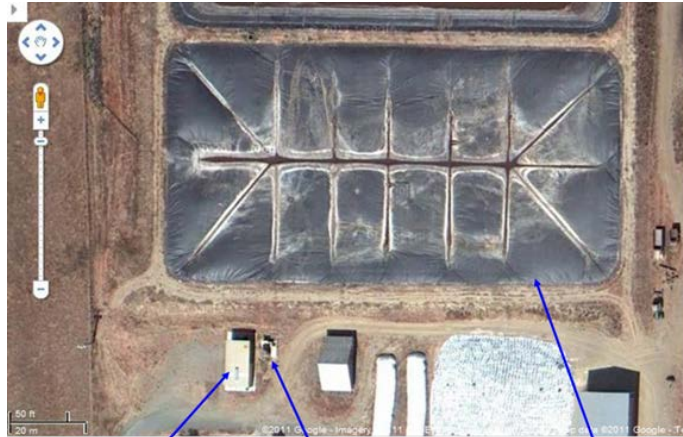
- FuelCell Energy (FCE) has completed the design of the SOFC Test Skid and begun the integration of the 2 kW<sub>e</sub> SOFC stack on a test skid



# Field Test Site # 1

## Cal DeNier Dairy Farm

### Cal DeNier Dairy Farm Layout



**ENGINE ROOM**  
60 kW, 480 V

**GAS TREATMENT**  
FLOW 20-30 SCFM  
INLET H<sub>2</sub>S 1000-2000 PPM  
OUTLET H<sub>2</sub>S 100-300 PPM

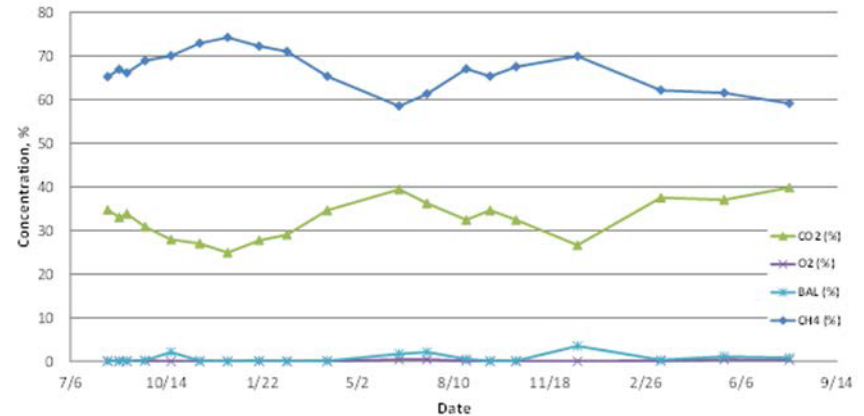
**DIGESTER**

### Engine Room

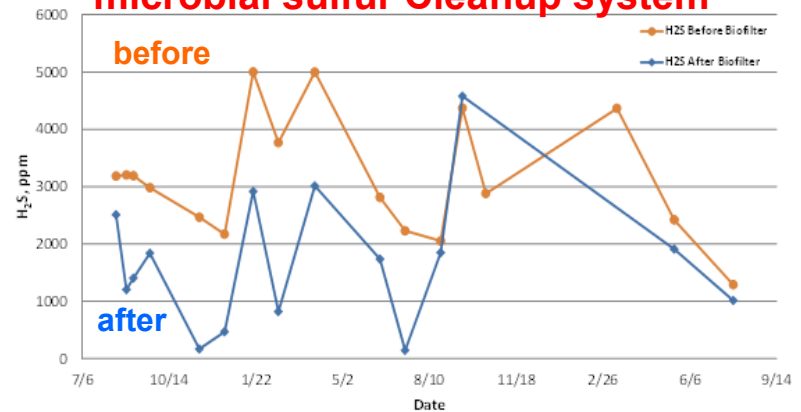


SPACE FOR FUEL CELL

### Biogas Composition



### H<sub>2</sub>S Concentration Before and after existing microbial sulfur Cleanup system



- FCE has initiated the subcontract with SMUD and SMUD has provided the historical ADG gas analysis data for the Cal-DeNier Dairy Farm

# Collaborations

## Packaged Desulfurizers



- TDA worked on providing a universal sorbent or desulfurizer for all applications and also identified alternate suppliers for raw materials
- Submitted several abstracts and papers to national conferences
- Received several enquiries about our sorbents for desulfurization of natural and biogas
- Initiated contact with several fuel cell manufacturers i.e., our potential customers
- Prepared and delivered sorbents and packaged desulfurizers for demonstration with fuel cells or reformers

## Lead/Lag Desulfurizer



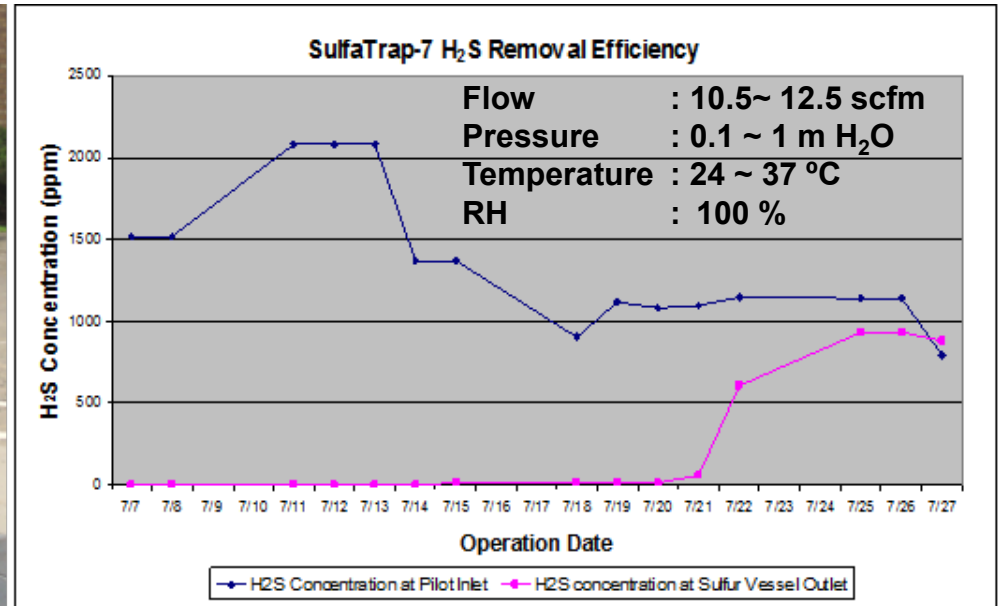


# Expendable Bulk Sorbent Field Test

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 the DOE project
- TDA sorbent achieved 17.5% wt. sulfur capacity (lb of sulfur per lb sorbent)
  - Two times higher than other commercially available sorbents, while reducing the sulfur concentration to undetectable levels i.e., sub ppmv levels

# Future Work

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## FY 2012 – Q3

- FCE will begin assembling/fabricating the SOFC test skid
- FCE will assist SMUD with the air permitting process as required
- SMUD will provide the electrical drawings and the ADG interface connections
- A design review meeting will be held between TDA and FCE to define tie in requirements and gas clean up skid and SOFC module communication links

## FY 2012 – Q4

- Complete integration of the two skids and complete shakedown tests
- A Hazop analysis on the SOFC module will be conducted

## FY 2013

- Field tests of the integrated system will be carried out in FY 2013
- 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

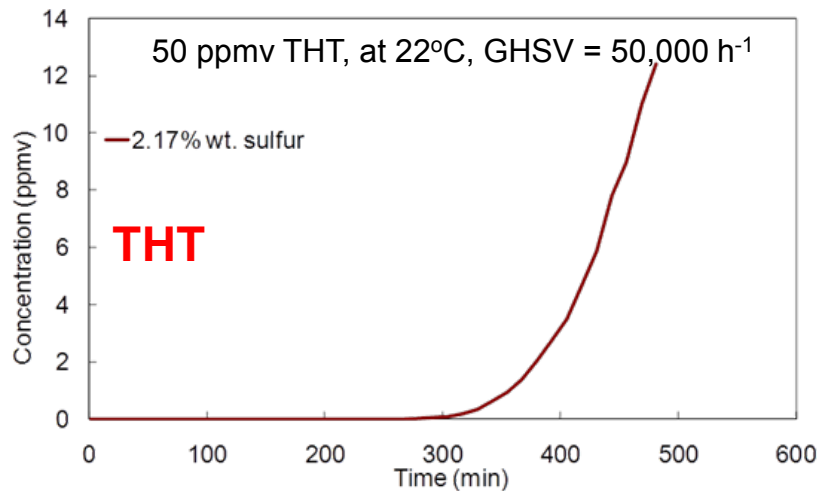
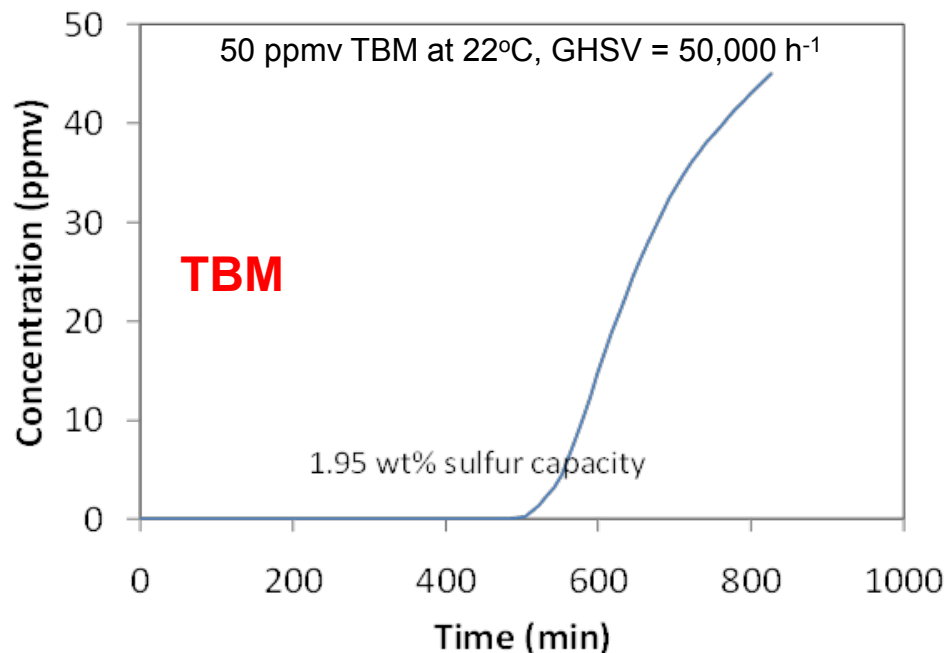
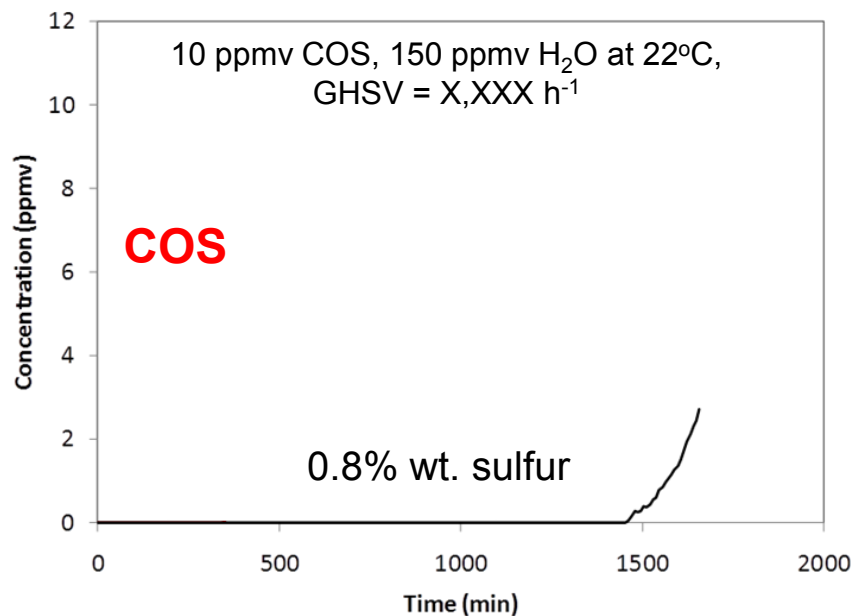
# Project Summary

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- **Relevance** - Promotes the use of fuel cells in waste-to-energy applications through eliminating some of the barriers such as contaminants present in biogas and increased fuel cell efficiency
- **Approach** - Our Experienced Team Will:
  - TDA leverage its experience with sulfur removal for natural gas to: systematically develop an universal gas cleanup system for biogas that removes all contaminants to ppb levels
  - FCE will leverage their experience in operating MCFCs using biogas to develop a robust and more efficient SOFC for biogas application
  - TDA, FCE and SMUD will carry out Field tests under biogas generated from different waste streams to demonstrate the technical and economic feasibility of using SOFCs for power generation in waste-to-energy applications
- **Accomplishments** – Completed sorbent scaleup, built the gas cleanup skid, completed design of the SOFC skid, Site identified and contact established, initial demonstration of the gas cleanup sorbent is successful at a wastewater treatment plant
- **Collaboration** – Active Partnerships with FCE, SMUD, Degremont and MWV, contacts established and providing sorbent samples for evaluations to other fuel cell developers
- **Future Work** - Complete SOFC test skid, the field tests and economic analysis

# Technical Back-Up Slides

# Removal of Other Sulfur Compounds



- We optimized our sorbent formulations to remove all the organic and inorganic sulfur species such as H<sub>2</sub>S, COS, mercaptans (TBM) and thiophenes (THT) from the ADG