Fuel Quality Effects on Stationary Fuel Cell Systems

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Presented at the 2011 Hydrogen Program Annual Merit Review Meeting
Washington DC, May 10, 2011

Project ID: AN010

Project Overview

Timeline

- Project Start: 2006
- Project End: 9/2011*

Budget

- FY 09: $200 K
- FY 10: $200 K
- FY 11: $200 K

* Project continuation and direction determined annually by DOE

Barriers

- B. Stove-Piped/Siloed Analytical Capability
- D. Suite of Models and Tools

Collaborations

- Energy Companies (BP, GTI)
- National Laboratories (NREL)
- Fuel Cell Companies
- International
  - Japan Gas Association
  - International Standards Org

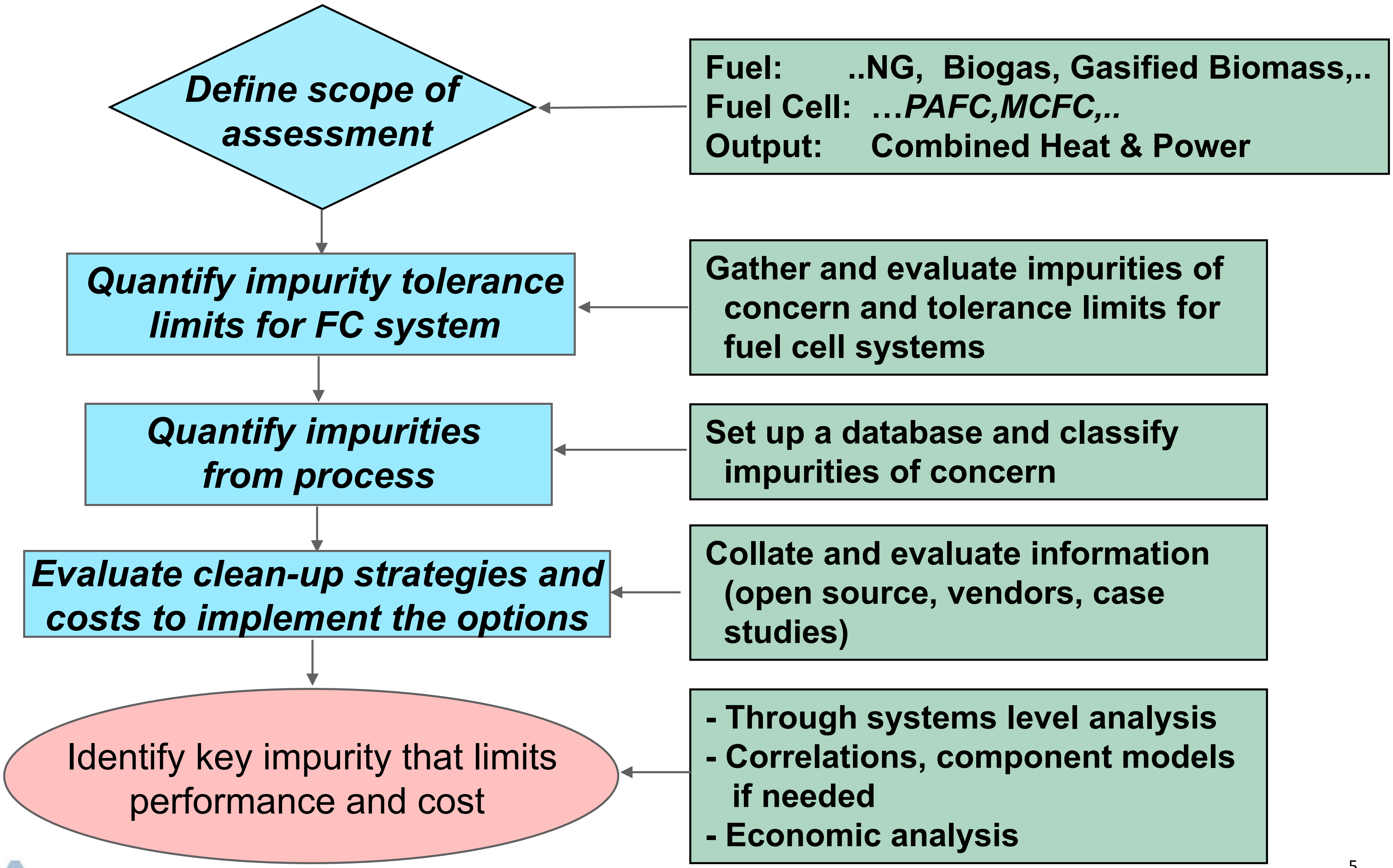
Relevance - Impurities in hydrogen affect the performance, life, and cost of fuel cell systems

- Fuel Cell systems operate on hydrogen and H_2-rich reformates that contain impurities
  - Inerts / diluents, reversible / irreversible poisons
- The effect of impurities depends on the type of fuel cell
  - Varies with electrolyte and anode materials, temperature, impurity level
- The impurities usually enter the fuel cell system with the feedstock
  - Natural gas, landfill gas, bio-derived liquid, etc.
- The critical impurities are removed before the vulnerable component
  - e.g., sulfur before reforming catalyst, ammonia before fuel cell anode, etc.
- Impurity removal adds to the lifecycle cost of the fuel cell
  - Existing clean-up strategies are often expensive or burdensome
    - E.g., low sorbent capacity, regeneration or waste disposal
  - Newer clean-up technologies will accelerate deployment of fuel cell systems

Objective

- Study the impact of impurities on fuel cell systems
  - Loss of performance and life
  - Clean-up strategies and their cost factors
  - Identify impurity – system configurations that are most constrained by impurity effects
- Correlate the cost of electricity to impurity concentrations
- Recommend R&D that can
  - Mitigate the deleterious effects
  - Provide alternative and less expensive clean-up options

Approach


Define scope of assessment
Fuel: ..NG, Biogas, Gasified Biomass,..
Fuel Cell: …PAFC,MCFC,..
Output: Combined Heat & Power
Quantify impurity tolerance limits for FC system
Gather and evaluate impurities of concern and tolerance limits for fuel cell systems
Quantify impurities from process
Set up a database and classify impurities of concern
Evaluate clean-up strategies and costs to implement the options
Collate and evaluate information (open source, vendors, case studies)
Identify key impurity that limits performance and cost
- Through systems level analysis
- Correlations, component models if needed
- Economic analysis

- Technical Accomplishments and Progress
Available information on fuel cells and impurities has been catalogued into databases

Each application is classified in terms of

- Type of fuel cell system

- Effects of different impurities on the performance of the fuel cell
  - *Includes data for phosphoric acid, molten carbonate, and solid oxide fuel cells (PAFC, MCFC, SOFC)*
  - *Includes effects of impurity concentration, fuel used, degradation rate*

- Impurities in the feedstock fuel and the reformate derived from it
  - Natural gas (NG), gasified biomass, coal gas, landfill gas (LFG), anaerobic digester gas (ADG)

- Impurity control or management techniques currently used or planned

Sulfur is common in all biogas

- Large variability of trace impurities from different biogas source
  - *Factors affecting concentration include temperature, pressure, type/origin of waste, age of waste (LFG)*
- **Sulfur**
  - Landfill gas (LFG) and digester gas from waste water treatment plants (WWTP) in ppm range
  - Highest levels in agricultural sector (typical values 0.05-0.6%)
  - H_2S bulk of sulfur species, organic sulfur ranges from ppb to ppm levels
    - Dimethyl sulfide (DMS) > Mercaptans > Carbonyl Sulfide (COS)
- **Siloxanes**
  - Biologically stable, found in many personal hygiene products, detergents, lubricants
  - Cyclic species (D3-D5), linear (L2-L4) and trimethylsilanol (TMS) most frequently encountered
  - Use of silicon-based products has been increasing over time
  - Analytical techniques are lab based and time consuming
- **VOC**
  - Aromatics, oxygenates, alkanes, halogens in the range of ppm
  - Distribution affected by waste and age of LFG
  - Halogens arise from volatilization of compounds in plastics foams, solvents, refrigerants,…
  - Chlororofluorocarbons (CFC’s) are stable compounds and evaporate slowly from landfill waste

- Technical Accomplishments and Progress

Data on impurity levels in landfill and digester gas have been compiled and categorized

- Database classifies impurities and their concentration levels
- Links to specific site and processes used
- Documents properties, links to NIST Chemistry WebBook

Class CAS Formula Chemical Name MW BP Vap.Pr. Solub.

Class	#	CAS	Formula	Chemical Name	Mw	T_{boil} (K)	P_{vap} (millibar)	H (mol/kg,bar)
Organosilicon	1	541-05-9	$C_6H_{18}O_3Si_3$	(D3) Hexamethylcyclotrisiloxane	222.46	407.0	5.8	-
Organosilicon	2	556-67-2	$C_8H_{24}O_4Si_4$	(D4) Octamethylcyclotetrasiloxane	296.62	448.0	1.3	-
Organosilicon	3	541-02-6	$C_{10}H_{30}O_5Si_5$	(D5) Decamethylcyclopentasiloxane	370.77	483.0	0.2	-
Organosilicon	4	540-97-6	$C_{12}H_{36}O_6Si_6$	(D6) Dodecamethylcyclohexasiloxane	444.92	518.0	0.0	-
Organosilicon	5	107-46-0	$C_6H_{18}OSi_2$	(L2) Hexamethyldisiloxane	162.38	373.0	55.7	-
⋮								
Sulfur	11	7783-06-4	H_2S	Hydrogen Sulfide	[illegible]			[illegible]
Sulfur	12	74-93-1	CH_4S	Methanethiol (Methyl Mercaptan)	48.108	279.1	-	0.200
Sulfur	13	463-58-1	COS	Carbonyl Sulfide	60.076	-	-	0.022
Sulfur	14	75-15-0	CS_2	Carbon Disulfide	76.143	319.2	478.5	0.055
Sulfur	15	75-18-3	C_2H_6S	Dimethyl Sulfide (DMS)	62.135	311.0	641.0	0.480
Sulfur	16	75-08-1	C_2H_6S	Ethanethiol (Ethyl mercaptan)	62.135	309.0	699.0	0.260
⋮								
Halocarbons	36	74-95-3	CH_2Br_2	Dibromomethane	173.835	370	58.9	0.930
Halocarbons	37	75-25-2	$CHBr_3$	Tribromomethane (Bromoform)	252.731	422.0	7.2	1.700
Halocarbons	38	106-93-4	$C_2H_4Br_2$	1,2-Dibromoethane	187.86	404.0	18.9	1.400
Halocarbons	39	108-86-1	C_6H_5Br	Bromobenzene	157.01	429.1	5.7	0.540
⋮								
Ketone	259	499-70-7	$C_{10}H_{18}O$	Cyclohexanone (Carvomenthone)	[illegible]			
Oxygenate	260	646-06-0	$C_3H_6O_2$	1,3-Dioxolane	74.0785	347.7	143.7	-
Oxygenate	261	110-00-9	C_4H_4O	Furan	68.074	304.7	799.3	-

- Technical Accomplishments and Progress

Data on impurity levels in landfill and digester gas have been compiled and categorized

- Documents by data source, gas supply location, and concentration range

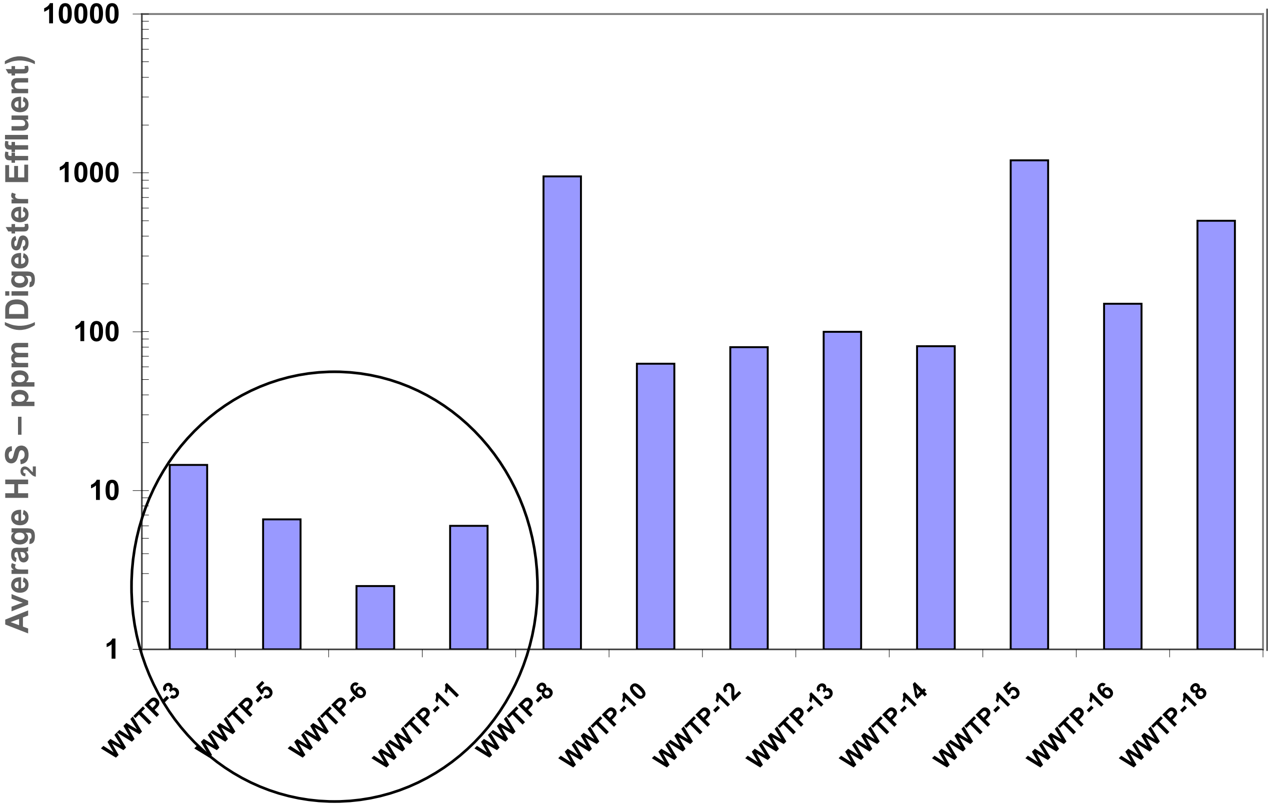
Abbreviations	Landfill characteristics/Comment	EPA Report	Spiege
b.d. = below detection limit	***Index #***	LFG-0	
n.m. = not measured	***Landfill Site***	EPA Data for Municipal Solid Waste Landfills across U.S	Grot
p.m. = peaks missed	***Activity***	Pre-1992 Landfills	Clo
blank = no data	***Refuse - Type***	Average value for U.S	Typical of m
STD = Standard deviation	***Refuse - Amount/Volume***	unknown	2 m
	Gas production rate (SLPM)	unknown	
	Analytical/Sampling	Grab Sampling, on-site	(Te
	Comments	Background Information Document for Updating AP42 Section 2.4 for Estimating Emissions from Municipal Solid Waste Landfills EPA/600/R-08-116, September 2008	Fuel cell opera the Groton, C gas was sam organic compo

Class	#	Formula	Chemical Name	Data Points	min (ppm)	max (ppm)	Average (ppm)	STD (ppm)	min (ppm)	(
Halocarbons	1	CH_3Br	Methyl Bromide (Bromomethane)	7	0.003	0.046	0.018	0.016	b.d.	
Halocarbons	2	CH_2Br_2	Dibromomethane	2	0.001	0.001	0.001	0.000		
Halocarbons	3	$CHBr_3$	Tribromomethane (Bromoform)	4	0.000	0.026	0.013	0.011	b.d.	
Halocarbons	4	$C_2H_4Br_2$	1,2-Dibromoethane	12	0.001	0.021	0.004	0.005		
Halocarbons	5	C_6H_5Br	Bromobenzene						b.d	
Halocarbons	6	HCl	Hydrogen Chloride	1	3.500		3.500			
Halocarbons	7	CH_3Cl	Methyl Chloride (Chloromethane)	14	0.002	1.260	0.217	0.323	0.06	
Halocarbons	8	CH_2Cl_2	Methylene Chloride (Dichloromethane)	50	0.005	40.100	5.150	7.570	b.d.	
Halocarbons	9	$CHCl_3$	Chloroform (Trichloromethane)	36	0.001	0.743	0.067	0.152	b.d.	
Halocarbons	10	CCl_4	Carbon Tetrachloride (Tetrachloromethane)	31	0.001	0.038	0.008	0.008	b.d.	
Halocarbons	11	C_2H_3Cl	Chloroethene (Vinyl Chloride)	48	0.006	15.600	1.230	2.430	0.33	

- Technical Accomplishments and Progress

The bulk of total sulfur in the digester gas is mainly as H_2S

The information are excerpts the database

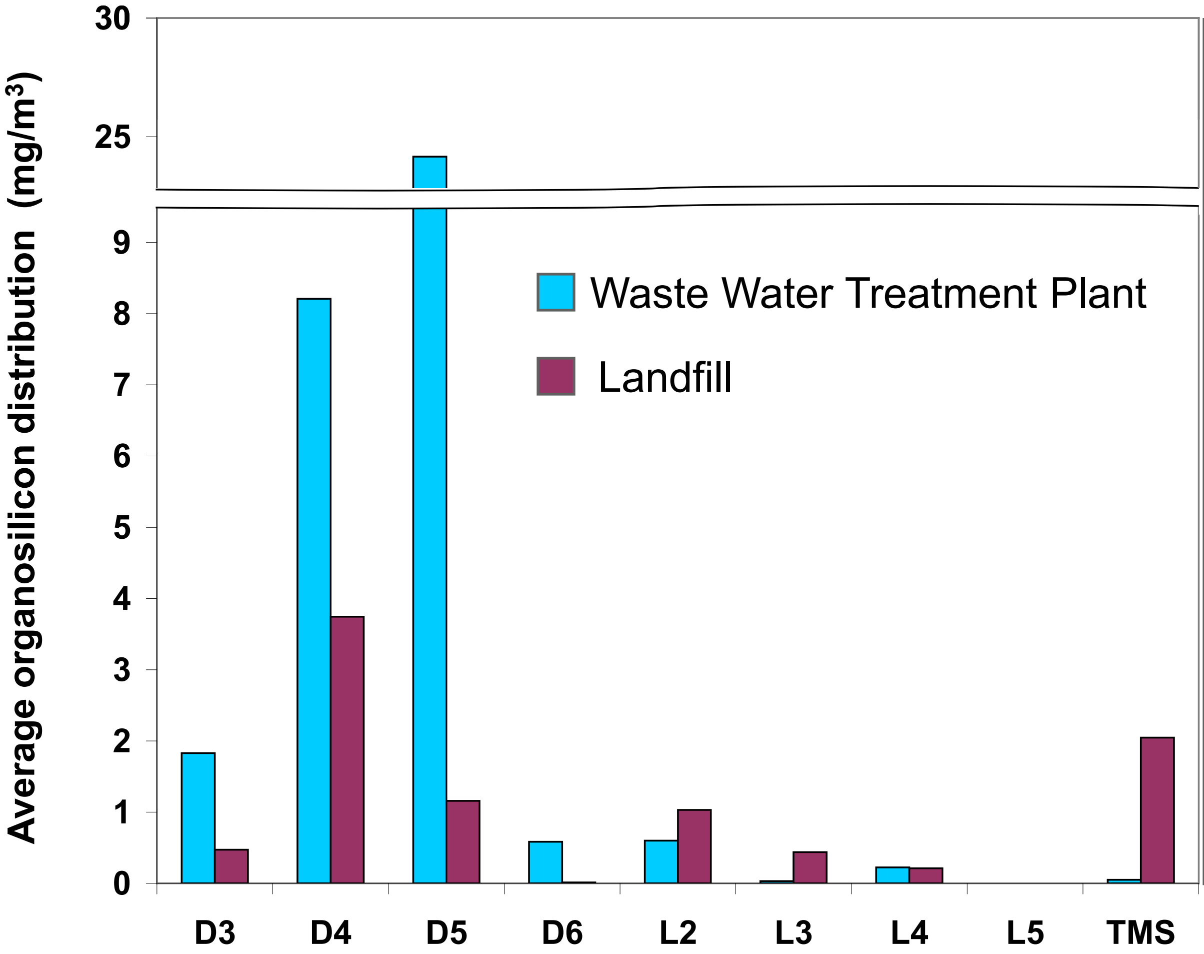


- H_2S shows variability in the order of 10 to 1000 ppm
- DMS and mercaptans can vary from ppb to ppm levels
- Iron salts used in the water treatment process sequester sulfide
- Impacts reformer/fuel cell catalyst/electrolyte. Sulfur impurities need to be reduced to levels of ~0.1-1 ppm

Low H_2S content due to iron salt used in the waste water treatment plants (WWTP), i.e. for sludge thickening, phosphate precipitation

- Technical Accomplishments and Progress

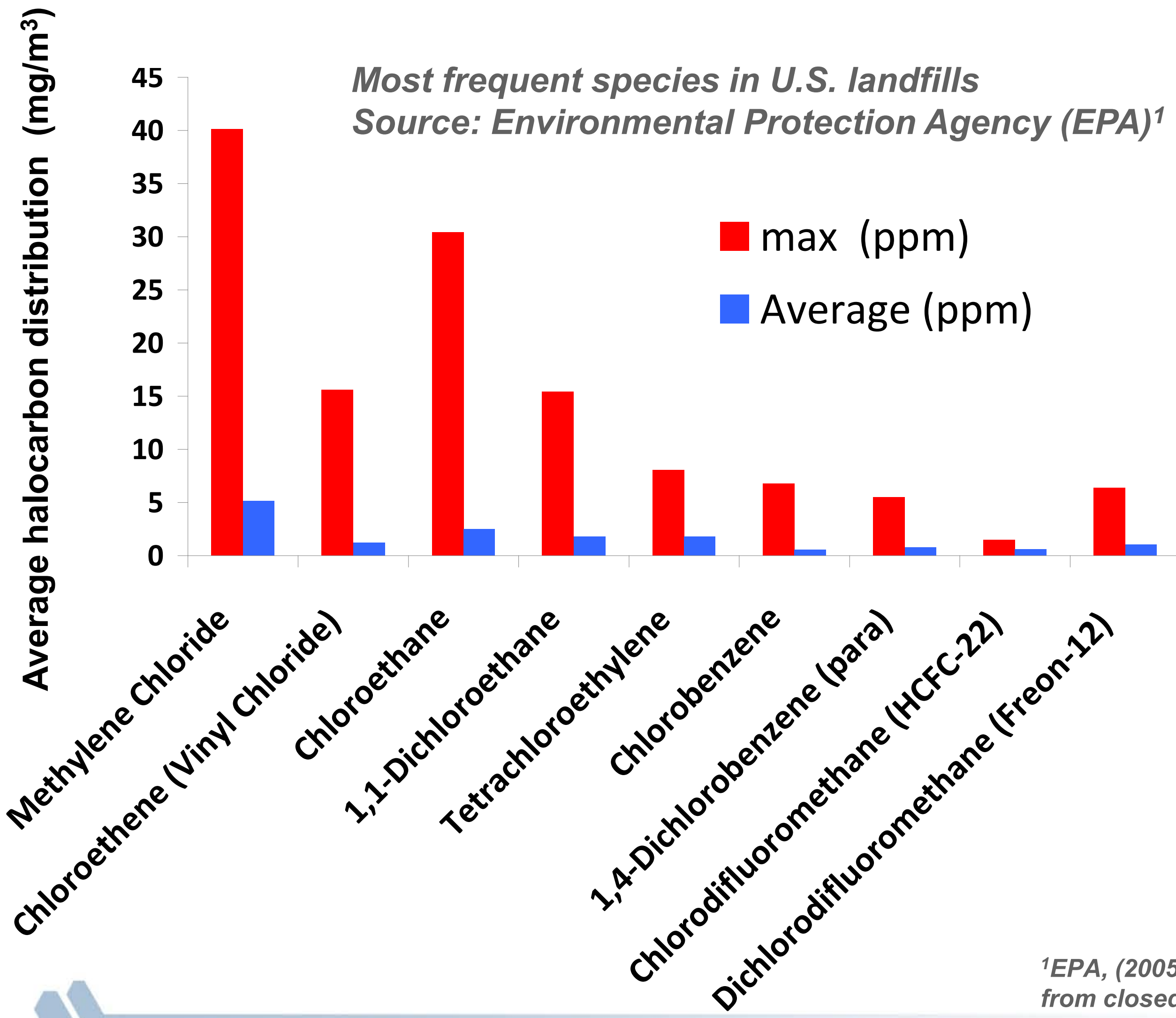
There are differences in siloxane concentrations for different biogas sources



- Siloxane concentration typically higher in WWTP gas than LFG
- Typical siloxane concentrations range from 2-30 mg/m^3
- Cyclic compounds (D3-D4) are dominant in WWTP gas
- Concentrations of linear compounds (L2-L5) and trimethylsilanol (TMS) are usually low
- ADG temperature affects speciation and concentration of siloxane compounds
- Solid silica deposits on surfaces. Tolerance levels often require "below detection limit"

The information are excerpts from the database

- Technical Accomplishments and Progress
LFG contains many different halogenated species



- Concentration of halogens is generally lower in WWTP than LFG gas
- Cl concentration generally most dominant, followed by F, then Br
- Form corrosive gases, HCl, HF, upon combustion or reforming
- Affect long-term performance of fuel cells

[1]EPA, (2005). Guidance for evaluating landfill gas emissions from closed or abandoned facilities. EPA-600/R-05/123a

- Technical Accomplishments and Progress

The impurity affects the fuel cell performance and ultimately the cost of electricity and plant life

- ***Sulfur***
  - Corrosive, affects catalyst and electrolyte
  - Rapid initial, then slower, voltage decay. Effect may be reversible
  - Tolerance limits 0.5-5 ppm
  - More severe effect with CH_4/CO rich fuels to fuel cell and anode recirculation
- ***Siloxanes***
  - Thermally decompose, forming glassy deposits
  - Foul surfaces (Heat exchangers, sensors, catalysts)
  - Few studies on the effects on FC's, but tolerance limits may be practically zero
- ***Halogens***
  - Corrosive, affect electrolyte
  - Long term degradation effects
  - Tolerance limits, 0.1-1 ppm
- ***Inerts***

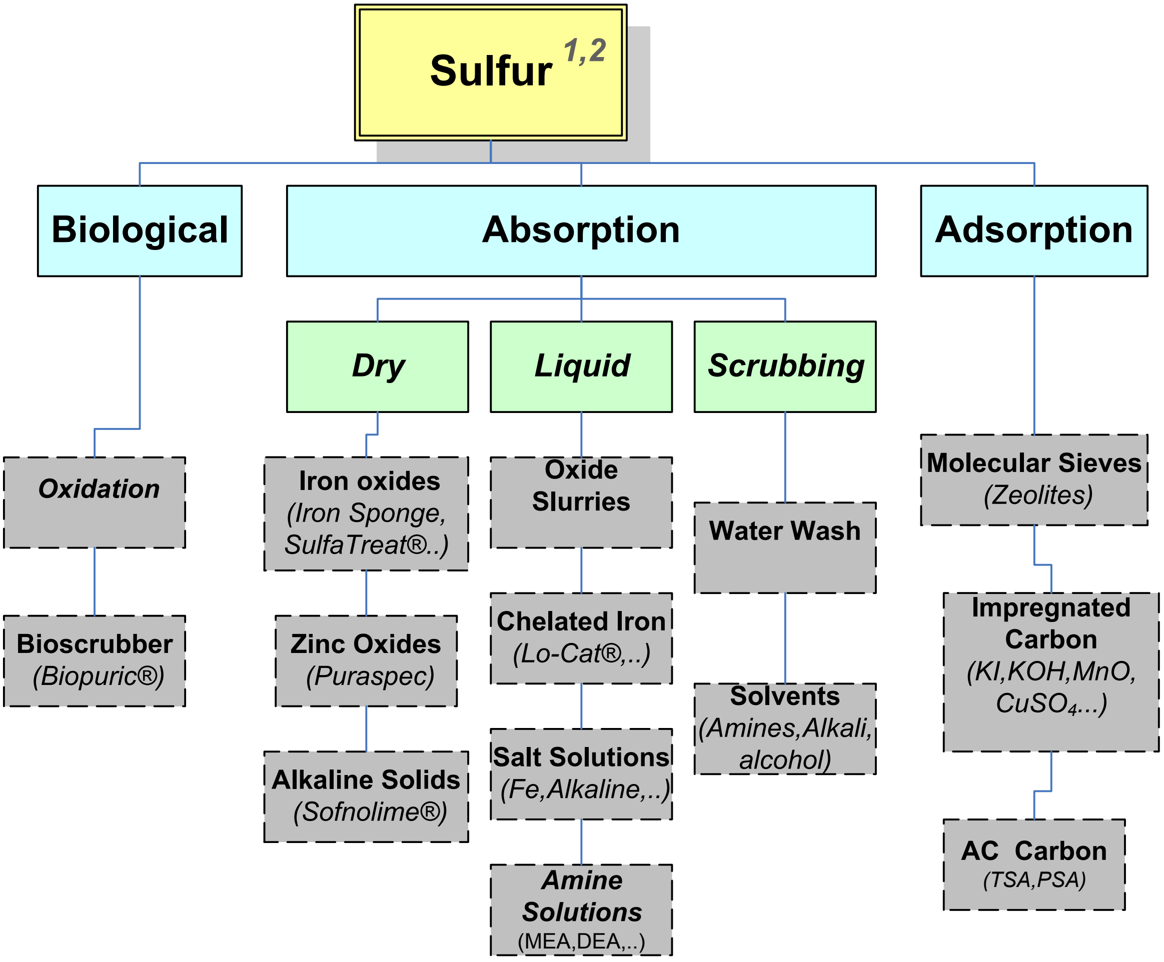
  - N_2 can catalytically react to form ammonia

  - Variable CO_2 content affects fuel heating value, complicating process control

Impurity	Tolerance	Reference
Molten Carbonate Fuel Cells		
H_2S	0.1 0.5 0.1-5 ppm	(Tomasi, *et al.*, 2006) (Abe, Chaytors, Clark, Marshall and Morgan, 2002) (Moreno, *et al.*, 2008) (Desiduri, 2003)
COS, CS_2, mercaptan	1 ppm	(Tomasi, Baratieri, Bosio, Arato and Baggio, 2006)
Organic Sulfur	<6 ppm	(Lampe, 2006)
H_2S, COS, CS_2	0.5-1 <10 ppm	(Cigolotti, 2009) (Lampe, 2006)
Halogens (HCl)	0.1-1 ppm	(Moreno, McPhail and Bove, 2008) (Desiduri, 2003), Lampe, 2006) (Abe, Chaytors, Clark, Marshall and Morgan, 2002)
Halides: HCl, HF	0.1-1 ppm	(Cigolotti, 2009)
Alkali Metals	1-10 ppm	(Tomasi, Baratieri, Bosio, Arato and Baggio, 2006) (Moreno, McPhail and Bove, 2008)
NH_3	1 1-3 %	(Moreno, McPhail and Bove, 2008) [Desiduri, 2002], [Fuel Cell Handbook, 2002] (Cigolotti, 2009)
[illegible]	[illegible]	(Moreno, McPhail and Bove, 2008)
Siloxanes: HDMS, D5	10-100 <1 ppm	(Cigolotti, 2009) (Lampe, 2006)
Tars	2000 ppm	(Cigolotti, 2009)
Heavy Metals: As, Pb, Zn, Cd,Hg	1-20 ppm	(Cigolotti, 2009)
Solid Oxide Fuel Cells		

- Technical Accomplishments and Progress

Numerous commercial solutions exist for sulfur removal



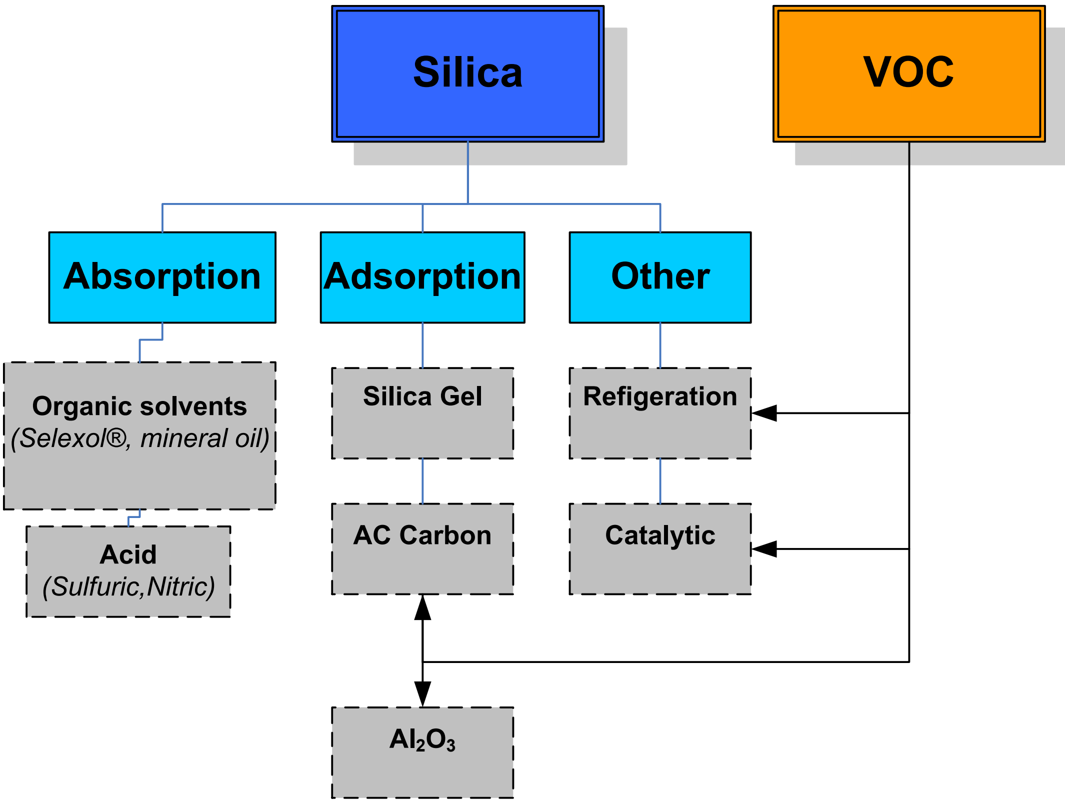
- Air dosing/ precipitation effective for high H_2S concentrations
  - *– Difficult to control large variations in H_2S concentration*
  - *- May affect digestion process*
- Scrubbing and regenerable options such as Bioscrubbers, Chelated iron solutions are capital intensive
  - *- Applicable for large flows, high sulfur content*
  - *- Scrubbing is energy intensive, good for upgrading to natural gas*
- Expenses for throw away solids are low but can incur high running costs
  - *- Iron oxides may be partially regenerable with air (highly exothermic)*
  - *-Adsorbents used for low concentrations /polishing*

1) GTI (2009). Pipeline Quality Biomethane, Task 1
2) EPRI (2006). Assessment of Fuel Gas Cleanup Systems for Waste Gas Fueled Power Generation

- Technical Accomplishments and Progress

Clean-up solutions are fewer for siloxanes and VOCs[1,2,3]

VOC – Volatile organic compounds



- Strong acid wash (T>60 C) excellent for siloxane removal
  - *Difficult strategy to implement in practice*
- Deep refrigeration needed for volatile species
  - Energy intensive, low temperature (-50^{o}C) and/or high pressure needed
  - Volatile siloxanes, L2,D3,L3 difficult to condense
- Adsorbents good for trapping small amounts of impurities
  - Gases are multi component mixtures, competitive adsorption **<u>Water</u>**>Aromatics>Siloxanes>Halocarbons
  - May need multiple adsorbents; resulting waste may be hazardous

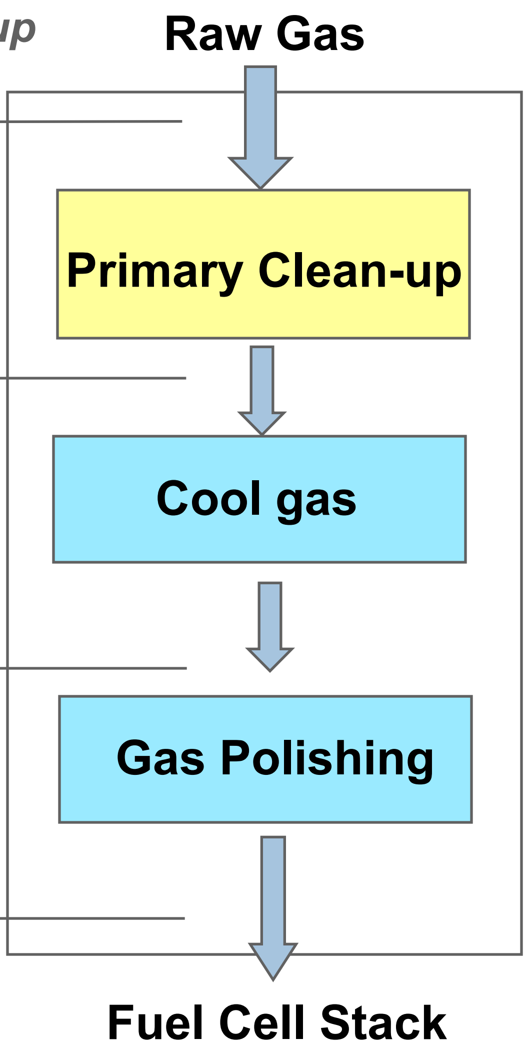
1) EPRI (2006). Assessment of Fuel Gas Cleanup Systems for Waste Gas Fueled Power Generation
2) Schweigkofler and Niessner (2001). J. Hazardous Materials, B83, 183-196
3) Arnold (2009). Reduction and monitoring of biogas trace compounds, ISBN 978-951-38-7314-1

- Technical Accomplishments and Progress

Clean up processes mostly rely on bulk removal and polishing solutions

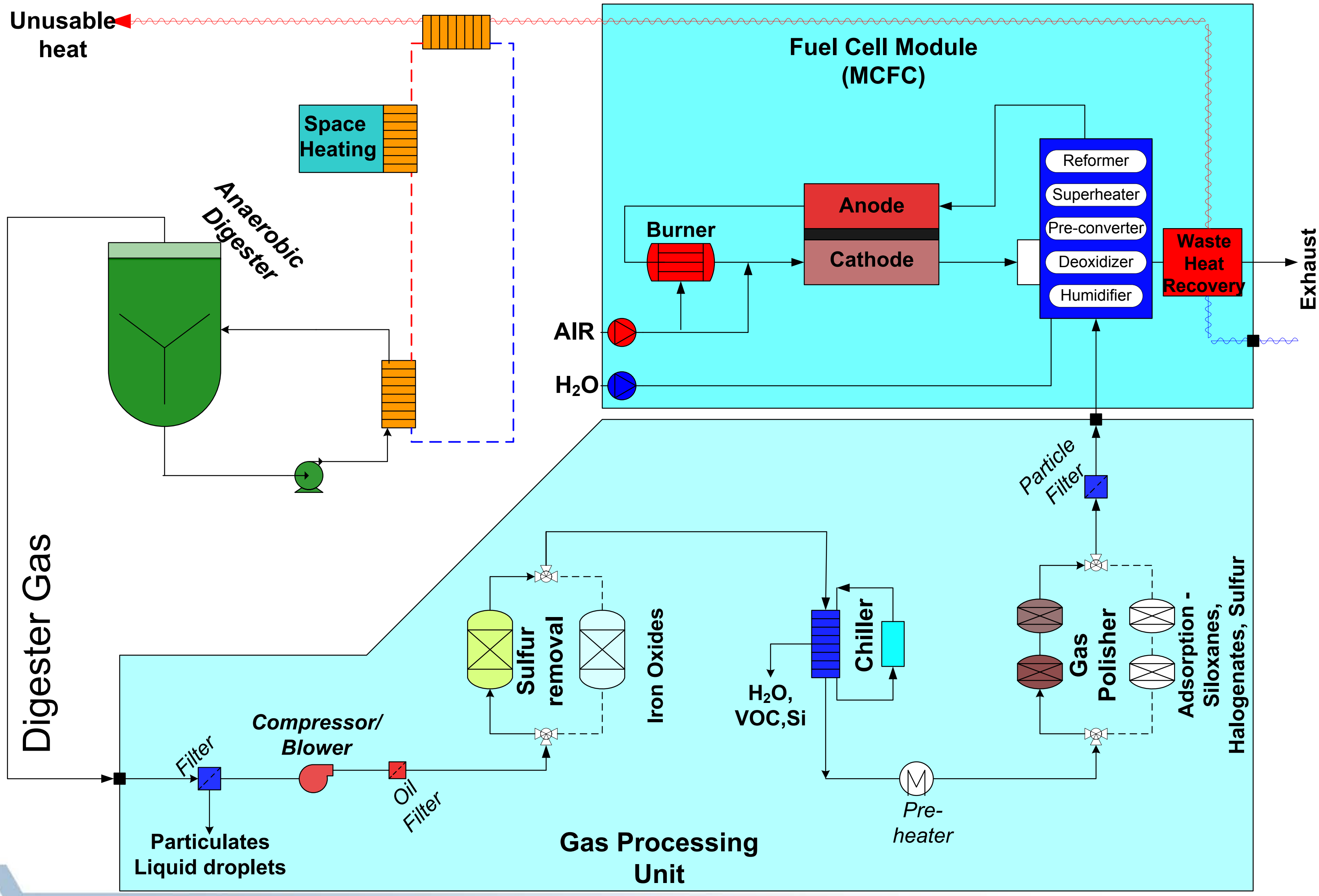
Example of strategy commonly employed for biogas clean-up

- Remove bulk of sulfur (to ~5-10 ppm)
  - **Precipitation, Iron oxides, Impregnated carbon**
  - *(Biological, washing)*
- Remove moisture (dry gas for polishing)
  - **Cooling also condenses some VOCs and siloxanes**
  - *(Deep refrigeration effective for some siloxanes)*
- Remove S, Halogens, Siloxanes
  - **Active carbon, Silica gel, Al_2O_3, ZnO ...**
  - **Throw away/ regenerable sorbent options**



- Technical Accomplishments and Progress

A base case system has been set-up to conduct cost analysis



The cost analysis will show the sensitivity of impurity levels in the fuel

Process

- Electricity demand (***kW***, MW)
- Credits
  - Usable heat production
  - Tax incentives
- Biogas source (LFG, ***WWTP***,..)
- Fuel Cell (PAFC, ***MCFC***,..)
- Clean-up option (regenerable, ***throw away***,)

Base Case

Cost Factors

- Utilities
- Calculating cost of electricity, heat from the FCS
- Cost contributors
  - Capital (installed), variable operating costs, maintenance

- We will study the effect of impurity on the cost of electricity
  - Cost analysis will be based on H2A (Fuel Cell Power Module)

Collaborations

- We acknowledge the technical support and guidance from
  - Fuel Cell Energy
  - Versa Power
  - Acumentrics
  - Nuvera
- Provided technical support on pressure swing adsorption (PSA) modeling to Directed Technologies

Summary

- A database documents the impurity levels and clean-up options for biogas sources
  - The data are classified on the basis of impurity classes, biogas source (LFG,ADG), the unit operations and processes of the system
- A database documents the impurities encountered in stationary fuel cell systems and effects
  - Sulfur, siloxanes, and halides are detrimental for all fuel cells
  - Higher hydrocarbons reduce clean-up capacity of adsorbents
  - Variability of biogas heating value increase complexity and cost for process control
- A base case process has been set-up for the economic analysis
  - System considers MCFC/ADG process (300 kWe), Absorption/Adsorption based clean-up strategy
  - Economic analysis for the base case system on track (by September)

Future Work

- Complete cost analysis for base case system (September)
- Determine costs for
  - Type of fuel cell
  - Biogas source
  - Clean-up options
- Validate results

- Trade-off analysis of cost of clean-up vs. cost of electricity due to power loss
- R&D recommendations to DOE
  - Develop on-line monitoring technology for siloxane
  - Develop strategies to measure / improve capacity and disposal of spent clean-up media