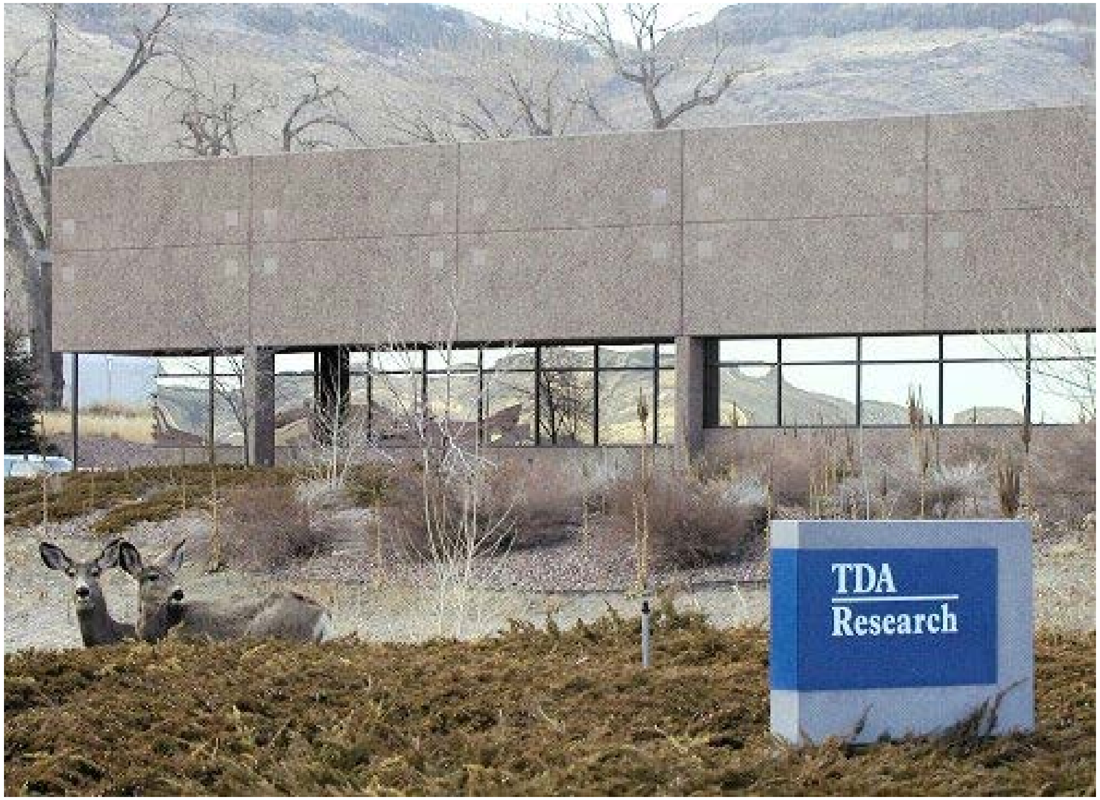
Warm Gas Multi-contaminant Removal System
(Contract No. DE-SC0008243)



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2019 Crosscutting Research Program Gasification Systems Project Review

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Project Objectives

- **The project objective is to demonstrate techno-economic viability of a synthesis gas purification system to eliminate potential catalyst poisons and environmental pollutants from coal-derived synthesis gas**
  - A high temperature sorbent is used for operation above the dew point of the synthesis gas
  - The sorbent is operated in a regenerable manner for NH_3 and Hg
  - All other contaminants (trace metals, HCN etc.) is removed irreversibly
- **Project Tasks**
  - Scale-up the production of the sorbent
  - Carry out multiple cycle to demonstrate long-term durability of the sorbent
  - Design a slipstream test unit for proof-of concept evaluations
    - 1 to 10 SCFM raw synthesis gas treatment capacity
  - Complete a high fidelity process design and economic analysis
- **Project Duration**
  - 3 years
  - Completion Date – 08/01/2019

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Background

- **Coal-derived synthesis gas contains a myriad of trace metal contaminants**

Typical Metal Contaminants in Coal

Coal Type	Hg (ppm)	As (ppm)	Se (ppm)	Cd (ppm)
Pittsburg	0.11	4.1	0.6	0.06
Elkhorn/Hazard	0.13	4.0	3.1	0.31
Illinois No.6	0.22	2.7	2.2	0.15
Wyodak	0.19	1.3	1.6	0.30

Bool et al., 1997

- **Removal of trace metals is critical to control emissions from advanced power cycles that use coal-derived synthesis gas feed**
  - Mercury is singled-out for particular scrutiny because of its effects on humans and wildlife
- **The nitrogen in the coal is converted to the NH_3 and HCN which will be converted into NOx in an IGCC plant**
- **Removal of metal contaminants and NH_3/HCN is also important for chemical manufacturing processes**
  - Arsenic, HCN, NH_3 are a potent poisons for the catalysts used in the WGS and Fischer Tropsch synthesis

Warm Gas Contaminant Removal

- NH_3 removal is commonly accomplished by using a water scrubber, where NH_3 is reacted with a mildly acidic solution to be converted into a stable salt solution
- These scrubbers typically run at low temperature to increase the NH_3 solubility (the critical first step is the dissolution of NH_3 in the scrubbing solution)
- These scrubbers do not reduce the NH_3 concentration to very low levels and do not remove contaminants such as hydrogen cyanide (HCN)
- For trace metals, the existing clean-up technologies based on physical adsorbents are also limited to low temperatures
- The objective is to develop a sorbent-based for warm gas clean-up technology
  - For a GE gasifier with water quench, the dew point is ~245^{o}C (480^{o}F)
- Warm temperature gas cleaning has major benefits:
  - Improves the efficiency of the power cycle
  - Eliminate the need for any heat exchange equipment
  - Eliminate the difficulties processing the condensate

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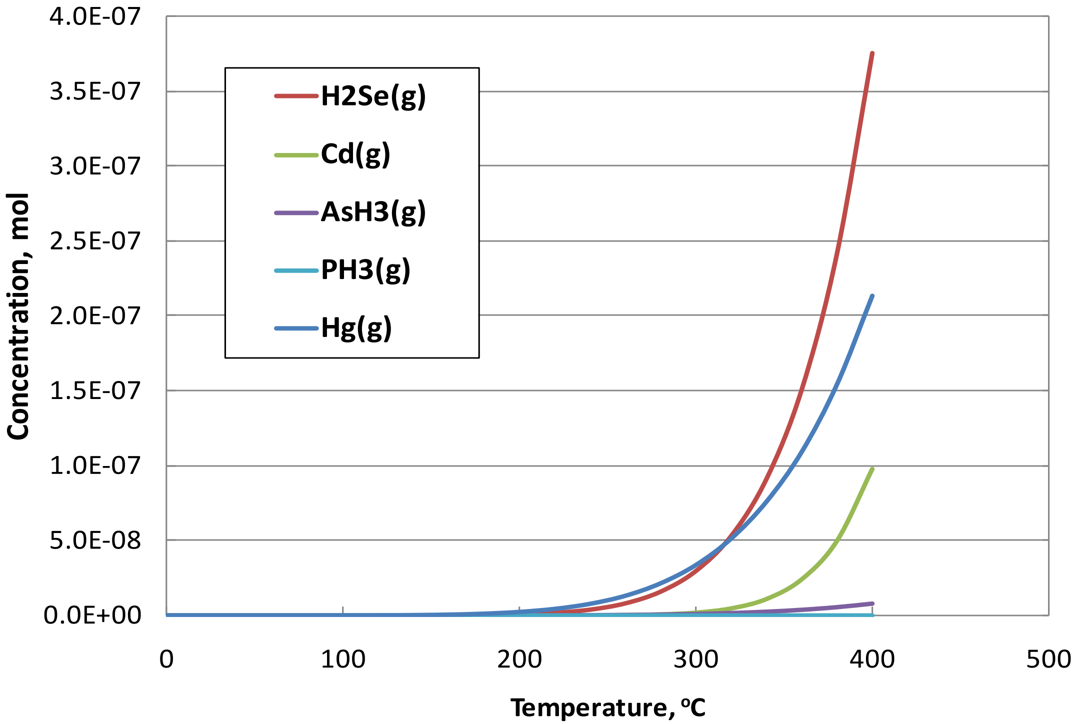
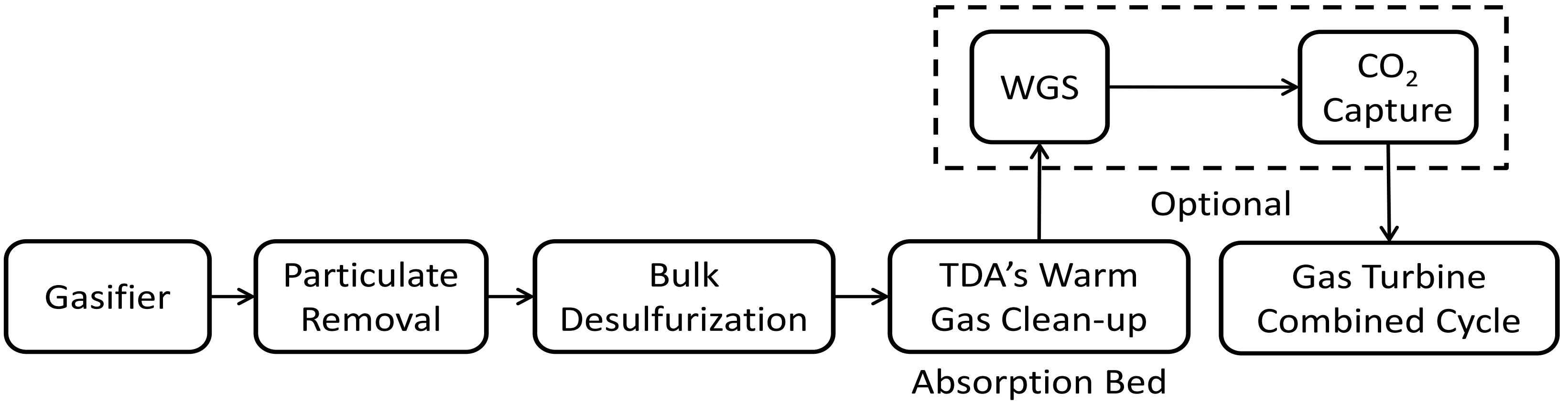
Equilibrium Compositions of Trace Metals Over New Sorbent

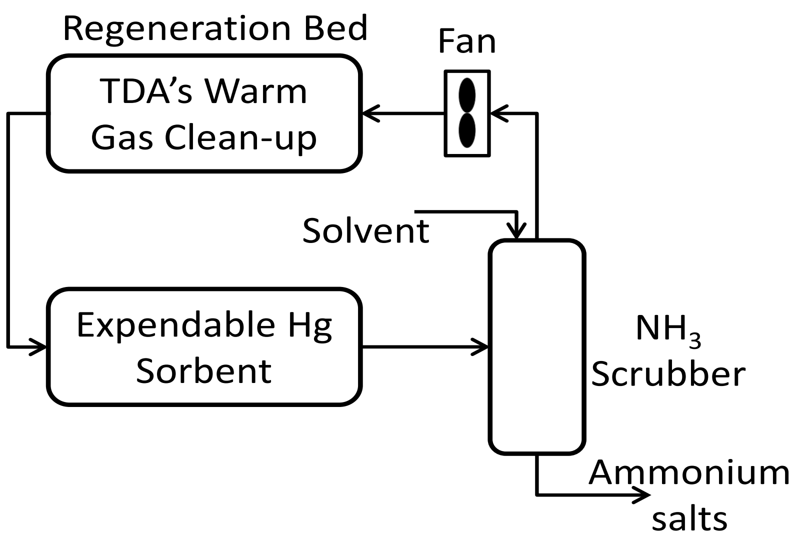


- **Hg (also Se) has a very high vapor pressure over any surface at 200ºC or higher temperatures (i.e., difficult to achieve high removal efficiency)**
  - The resulting low capacity increases the cost of using expendable sorbents
- **NH_3 removal using one-time use sorbents is also impractical as it is present in relatively high concentrations (200 to 1500 ppmv range)**

TDA's Multi-contaminant Removal Process

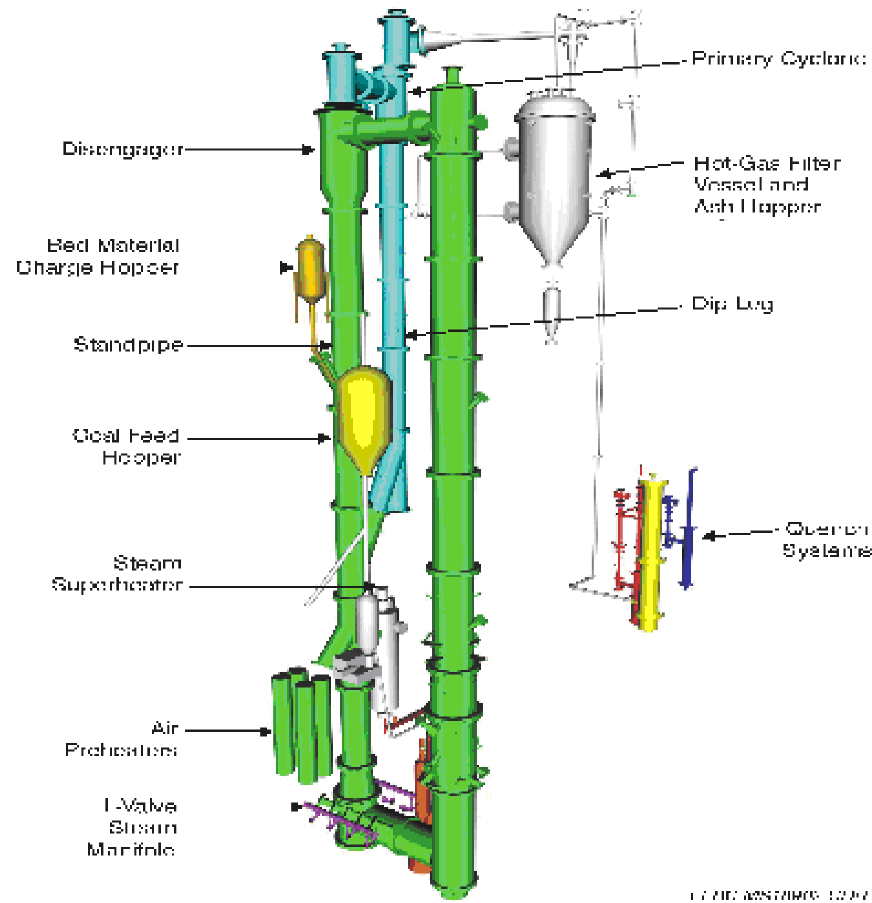


- **Hg and NH_3 are removed at high temperature**
- **The sorbent is regenerated using a combination of temperature and pressure swing**
- **The off-gas from the sorbent bed is cooled enabling the use of low temperature sorbents or scrubbers**



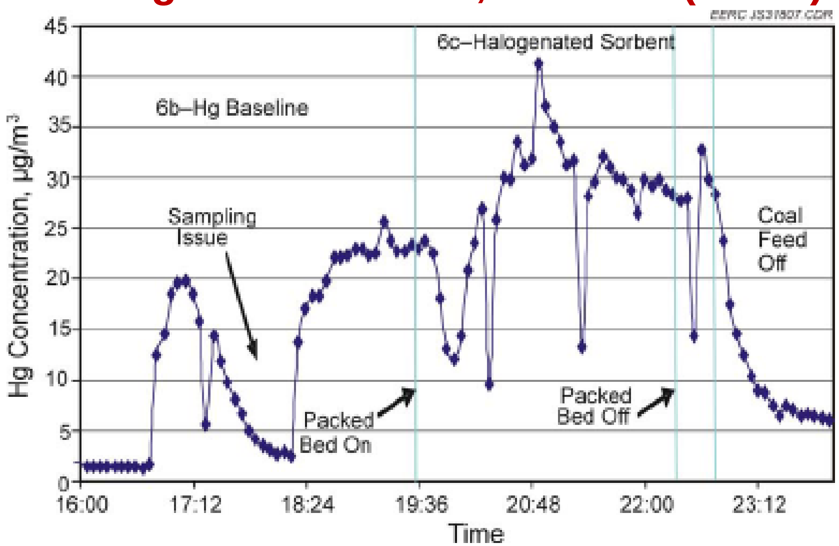
Early Testing at UNDEERC

- **Operation of the regenerable Hg sorbent has been demonstrated in two test campaigns at UNDEERC**
  - SUFCo bituminous (May 2008)
  - Oak Hills Lignite (June 2008)
- **Specifications of EERC Transport reactor demonstration unit (TRDU)**
  - Operating P=125 psig
  - 10,000 SCFH syngas treatment

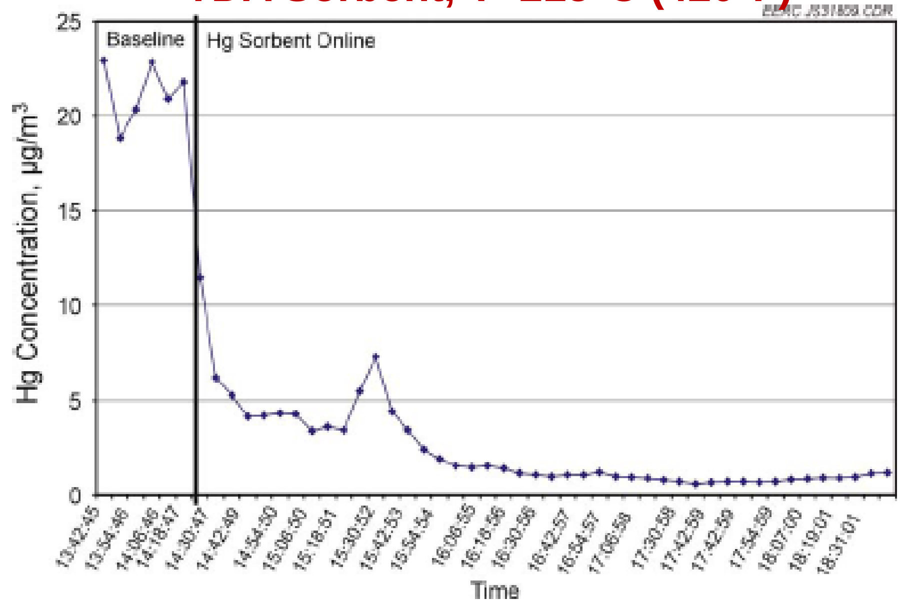


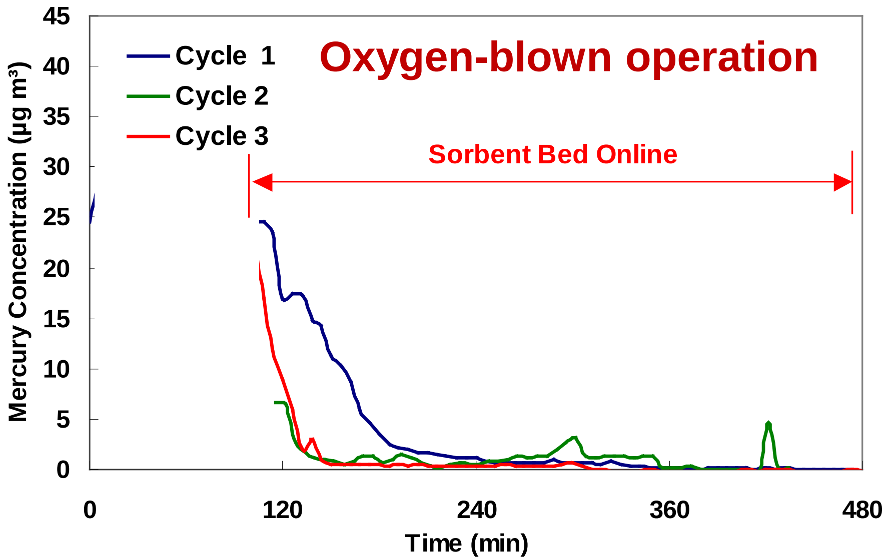
Test Results at UNDEERC

Halogenated Carbon, T=215ºC (420ºF)



TDA Sorbent, T=215ºC (420ºF)





- **TDA sorbent achieved over 95% Hg removal efficiency and outperformed commercial halogenated carbon**
  - EERC Report November 2007 "Gasification of Lignites to Produce Liquid Fuels, Hydrogen and Power"
- **Stable operation over 10 cycles at UNDEERC and over 30 at TDA**

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Key R&D Needs

- **Demonstrating the combined NH_3 and Hg removal capability using a regenerable sorbent**
  - Optimize and scale-up the sorbent
  - Laboratory experiments
  - Demonstrate long-term durability of the sorbent over many cycles
  - Slipstream evaluations using actual coal-derived synthesis gas for proof-of concept evaluations
  - Complete a high fidelity process design and economic analysis

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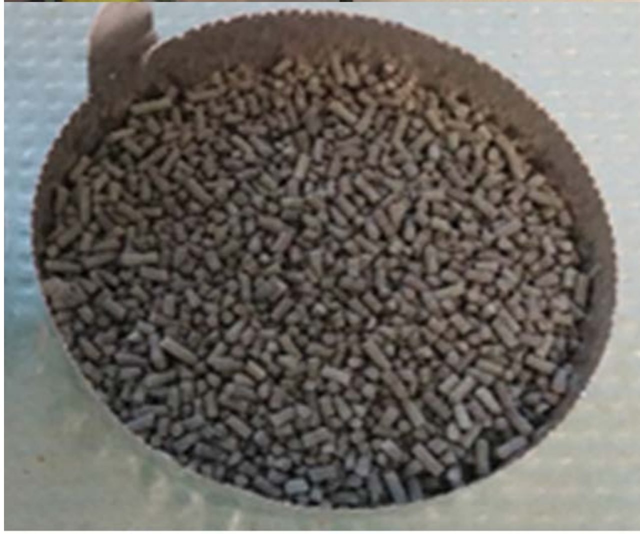
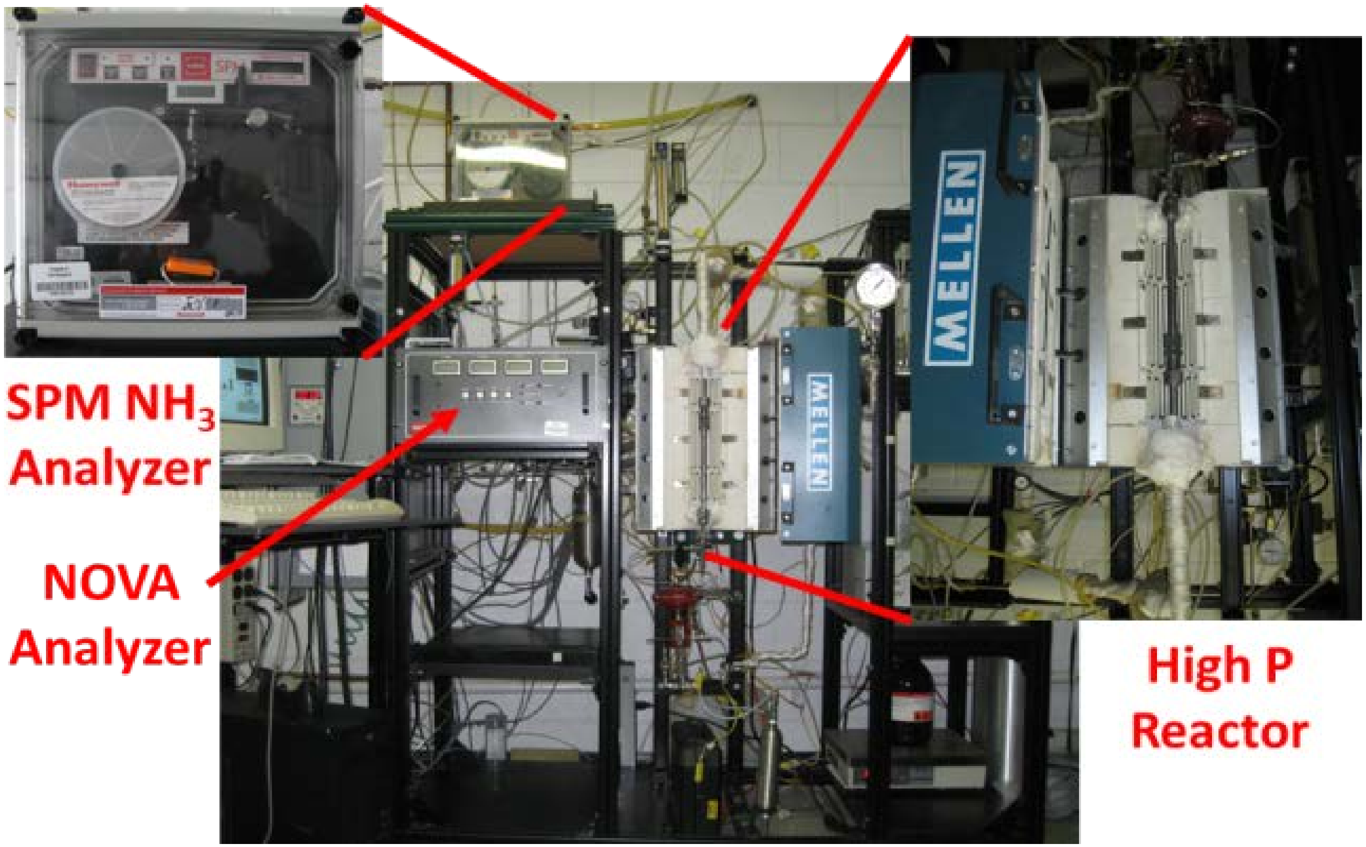
Sorbent Development and Scale-up



- Sorbent production was scaled up using high throughput manufacturing equipment
- Batch size 80 kg
- Final product 1/16” cylindrical extrudates with very high mechanical integrity
- Crush strength >2 lbf/mm
- (1/8” or ¼” size is also possible)



Setup Used in Contaminant Removal Tests



- High T/High P test rig capable of simulating synthesis gas compositions
- Nova Analyzer for H_2, CO, CO_2, CH_4 measurements
- SPM/Honeywell analyzer was used for AsH_3 and HCN detection
- Tekran 330 CEM for Hg analysis

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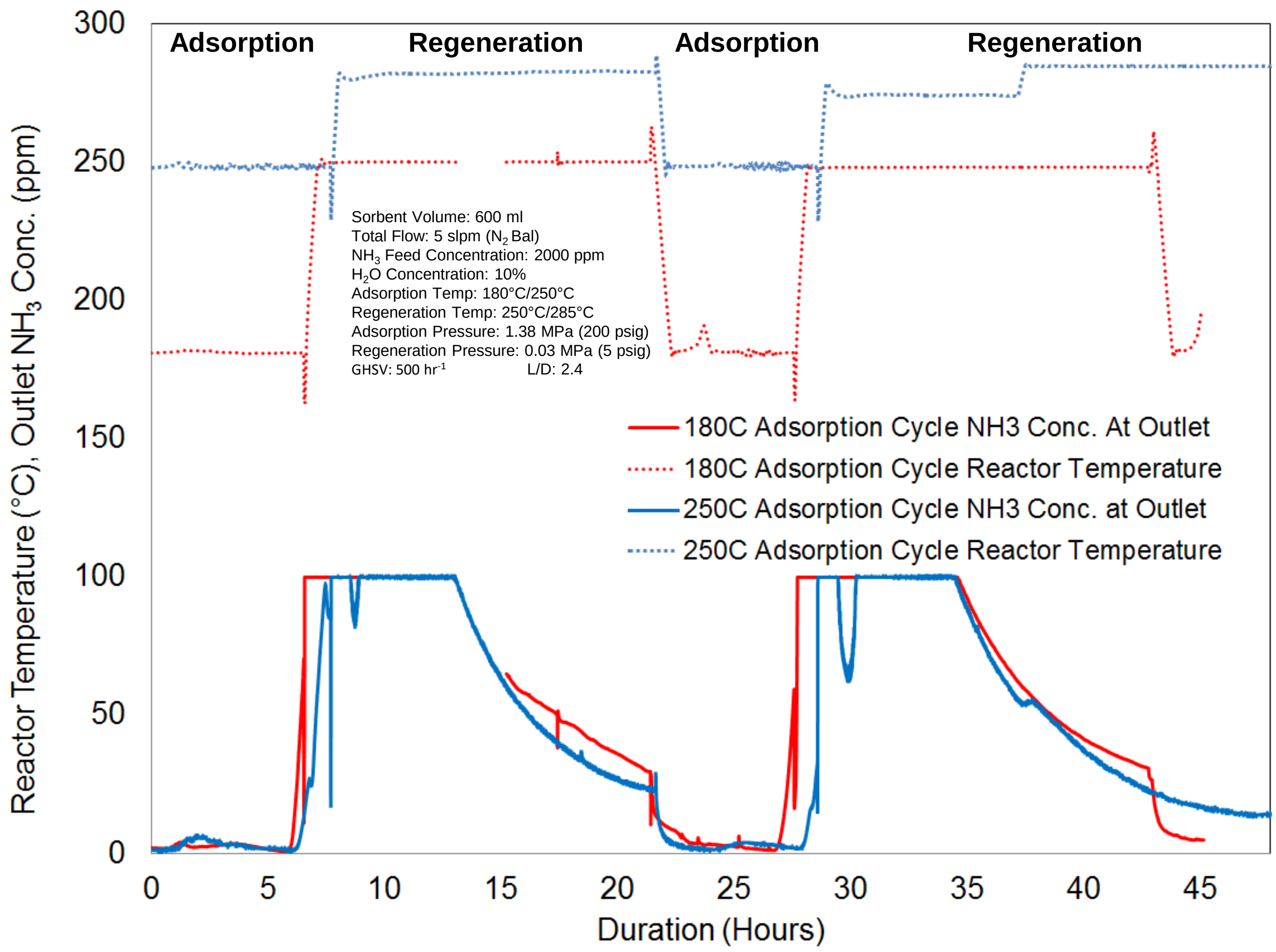
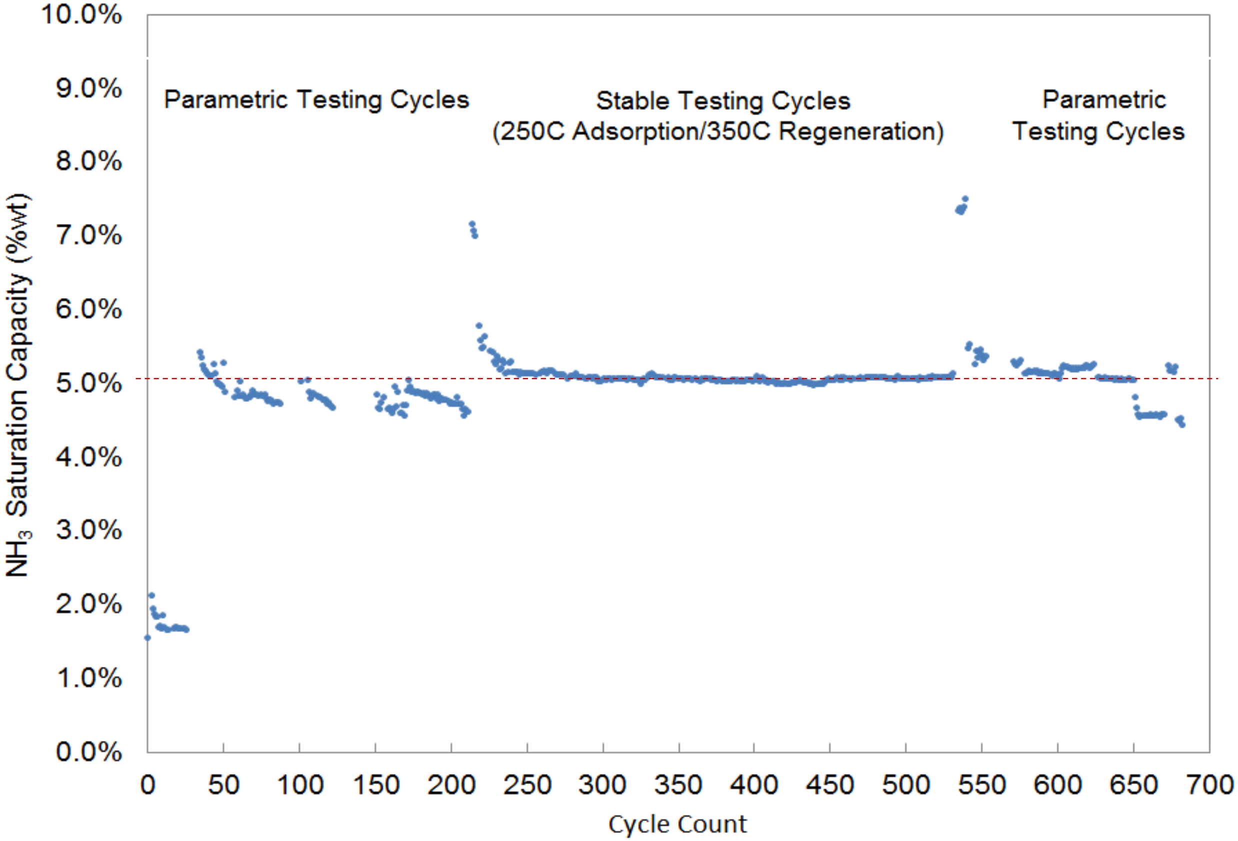
Typical Test Profile – NH_3 Removal



Regenerable NH_3 Removal

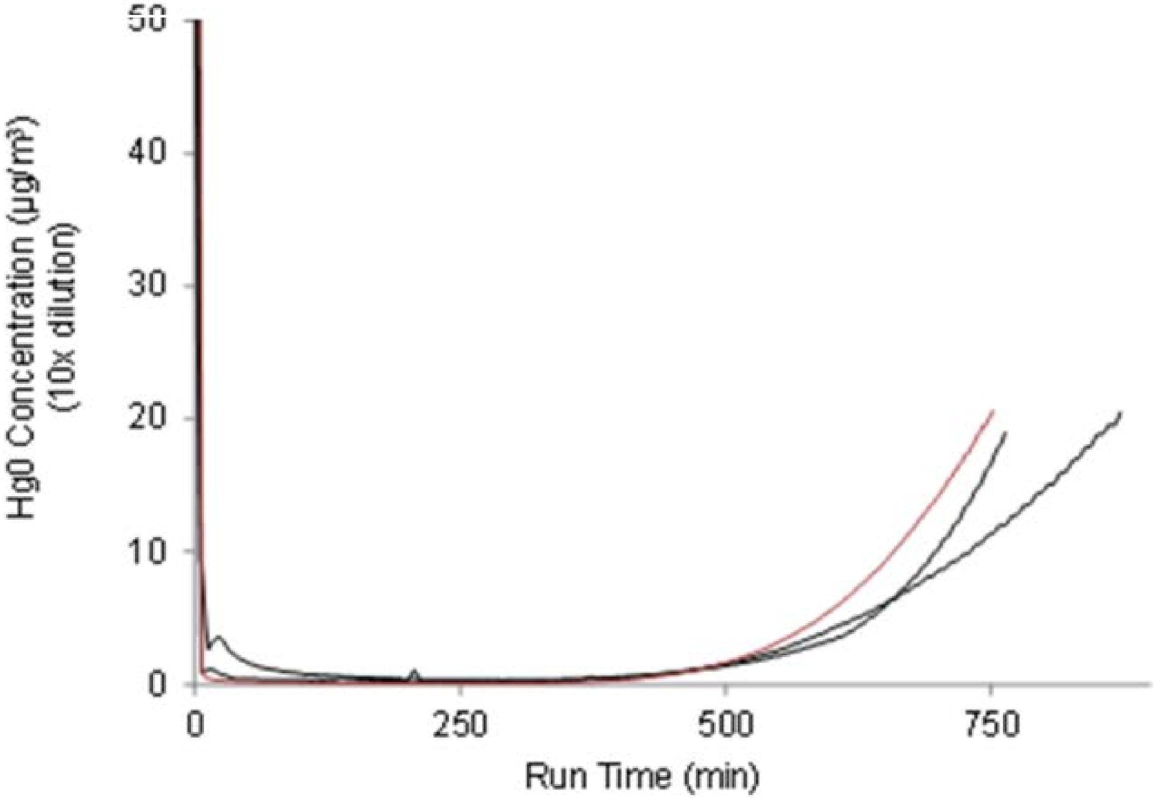
Adsorption: T=200-250°C, P= 100 psig, NH_3 Inlet = 2,000 ppmv, GHSV = 2,000 h^{-1}, simulated synthesis gas
Regeneration: T= 250-300°C, P=10 psig under N_2 flow, GHSV = 200 h^{-1}



- **TDA sorbent maintained a stable capacity ~700 cycles (achieving over 5% wt. NH_3 capacity)**

Hg Removal

Absorption: T= 240°C, P = 2.5 psig, Hg = 70 ug/m^3, GHSV = 3,000 h^{-1}
Regeneration: T= 280^{o}C, P=1 psig under N_2 flow, GHSV = 200 h^{-1}



- **TDA sorbent also maintains a stable capacity for Hg over multiple cycles (3 cycles were completed to demonstrate the concept)**

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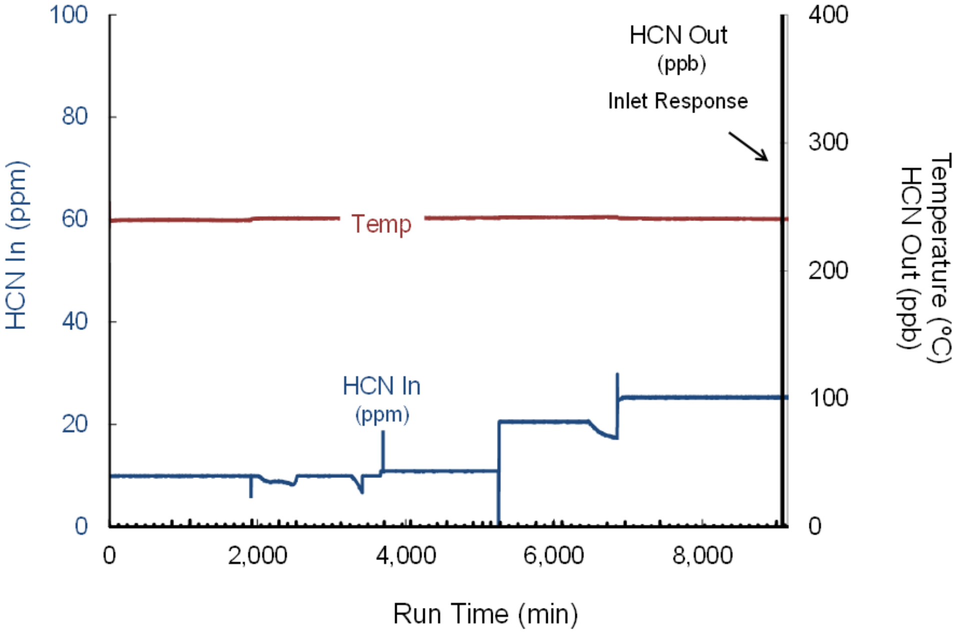
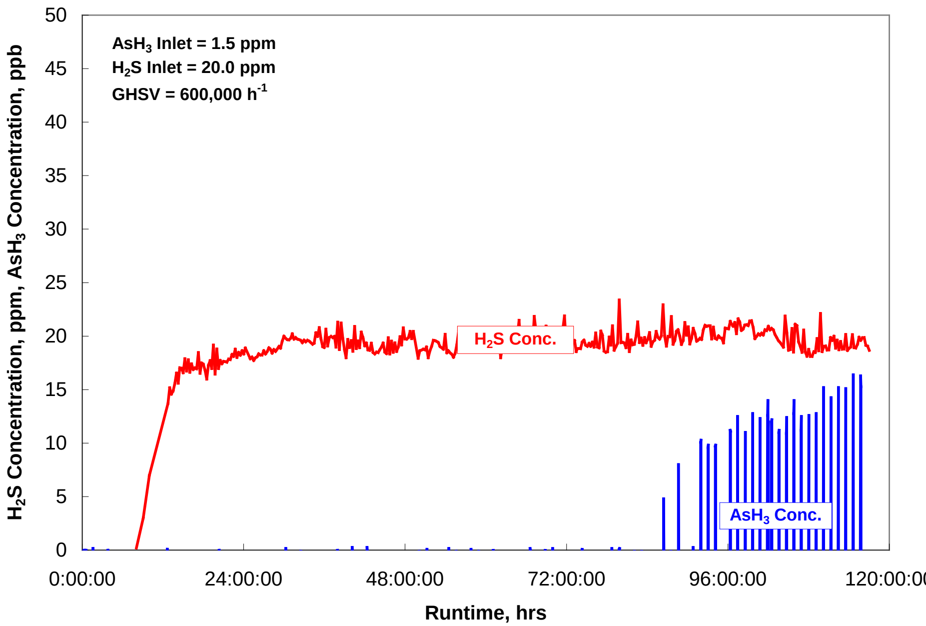
HCN and AsH_3 Removal

T = 240°C, HCN = 10 ppmv, P= 300 psig, GHSV = 7,500 h^{-1}



- Sorbent also achieved over 3% wt. HCN capacity with very high removal efficiency

T= 245°C, P= 350 psig, AsH_3 Inlet= 1.22 ppmv, H_2S Inlet= 20-4,800 ppmv, GHSV= 180,000 h^{-1}



- In presence of 20 ppmv H_2S, 7.1% wt. capacity was achieved (at breakthrough)
  - Sorbent also achieved 8.5% wt. sulfur capacity

Testing at NCCC/PSDF In a 4-Bed PSA

4-bed PSA Skid

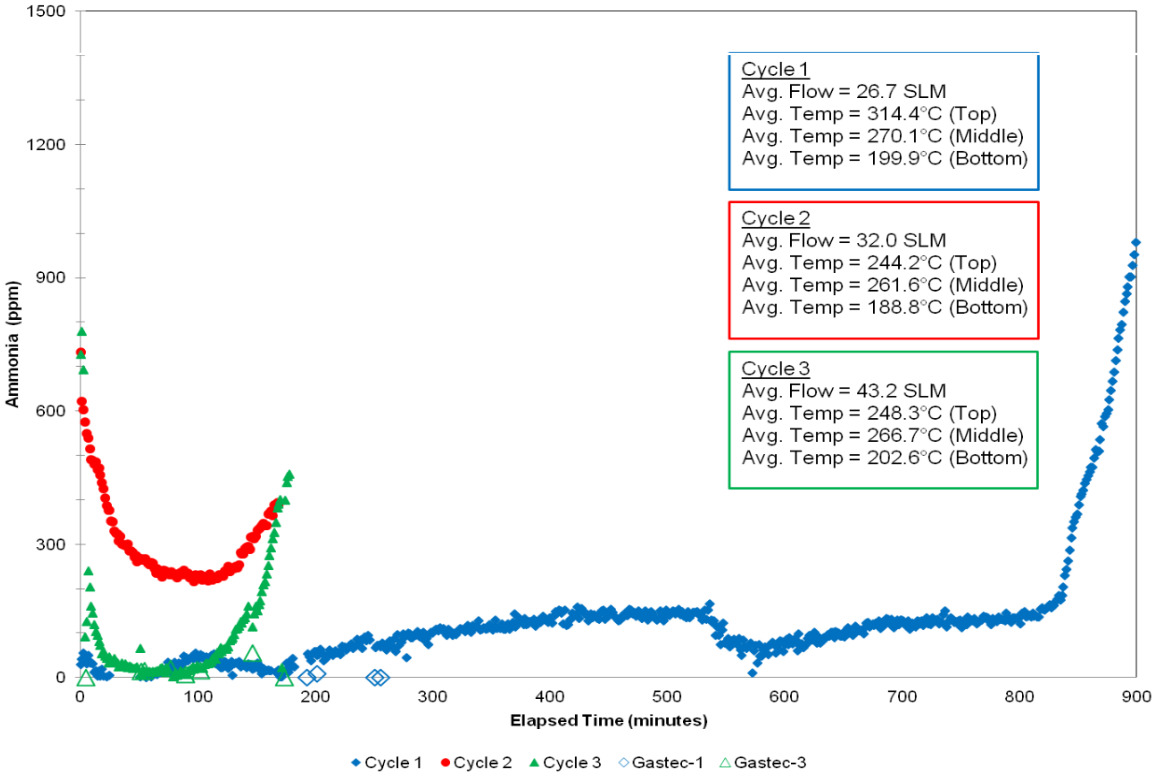
Gas Conditioning Skid

- A 4-bed PSA field unit designed to evaluate a pre-combustion CO_2 removal sorbent qualified for use at NCCC/PSDF is used for proof-of-concept evaluations

Field Test Units Installed at NCCC

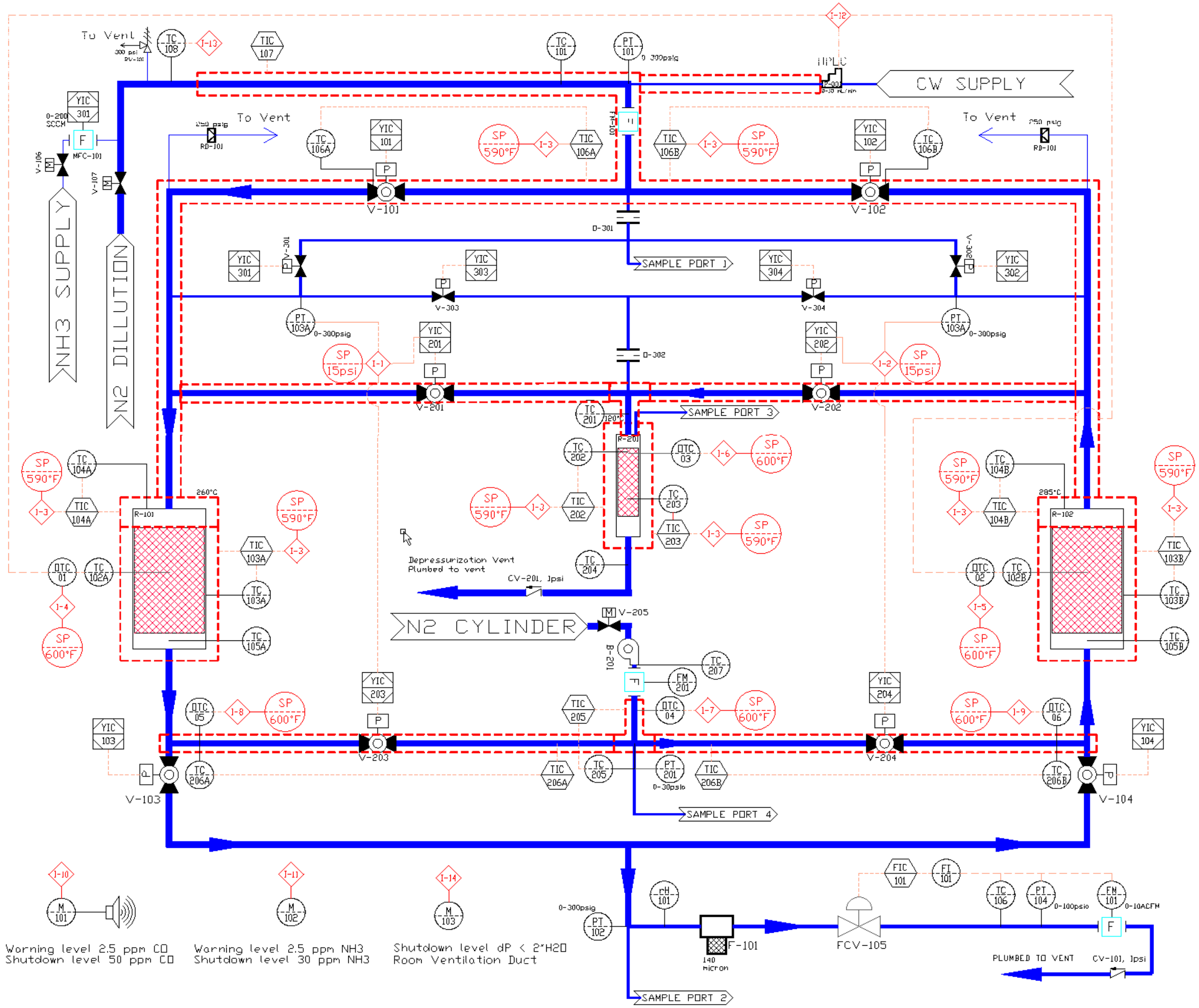
NCCC Test Results

Adsorption: T=200-250ºC, P= 100 psig, NH_3 Inlet = 2,000 ppmv, GHSV = 2,000 h^{-1}, simulated synthesis gas
Regeneration: T= 250-300ºC, P=10 psig under N_2 flow, GHSV = 200 h^{-1}



- **Three cycles were performed by "only" applying pressure swing**
- **First cycle had a very high capacity as in the consecutive ones sorbent is not fully regenerated**

P&ID of the New Test Unit



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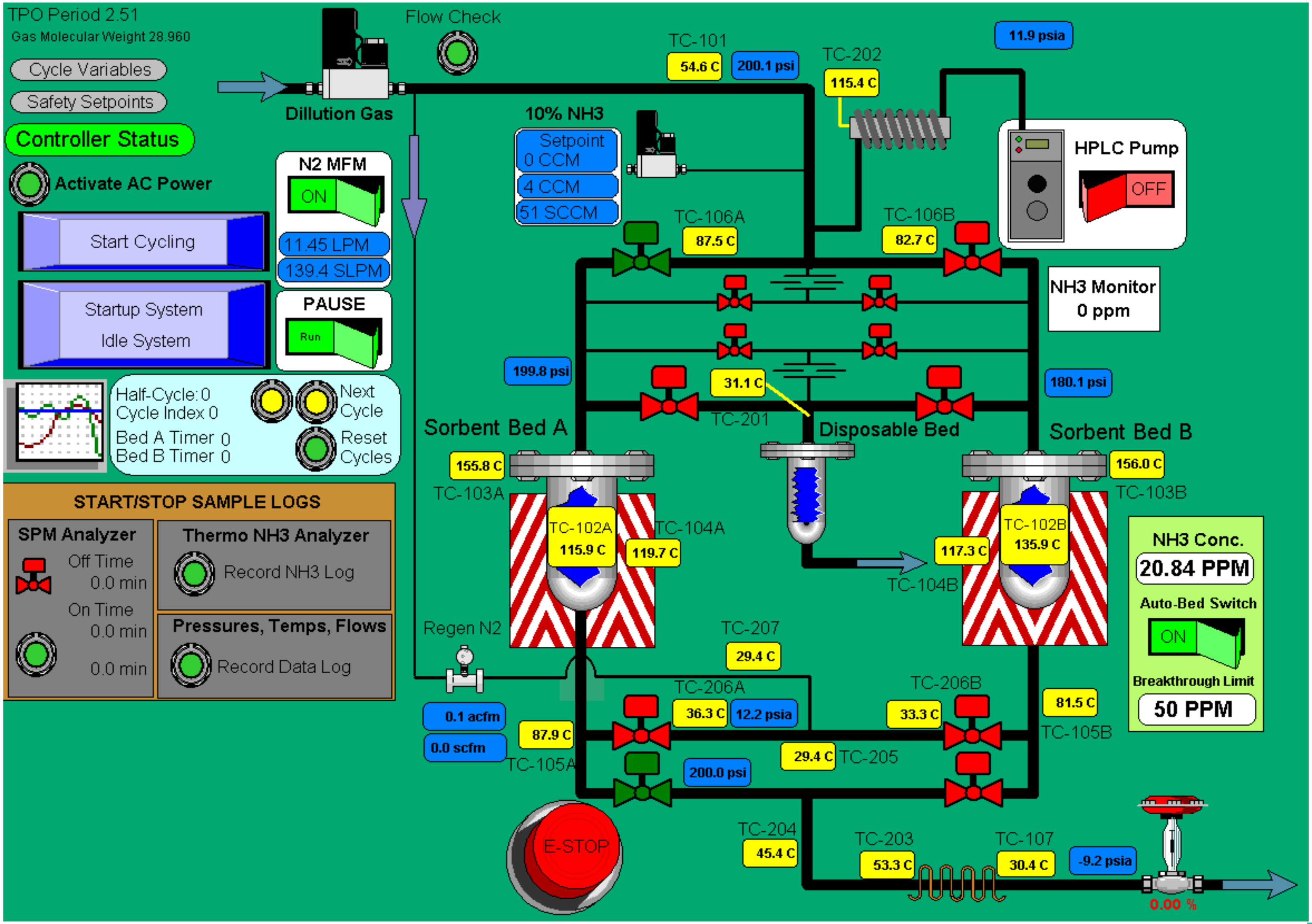
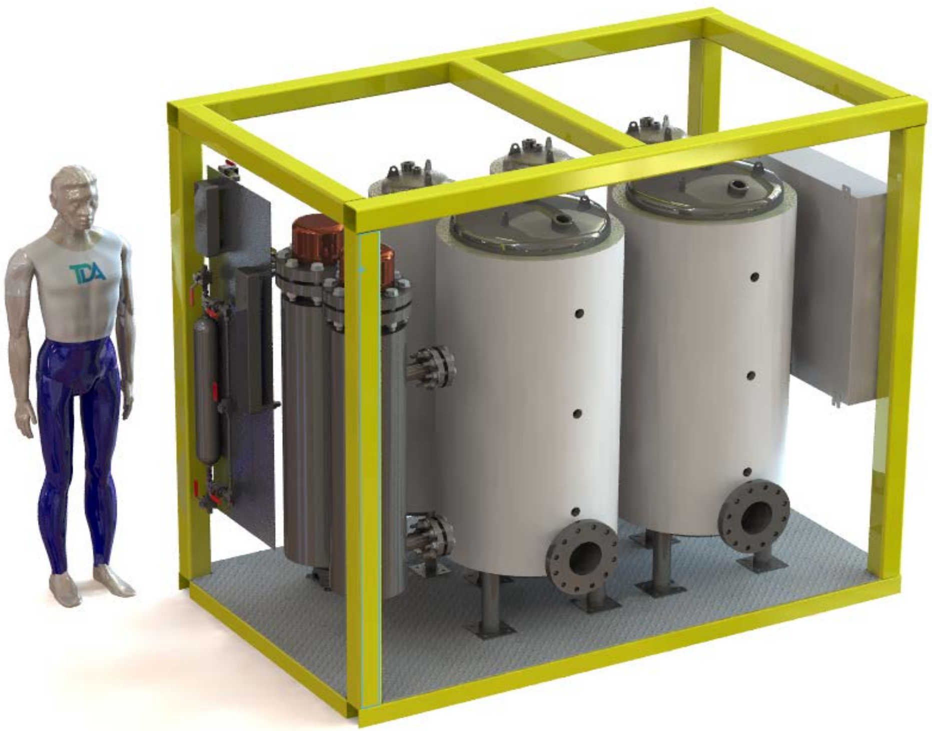
Prototype Control System



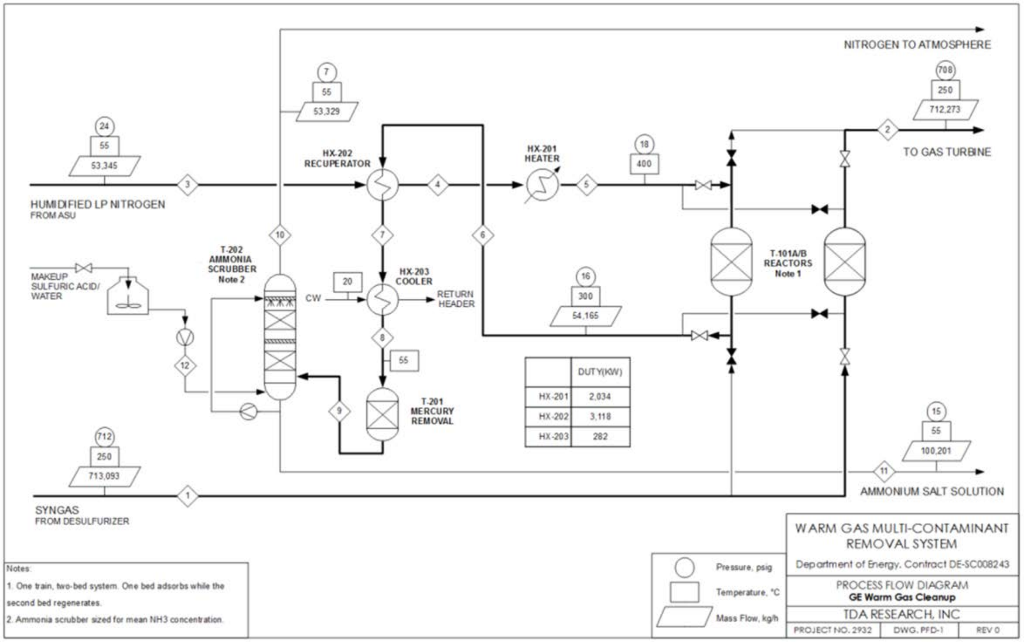
Fabrication of the Test Unit



- A slipstream test unit is being fabricated to demonstrate continuous removal of NH_3 and Hg using coal derived synthesis gas
- Originally, we have designed a unit that is capable of treating 10 SCFM of synthesis gas for testing at the NCCC
- A smaller unit is now being built to treat up to 1 SCFM synthesis gas

Engineering and Cost Analysis

- **Design Basis = 550 MW IGCC Plant**
  - NH_3 Concentration = 1,300 ppmw
  - Hg Concentration = 52 ppbw
  - AsH_3 Concentration = 1 ppmw
  - HCN Concentration = 1 ppmw



Labor Cost	**$**	**212,212**	
Operating Labor	$	124,830	1 person-3 shift/$20/hr
Supervising Labor	$	18,725	15% operating labor
Maintenance Labor	$	68,657	55% operating labor
Maintenance Materials		**395,351**	1% of TCC
Sorbent Replacement Cost	**$**	**1,228,241**	
Regenerable Sorbent Cost			$12/L
Expendable Sorbent Cost			$7.5/L
NH3 Scrubbing Solution Cost		**$45,261**	
Scrubbing Solution Unit Cost			$200/tonne
Power Cost		**423,142**	@ $0.05/kWh
Overhead		**121,512**	20% of Direct O&M Labor Cost
Taxes, Insurance, Administrative		**1,281,405**	4% of the Capital Cost
Total O&M Cost	**$**	**3,707,124**	
Total Capital Cost	**$**	**32,035,125**	
Capital Recovery Cost	**$**	**6,407,025**	20% capital recovery factor
Annual Operating Cost	**$**	**10,114,149**	

- **The cost of removing NH_3, Hg, AsH_3 and HCN contaminants are estimated as ~$3.7 MM per year ($10.1 MM with annualized capital cost)**

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Acknowledgement

- NETL, Project Manager, Diane Madden
- Frank Morton, NCCC