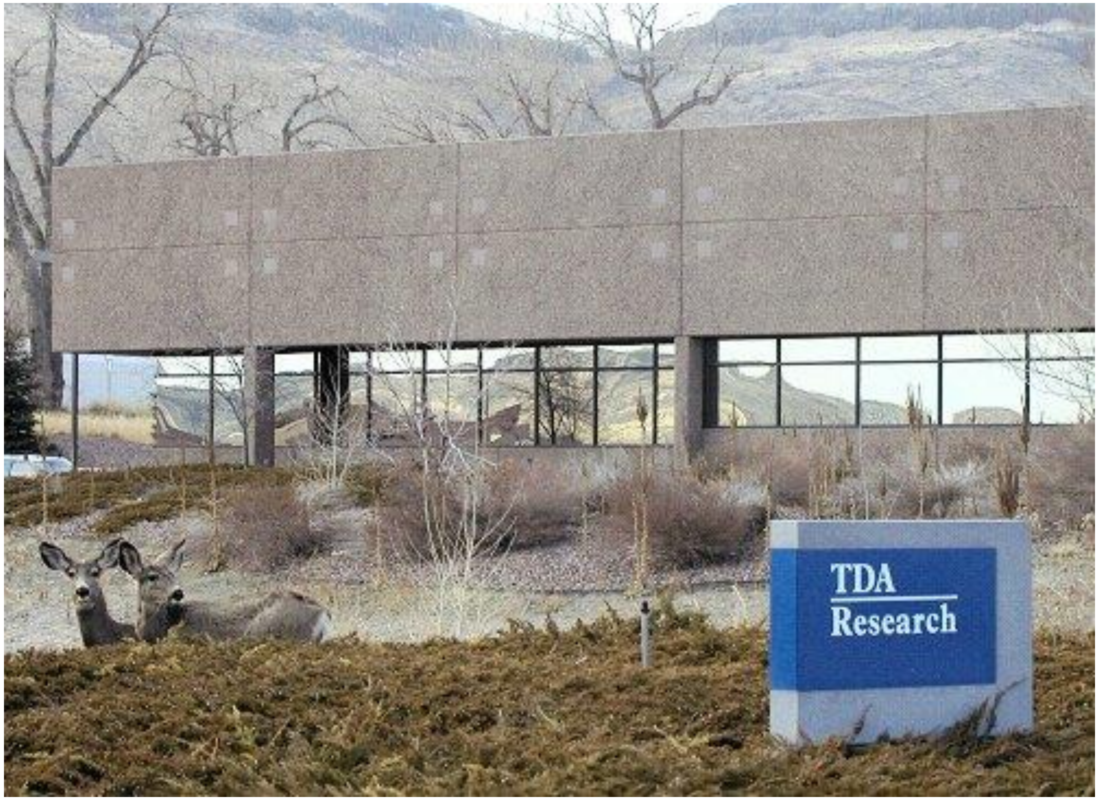
Warm Gas Multi-contaminant Removal System
(Contract No. DE-SC0008243)



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Gasification Virtual Project Review Meeting

September 3, 2020

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**
  - Completion Date – 08/31/2020

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
- **Nitrogen in the coal is converted to the NH_3 and HCN which could be oxidized 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 also potent poisons for the catalysts used in the WGS and Fischer Tropsch synthesis

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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 and converted into a stable salt**
- **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 are not effective for contaminants such as 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 <u>warm gas</u> clean-up technology**
  - **For a gasifier with water quench, the dew point is ~245°C (480°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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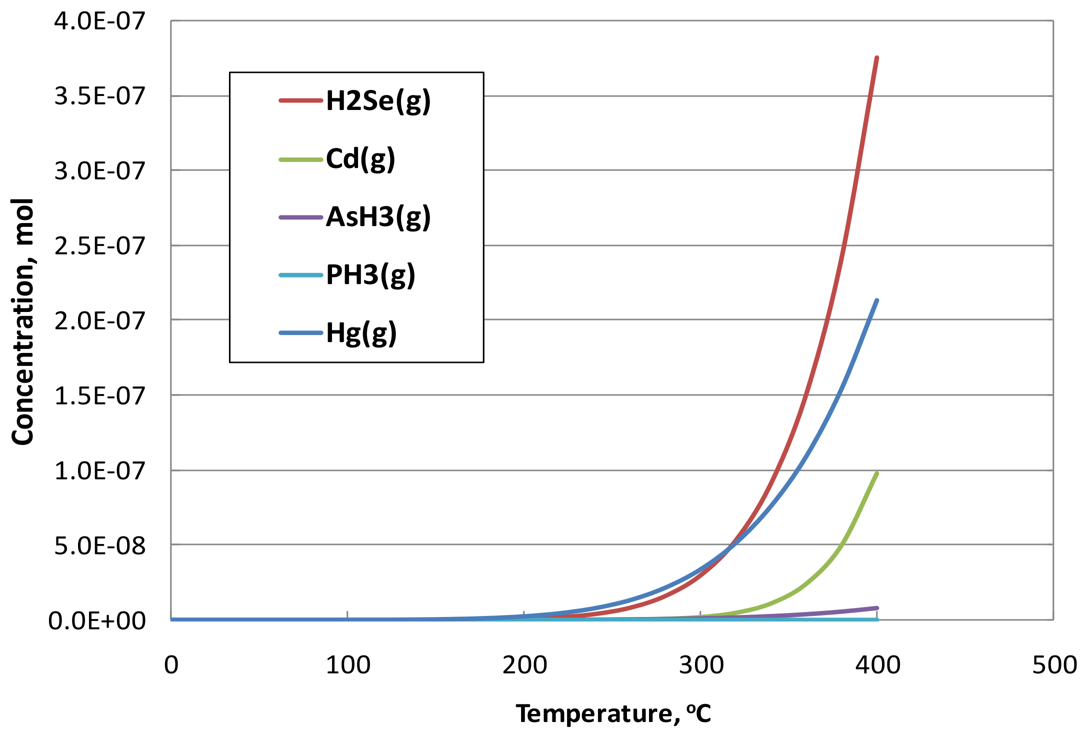
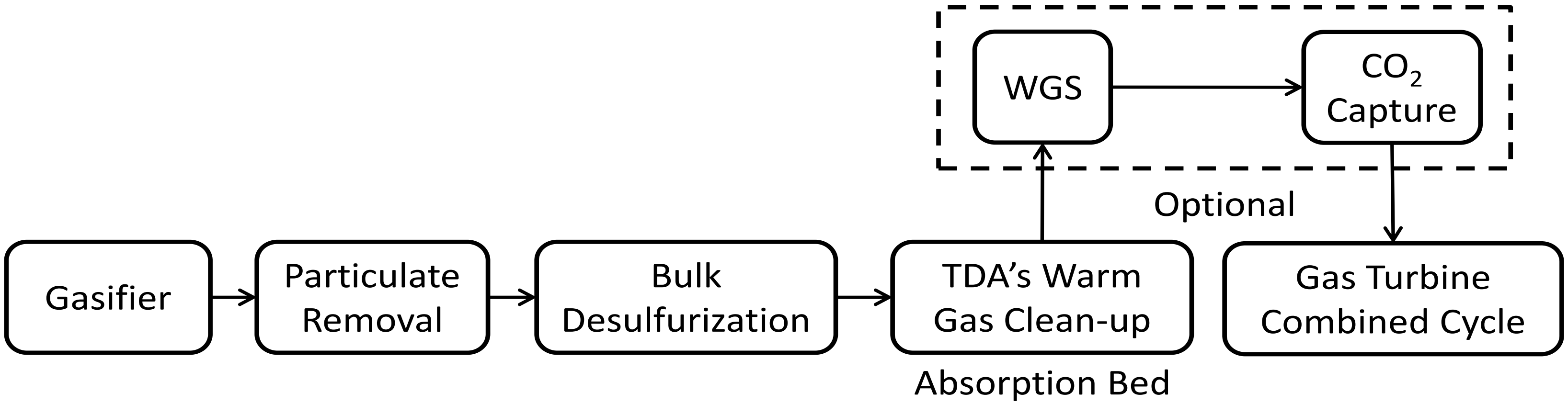
Equilibrium Compositions of Trace Metals Over New Sorbent

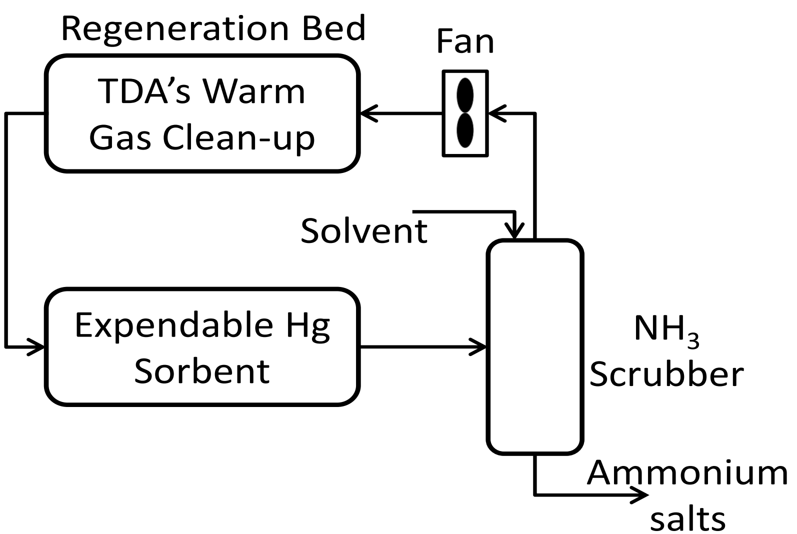


- **Hg (also Se) has a very high vapor pressure over any surface at 200ºC or higher temperatures (i.e., difficult to achieve high removal efficiency)**
  - The resulting low capacity increases the cost of using expendable sorbents
- **NH_3 removal using one-time use sorbents is also impractical as it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

TDA's Multi-contaminant Removal Process

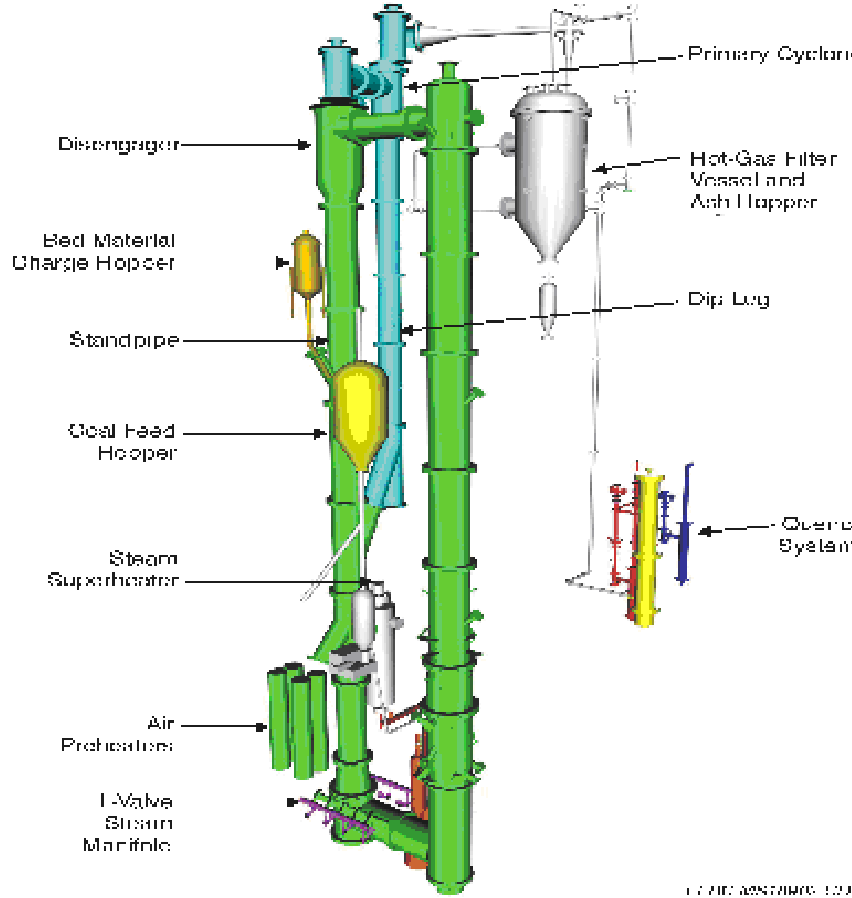


- **Hg and NH_3 are removed at high temperature**
- **The sorbent is regenerated using a combination of temperature and pressure swing**
- **The off-gas from the sorbent bed is cooled enabling the use of low temperature sorbents or scrubbers**



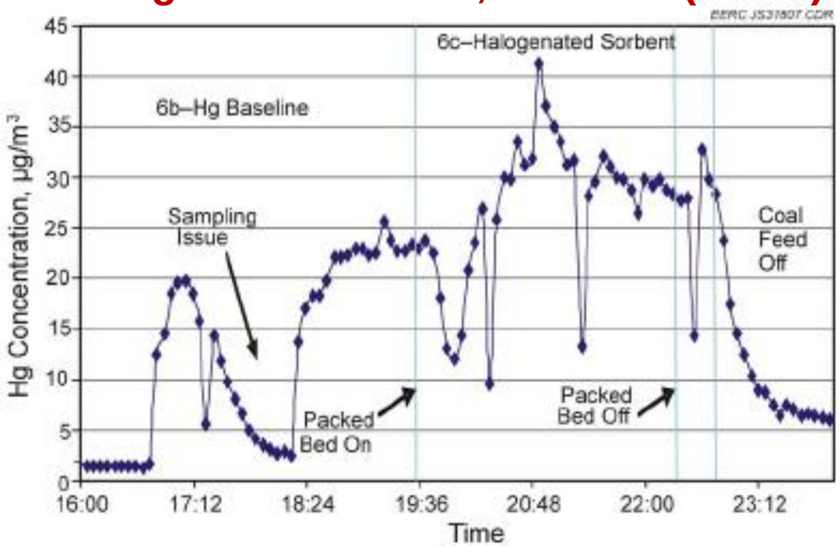
Early Testing at UNDEERC

- **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

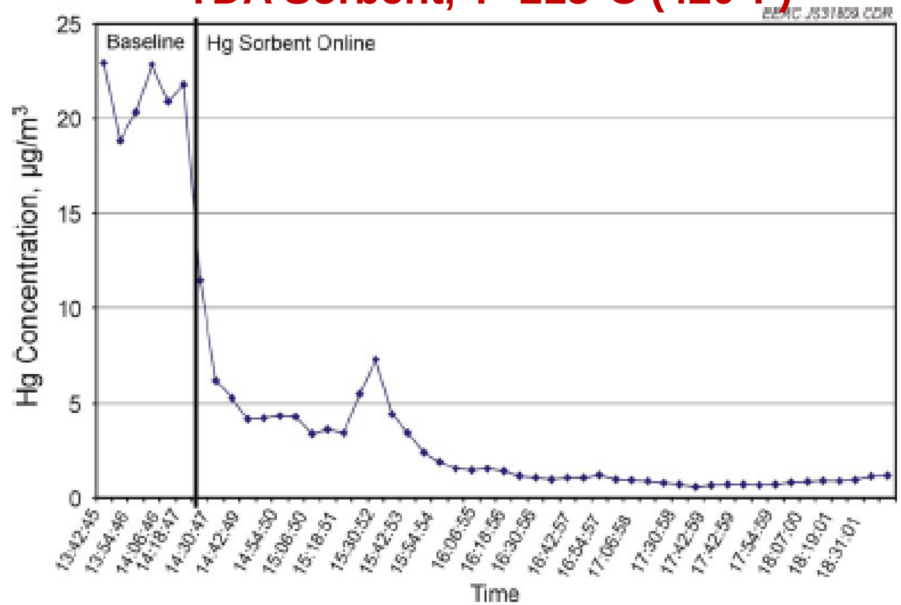


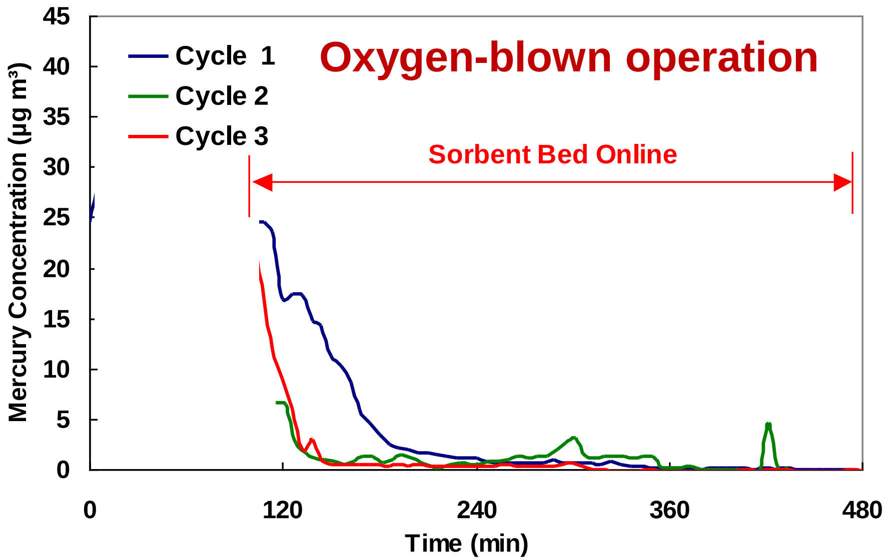
Test Results at UNDEERC

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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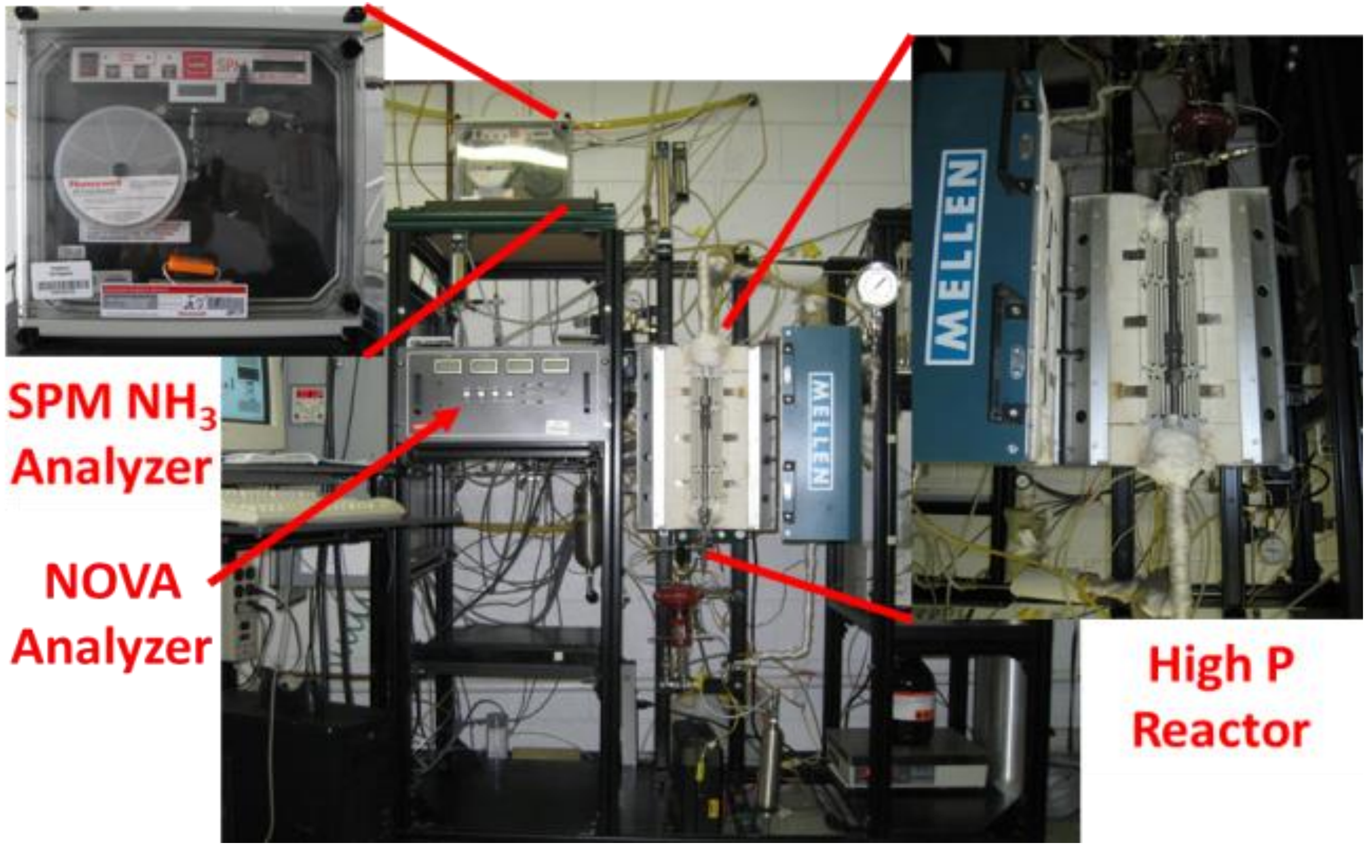
Sorbent Development and Scale-up

- **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)**

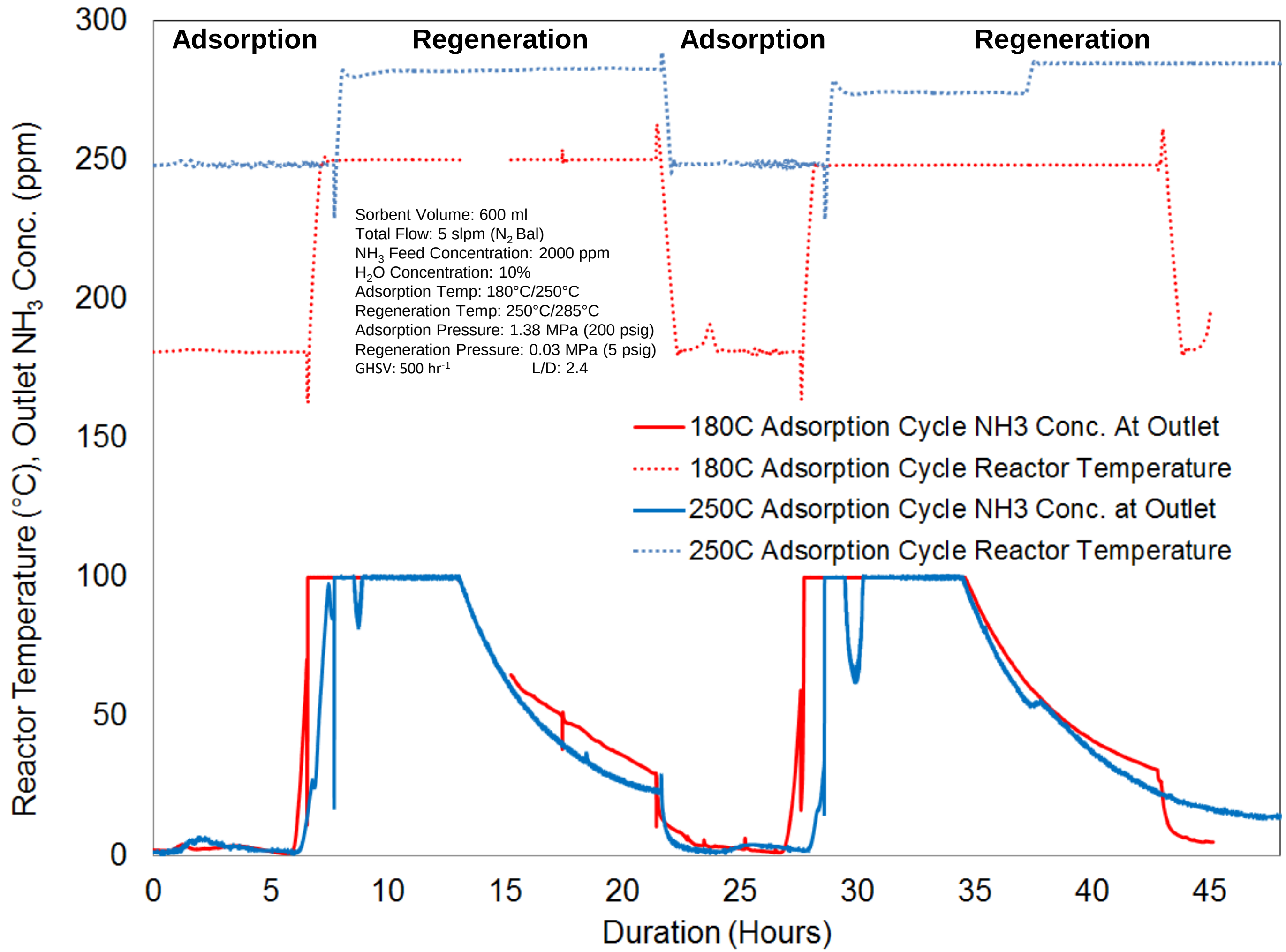
Setup Used in Contaminant Removal Tests



- 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

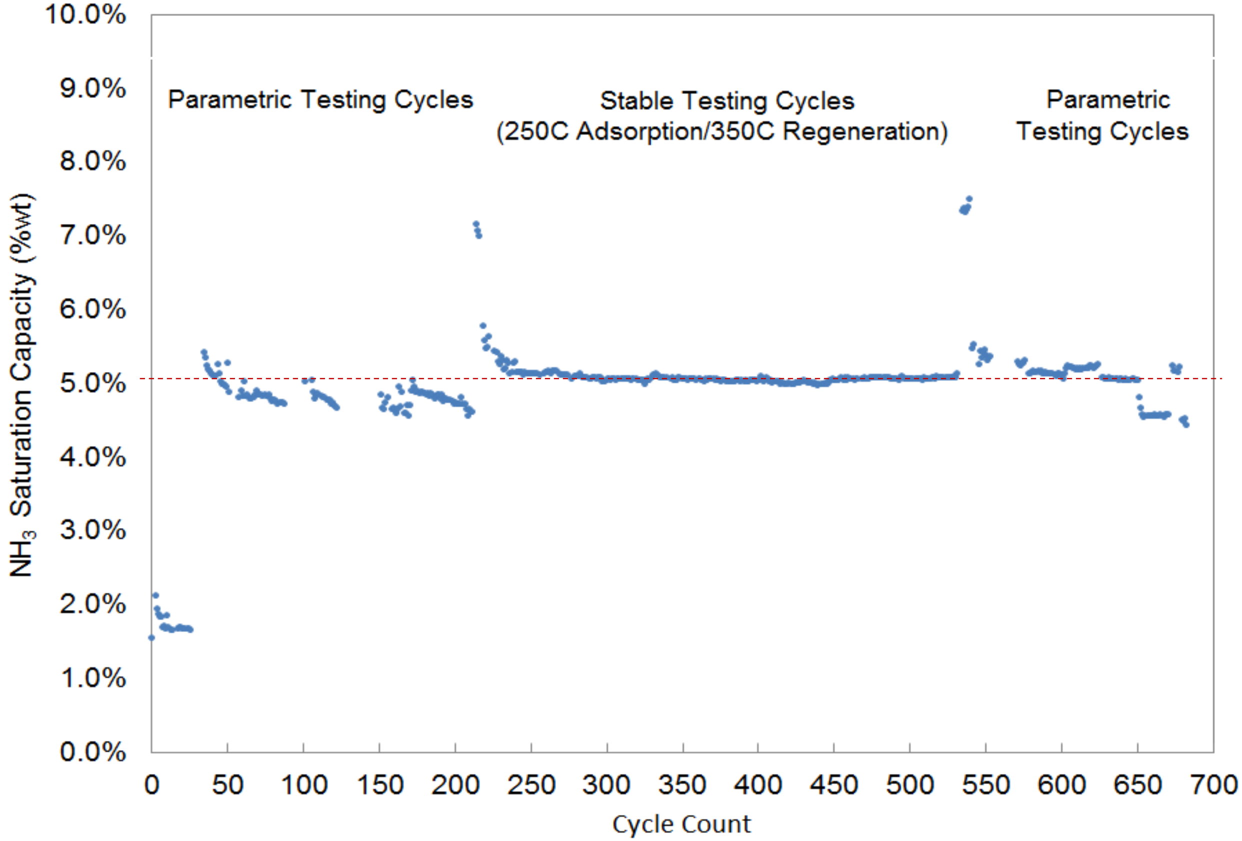
Typical Test Profile – NH_3 Removal

NH_3 Feed Concentration = 2,000 ppmv, H_2O = 10% vol., P = 200 psig, simulated syngas



Regenerable NH_3 Removal

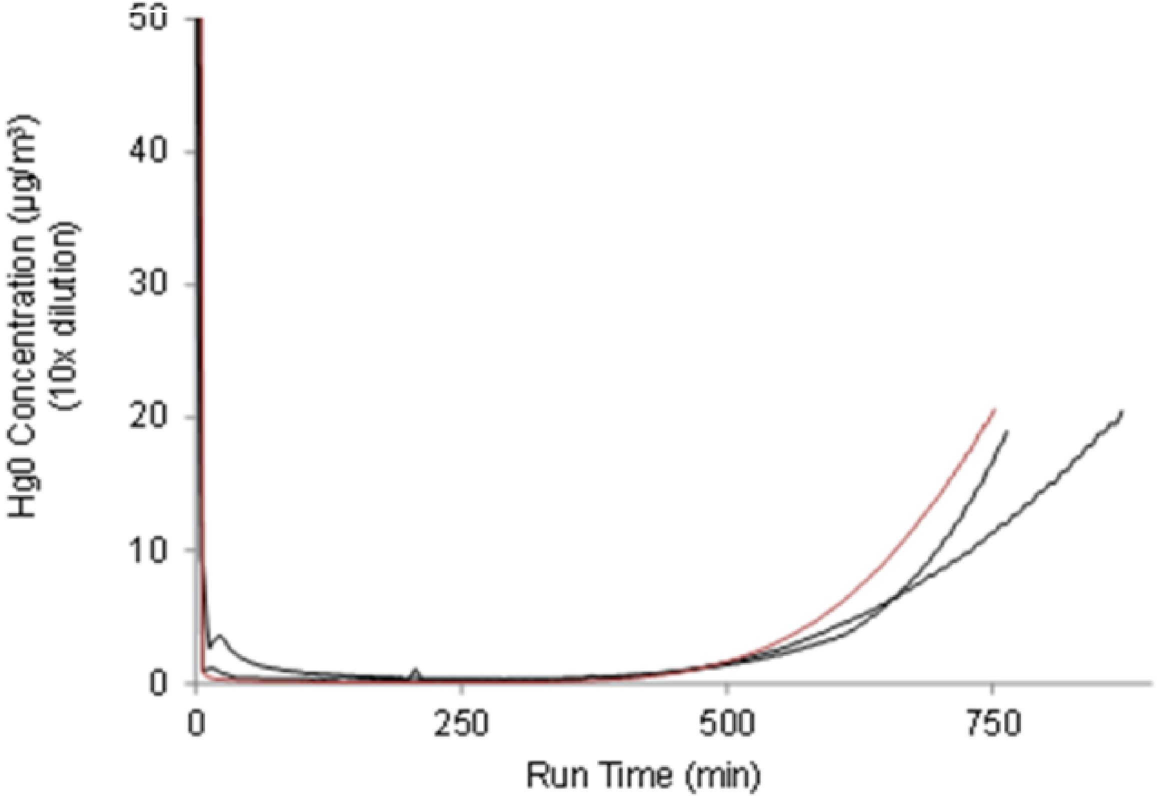
Adsorption: T=200-250°C, P= 100 psig, NH_3 Inlet = 2,000 ppmv, GHSV = 2,000 h^{-1}, simulated synthesis gas
Regeneration: T= 250-300°C, P=10 psig under N_2 flow, GHSV = 200 h^{-1}



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

Hg Removal

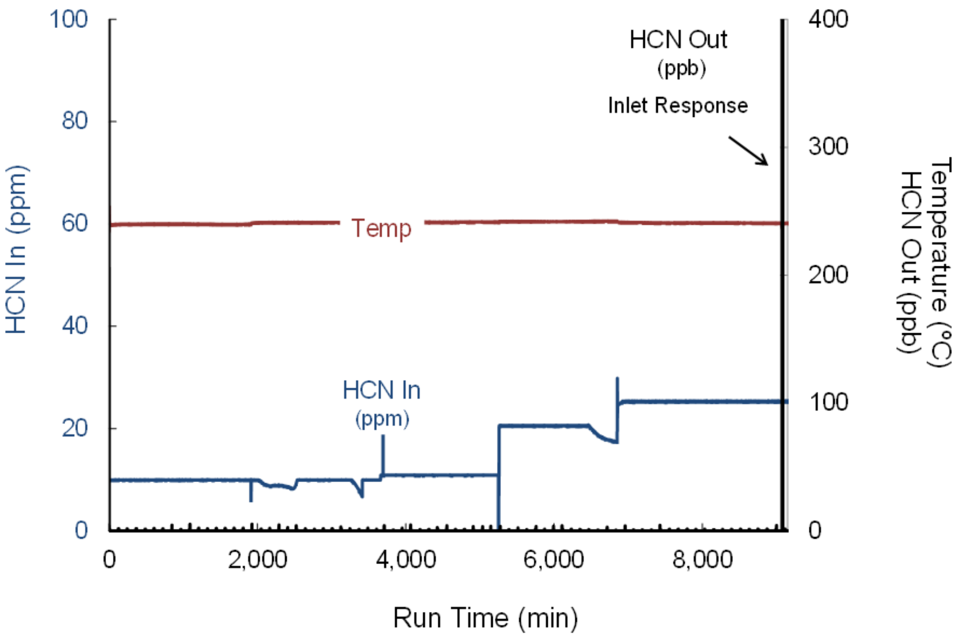
Absorption: T= 240°C, P = 2.5 psig, Hg = 70 ug/m^3, GHSV = 3,000 h^{-1}
Regeneration: T= 280^{o}C, P=1 psig under N_2 flow, GHSV = 200 h^{-1}



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

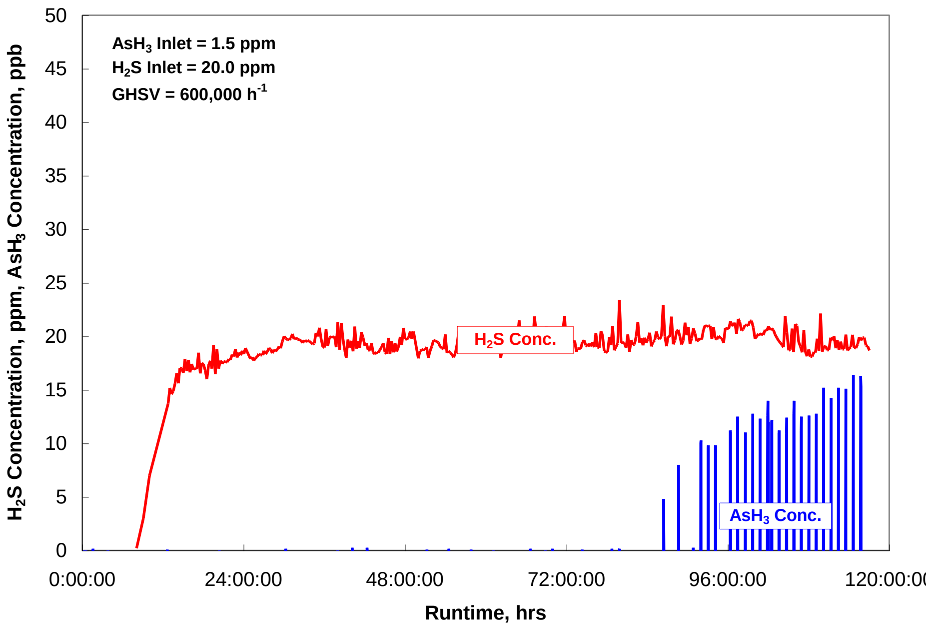
HCN and AsH_3 Removal

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

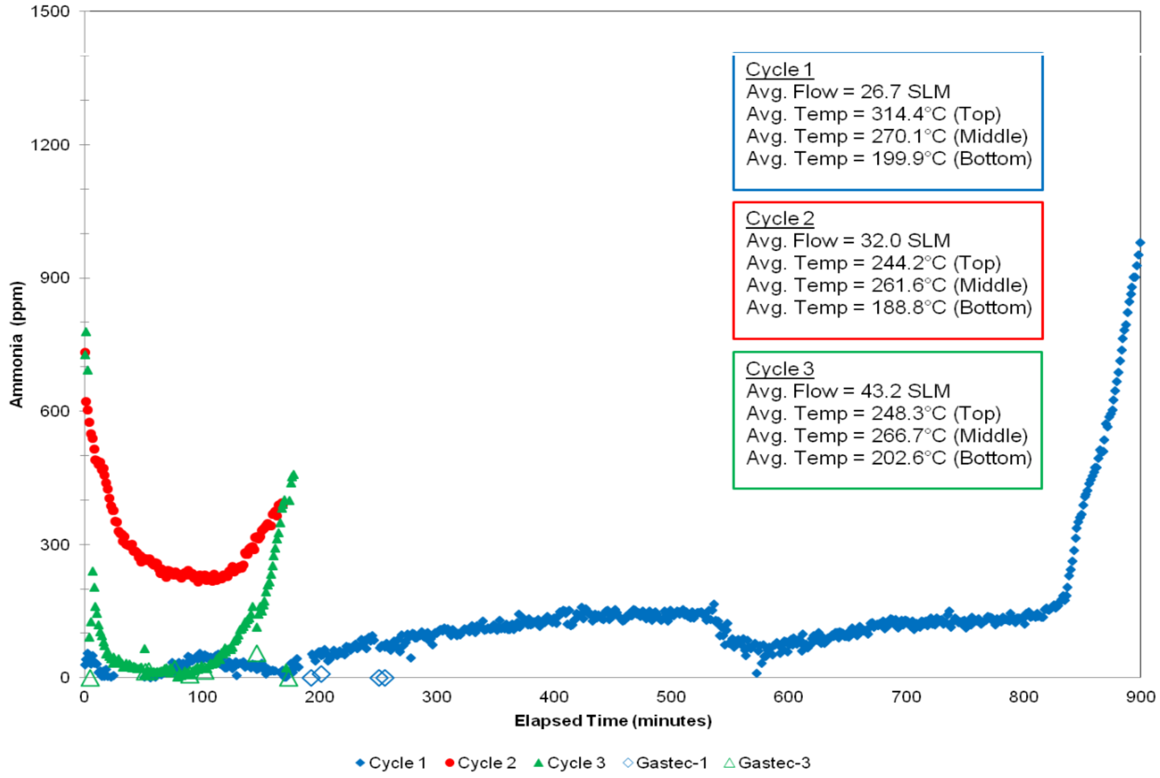
- **A 4-bed PSA field unit designed to evaluate a pre-combustion CO_2 removal sorbent qualified for use at NCCC/PSDF is used for proof-of-concept evaluations**

TDA RESEARCH

Field Test Units Installed at NCCC

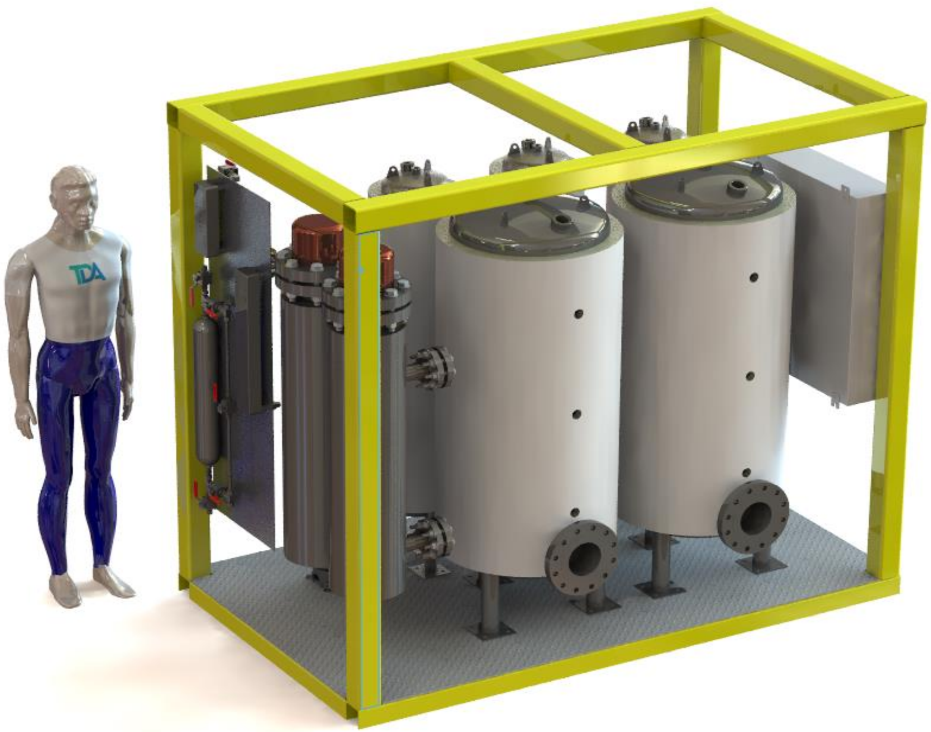
NCCC Test Results

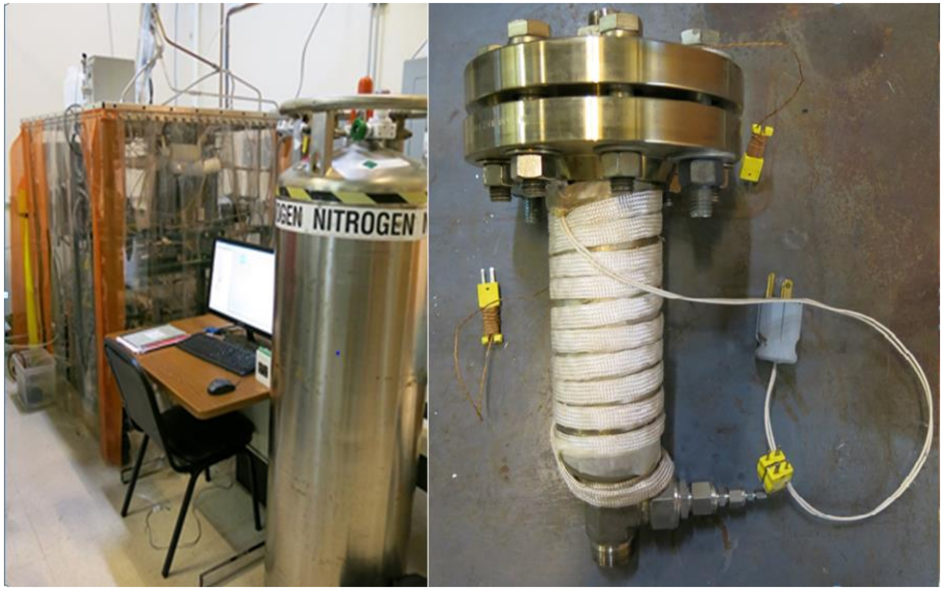
Adsorption: T=200-250°C, P= 100 psig, NH_3 Inlet = 2,000 ppmv, GHSV = 2,000 h^{-1}, simulated synthesis gas
Regeneration: T= 250-300°C, P=10 psig under N_2 flow, GHSV = 200 h^{-1}



- **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**

Fabrication of the Test Unit

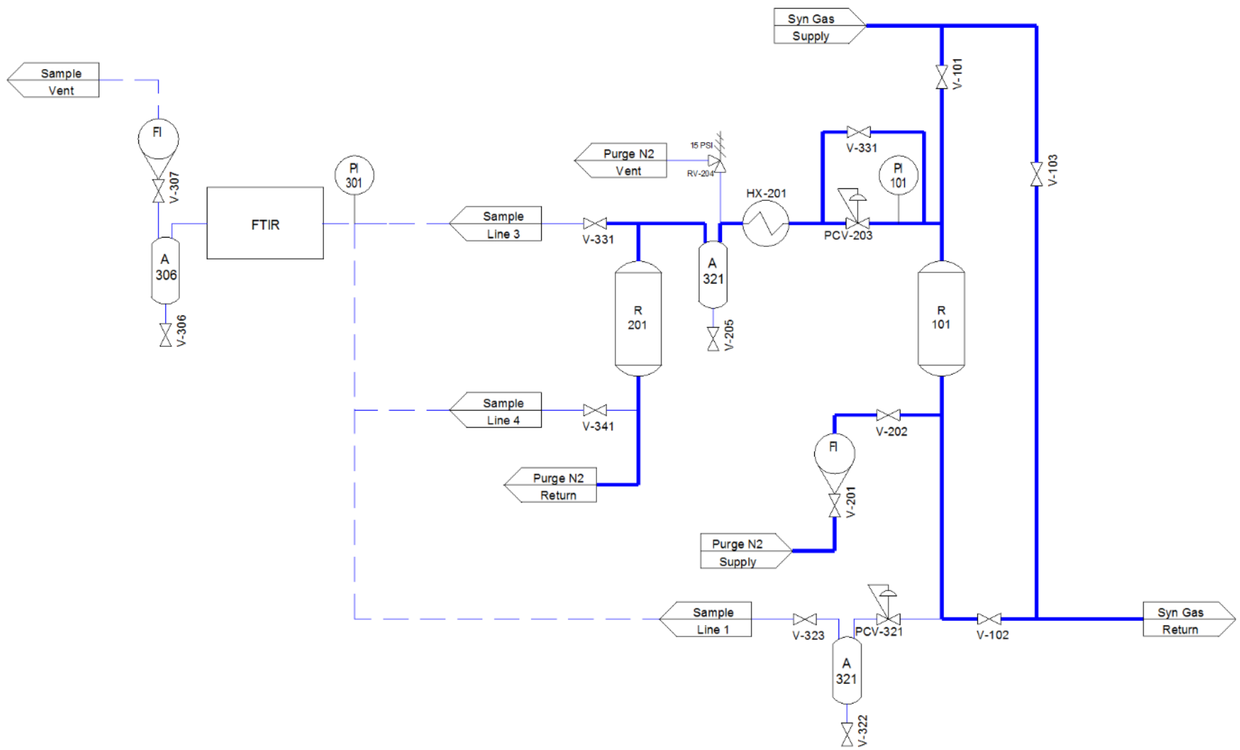


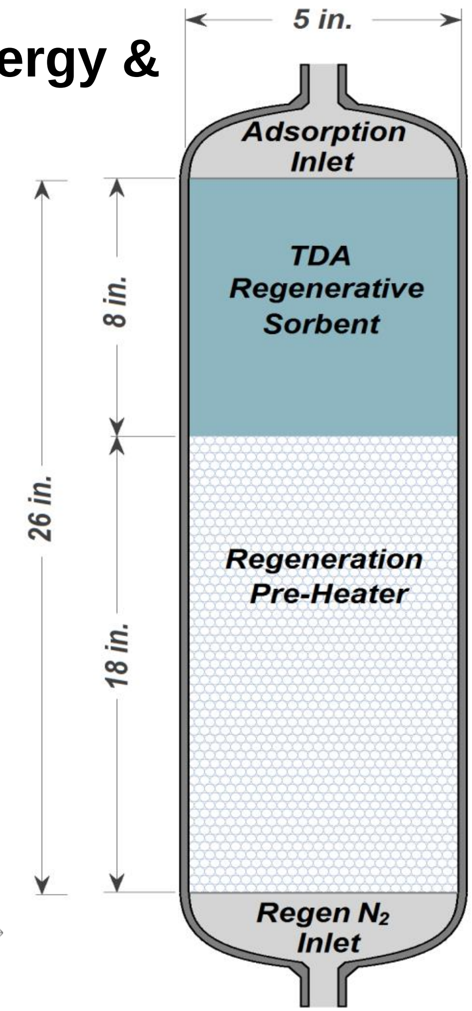


- **A slipstream test unit is designed to demonstrate continuous removal of NH_3 and Hg using coal derived synthesis gas**
- **Originally, we designed a unit that is capable of treating 10 SCFM of synthesis gas for testing at the NCCC**
- **After PSDF was shutdown, we have explored other potential sites**

UNDEERC Field Test Summary

- **Conducted at the University of North Dakota Energy & Environmental Research Center 11/13-27/2020**
- **Single 8 L sorbent bed**
- **Processed 0.3 m^3/h syngas at 5 MPa & 210°C**

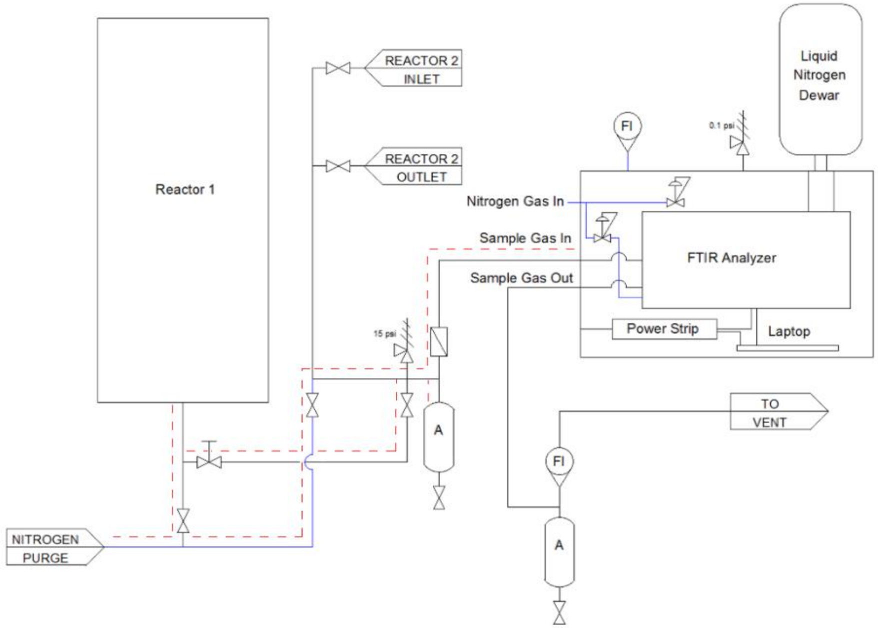




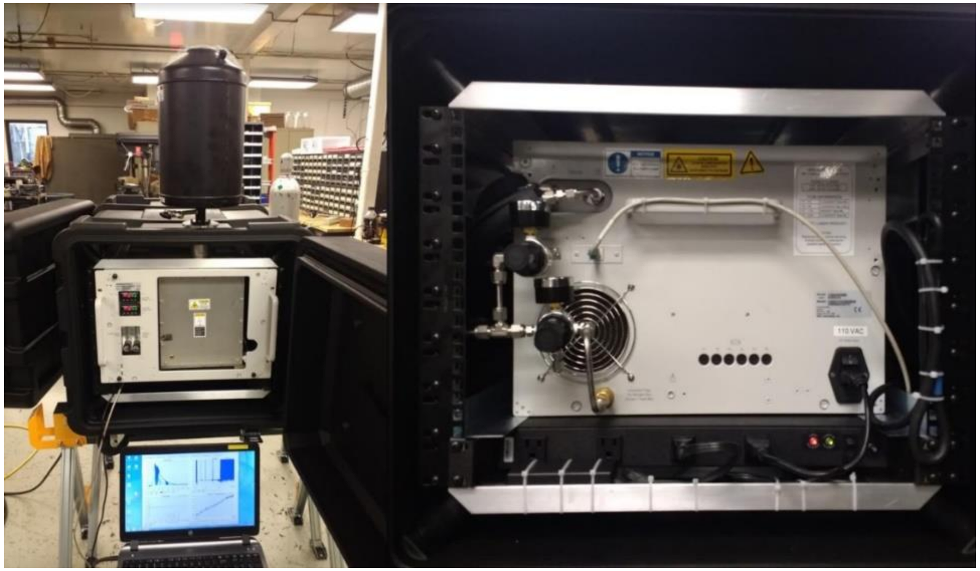
Piping & instrumentation diagram and bed dimensions for UNDEERC field test

UNDEERC Analytical Equipment

- One of TDA's liquid nitrogen-cooled FTIR analyzers was used to provide the best real-time syngas composition measurements
- TDA equipped the FTIR with a nitrogen purge container for use in the explosive environment



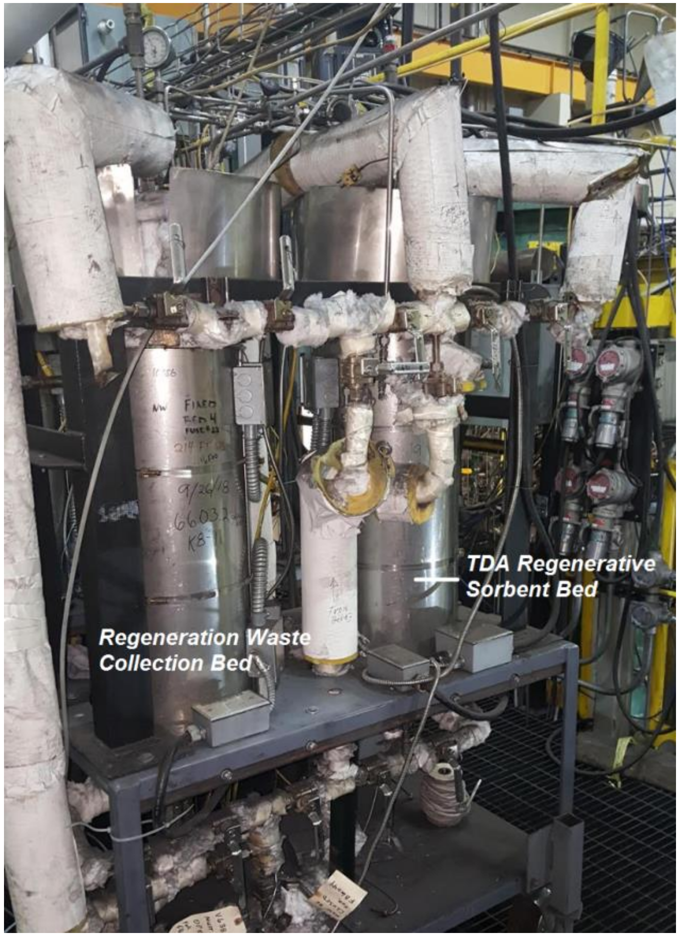
Sampling System for UNDEERC field test



TDA's FTIR analyzer in purge container with liquid nitrogen dewar attached

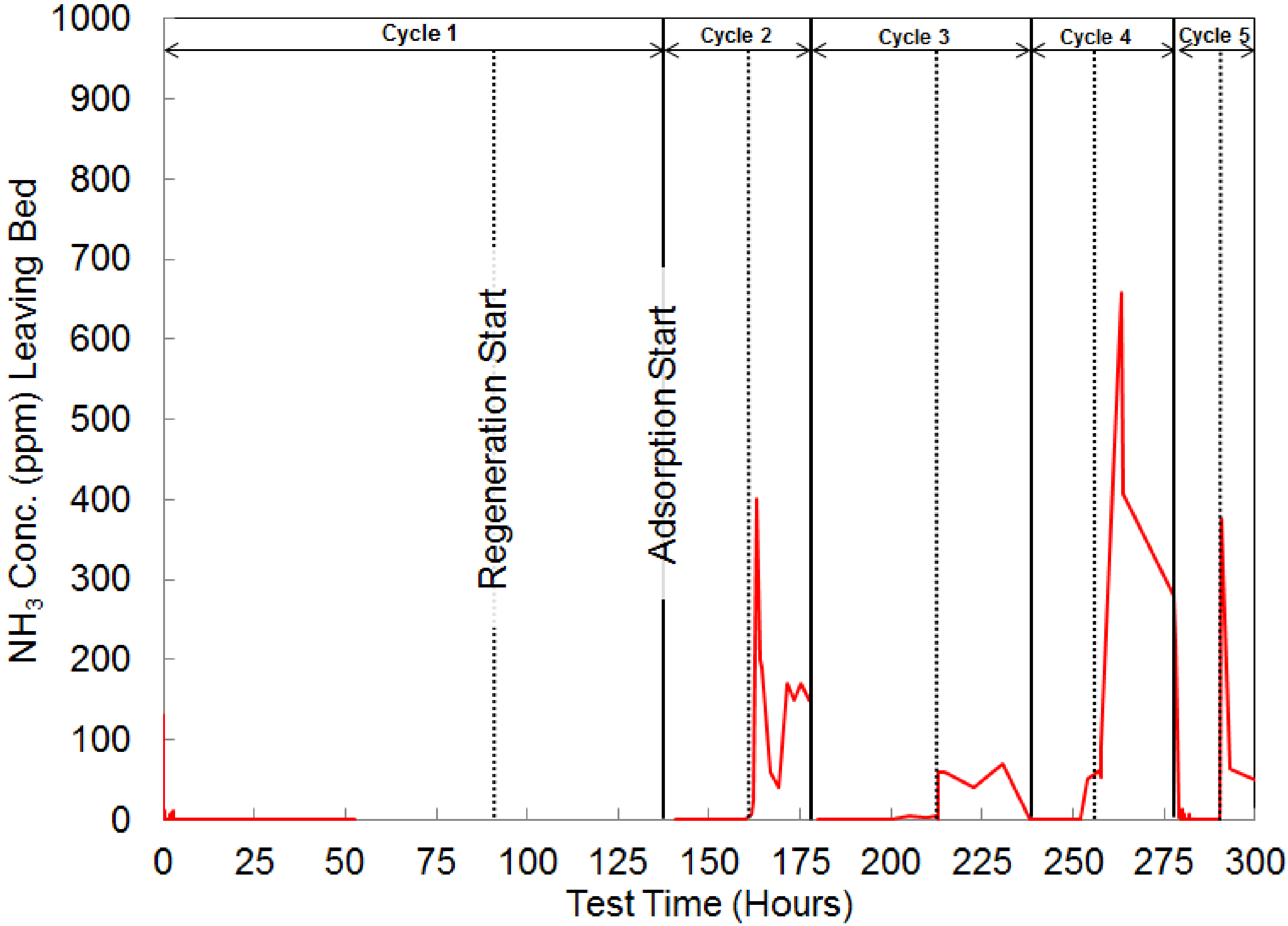
Notes on UNDEERC Field Test

- TDA sorbent was evaluated using an existing system designed to evaluated one-time use expendable sorbents
- The bed modifications was completed to enable heating
- The ammonia analysis carried out by UNDEERC indicated 2500-3000 NH_3 ppm in the feed gas (TDA determined that concentrations as lows as 700 ppm)
- The maximum flow of syngas into TDA reactor was 10 SCFH
- Multiple tests were underway and this was to ensure to provide sufficient gas flow to the other experiments
- Bed size could not be reduced as no work was allowed on the system while the gasifier was online
- As a result, we were not able to carry out as many cycles as initially designed



Regenerative and disposable bed at UNDEERC field test

UNDEERC Test Summary



- **~300 hr of testing was completed with 5 adsorption/regeneration cycles**

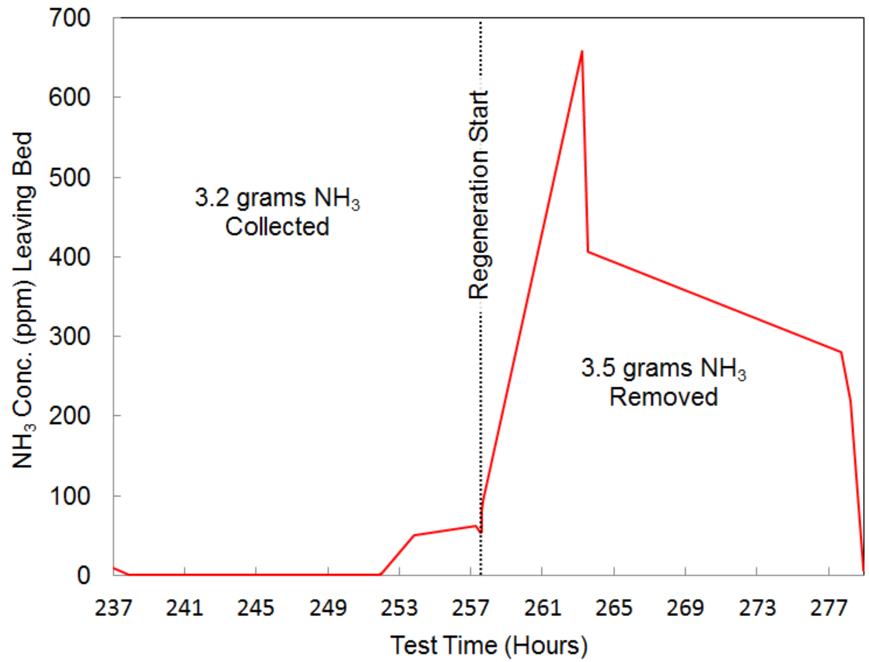
Test Summary

Cycle capacities achieved at UNDEERC

Cycle	Syngas Flow Start	Syngas Flow Stop	Total Flow (scfh)	NH_3 Conc. (ppm)	NH_3 Collected (g)	Capacity Achieved (%wt)
1	11/14/2019 21:13	11/18/2019 17:59	5	700	7.0	0.33%
2	11/20/2019 14:45	11/21/2019 15:00	5 to 10*	700	2.9	0.14%
3	11/22/2019 8:00	11/23/2019 18:00	5 to 10*	700	3.6	0.17%
4	11/24/2019 18:30	11/25/2019 15:00	10	700	3.2	0.15%
5	11/26/2019 12:10	11/26/2019 23:20	10	700	1.7	0.08%**

**UNDEERC adjusted flow up without notation. The time is uncertain, but will be included with data package from UNDEERC*

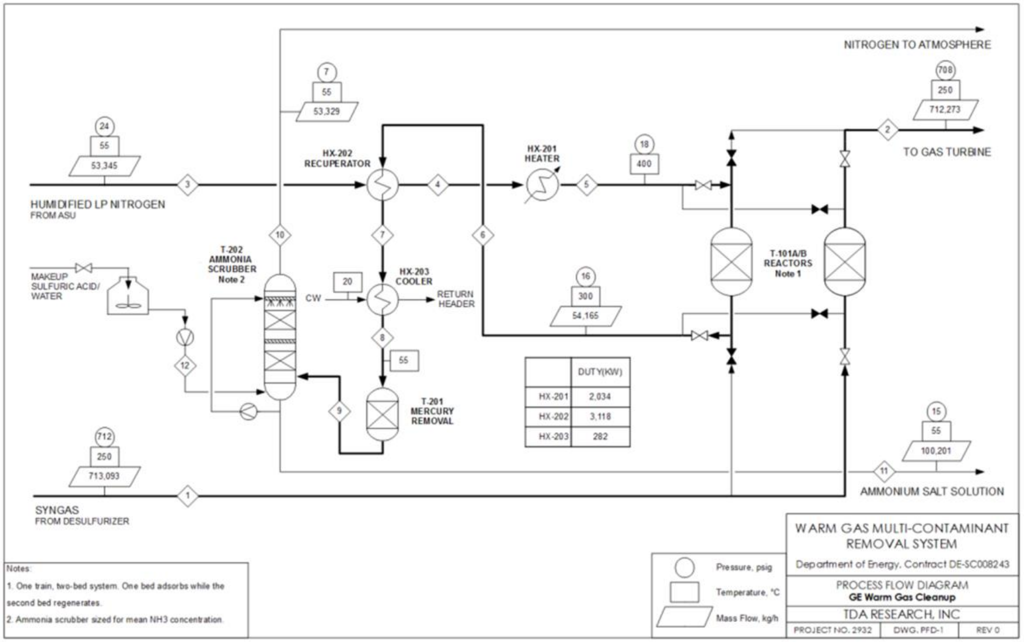
***Coal feeder jammed during final half-cycle adsorption, regeneration was completed*



- **Cycle 4 adsorption and regeneration ammonia concentrations shows a good closure of ammonia mass balance**

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)**

Acknowledgements

- NETL, Project Manager, Diane Madden Ravey
- Frank Morton, NCCC
- Michael Swanson, UNDEERC