Sorbents for High Temperature Removal of Trace Metals from Coal-Derived Synthesis Gas

Gökhan O. Alptekin, PhD

Pittsburgh Coal Conference

Pittsburgh, PA

September 14, 2005

TDA Research Inc. • Wheat Ridge, CO 80033 • www.tda.com

TDA Research, Inc.

- **Privately Owned / Began operations in 1987**
- **62 full-time technical staff**
  - Primarily chemists and engineers, 60% with advanced degrees

12345-12355 W 52nd Avenue

22,000 ft^2 offices and labs

Synthetic Chemistry, Catalyst/Sorbent Synthesis and Testing, Machine and Electronics Shops, SEM, TOF Mass Spec

4663 Table Mountain Drive

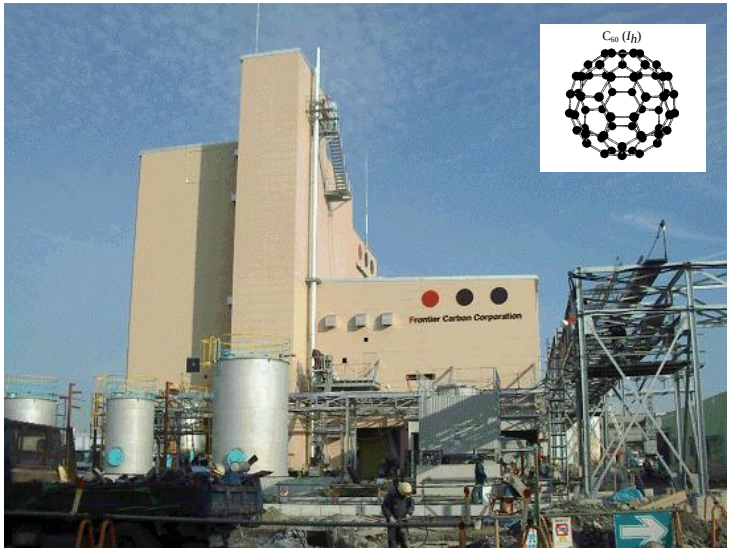
27,000 ft^2 offices and labs

27 fume hoods, Synthetic Chemistry, Catalytic Process Development

TDA Research

TDA Projects

TDA partial oxidation unit installed at the Whiting Petroleum Sable Gas Plant in Plains, TX.



TDA built and licensed all of the reactors for the Frontier Carbon Corp. 40 ton/year fullerene factory in Kitakyushu, Japan

Conducting polymers available through Sigma-Aldrich

TDA Research

Introduction

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

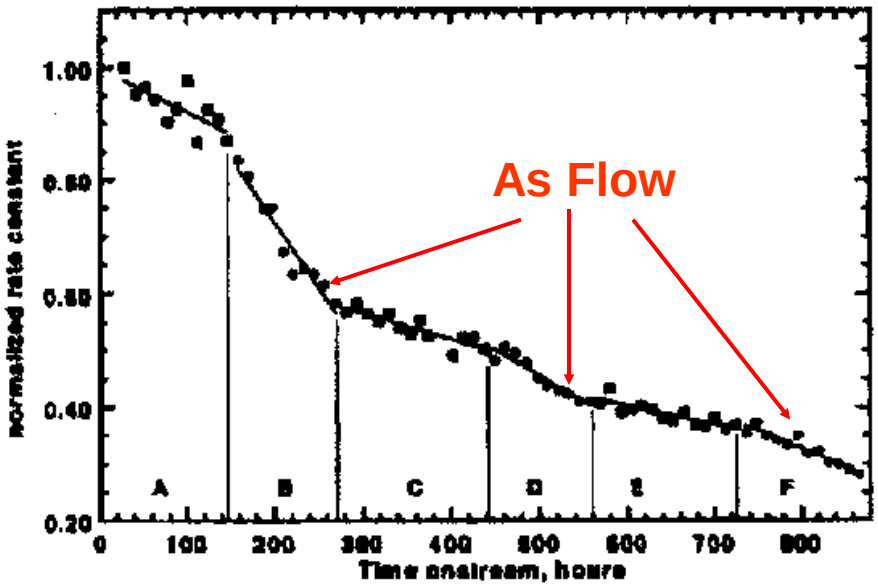
Typical Metal Contaminants in Coal

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

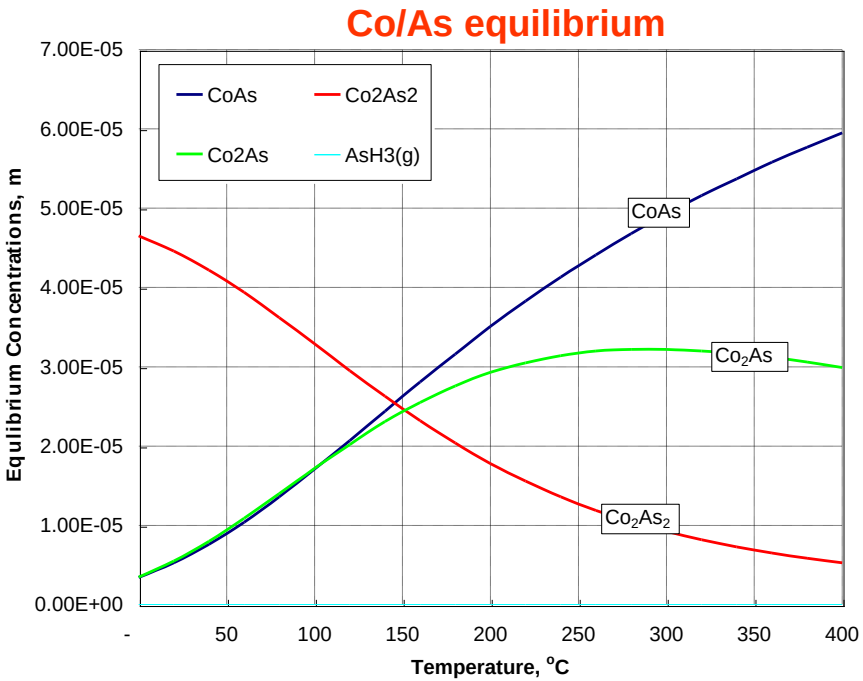
Bool et al., 1997

- **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
- **Removal of metal contaminants is also important for chemical manufacturing processes**
  - Arsenic is a known catalyst poison

Arsenic as a Catalyst Poison



Source: R. Quinn Applied Catalysis (2004)



- **During operation of the LPMeOH™ plant catalyst deactivation rates up to 0.2%/day was observed**
  - Some of this was attributed to the sintering of the $Cu/ZnO/Al_2O_3$ catalyst, but most to the As poisoning
  - Elemental analysis showed an increase in As concentration of the catalyst with use in the process
- **Arsenic also forms various complexes with metals like Fe, Co; key ingredients of WGS, and Fischer-Tropsch catalysts**
  - Blocking of active site by irreversible chemisorption (chem. reaction)
  - Increase sintering rates by promoting microfluxes

TDA Research

Conventional Control Technologies

- **Mercury Control Technologies**
  - **Physical adsorbents**
    - Reasonable capacity, but limited to low temperatures
    - Activated carbon (Granite et al., 2000)
    - Aluminosilicates (Granite et al., 2000)
    - Sulfided activated carbon (Livengood et al., 1996)
  - **Mercury amalgamation**
    - Wider temperature range, but cost is an issue
    - Gold and silver are too expensive even when coated over gauzes or monoliths (Constandi, 1992)

- **Arsenic Control Technologies**
  - **Physical adsorbents**
    - To protect process equipment
    - Chemically modified activated carbons
    - Manganese oxide

Project Objective

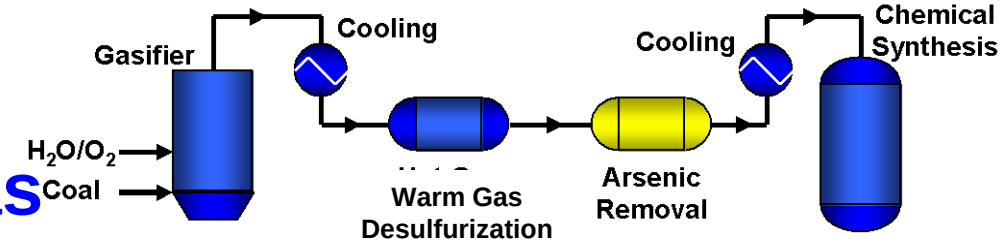
- **TDA Research, Inc. is developing a single-step process for high temperature trace metal removal from coal-derived synthesis gas**
  - The key for the process is an effective sorbent
- **Requirements on the sorbent**
  - High contaminant absorption capacity
  - Low cost
  - Reducing metal concentration to less than ppb levels to achieve greater than 95% removal of mercury and 99% for arsenic
  - High temperature operation under reducing conditions
  - Inactive for side reactions
  - Tolerant to possible coal gas contaminants

Test Apparatus

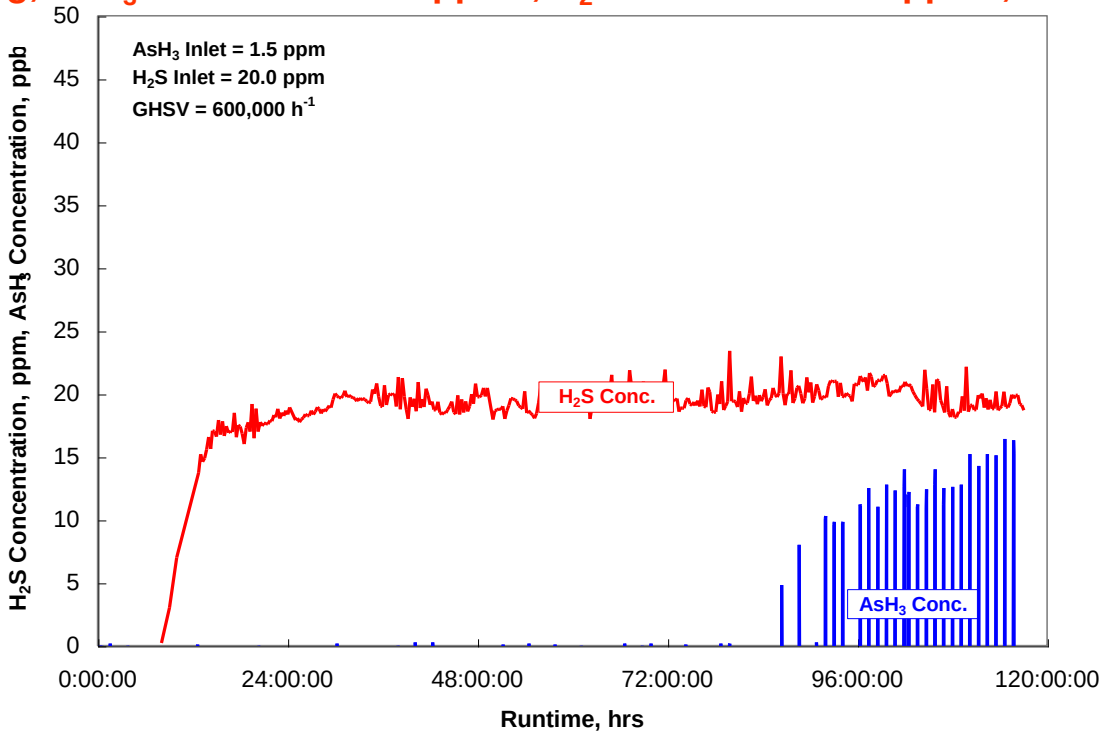
- **The apparatus could test 0.5 to 20.0 g samples**
  - In selected experiments, sorbents were tested in the form of pellets
- **A quartz insert with internal pressure stabilization housed the pellets**
  - P_{max} = 900 psig @ 260°C
- **A special coating was applied to the gas transfer lines to minimize steel catalyzed arsine decomposition**
  - $AsH_{3(g)} = As + 3/2H_{2(g)}$
- **An on-line analyzer is used to monitor AsH_3 and H_2Se concentrations with 10 ppbv detection sensitivity**
- **Accelerated tests at very short gas-solid contact times were conducted to quickly screen sorbent samples**

TDA Research

Sorbent Performance with Low Sulfur Syngas



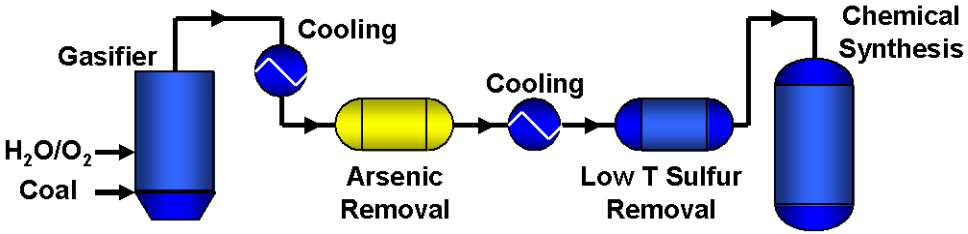
T=240°C, P= 450 psig, AsH_3 Inlet Conc.= 1.5 ppmv, H_2S Inlet Conc.= 20 ppmv, GHSV= 600,000 h^{-1}



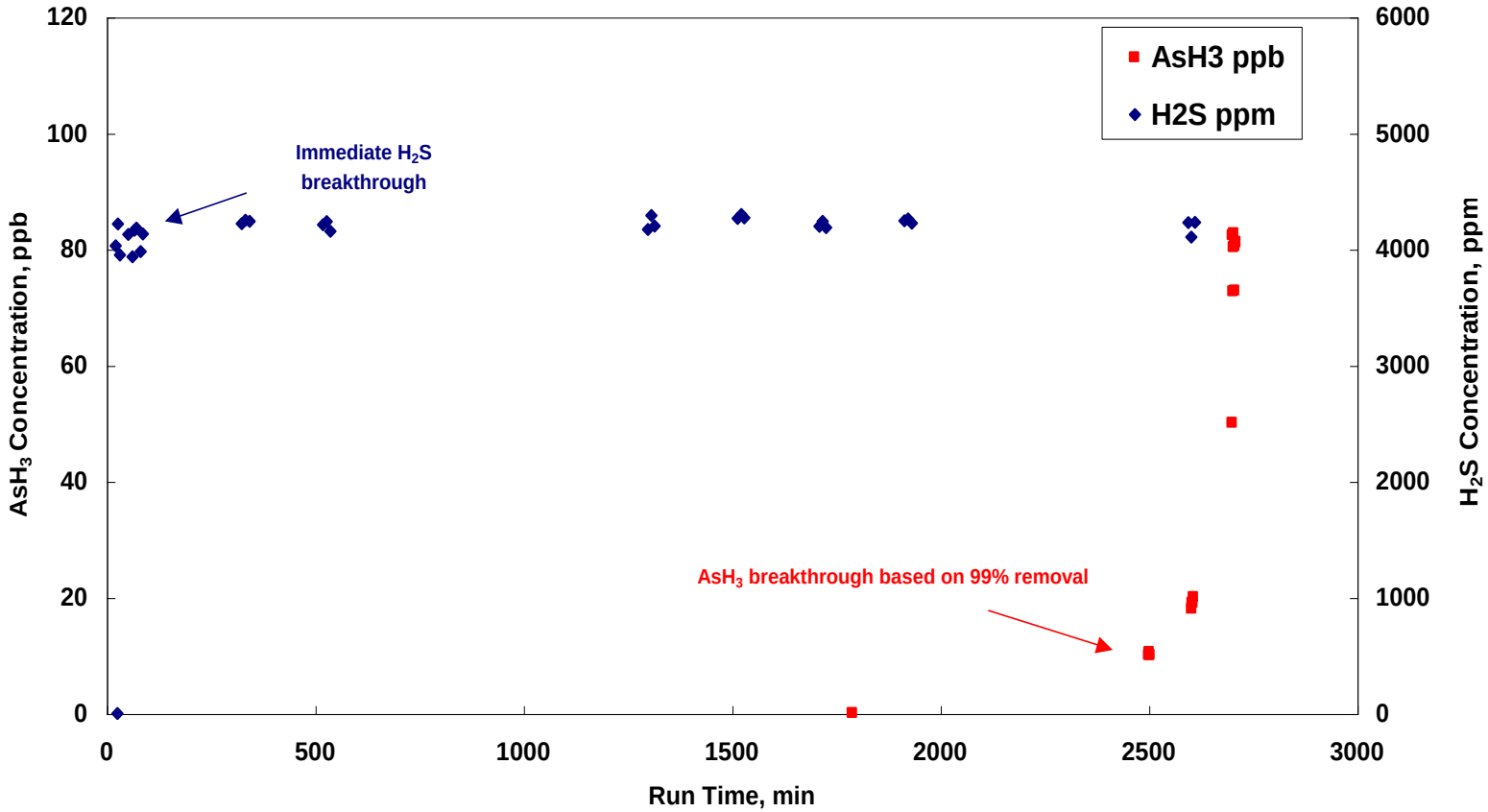
- **In the presence of 20 ppmv H_2S, sorbent achieved 7.1% wt. As absorption capacity at breakthrough**
- **At breakthrough the sorbent was still removing 99% of the AsH_3 indicating a much higher saturation capacity**
- **Sorbent also showed 8.5% wt. sulfur capacity**

TDA Research

Sorbent Performance with High Sulfur Syngas



T= 245°C, P= 350 psig, AsH_3 Inlet Conc.= 1.22 ppmv, GHSV= 180,000 h^{-1}

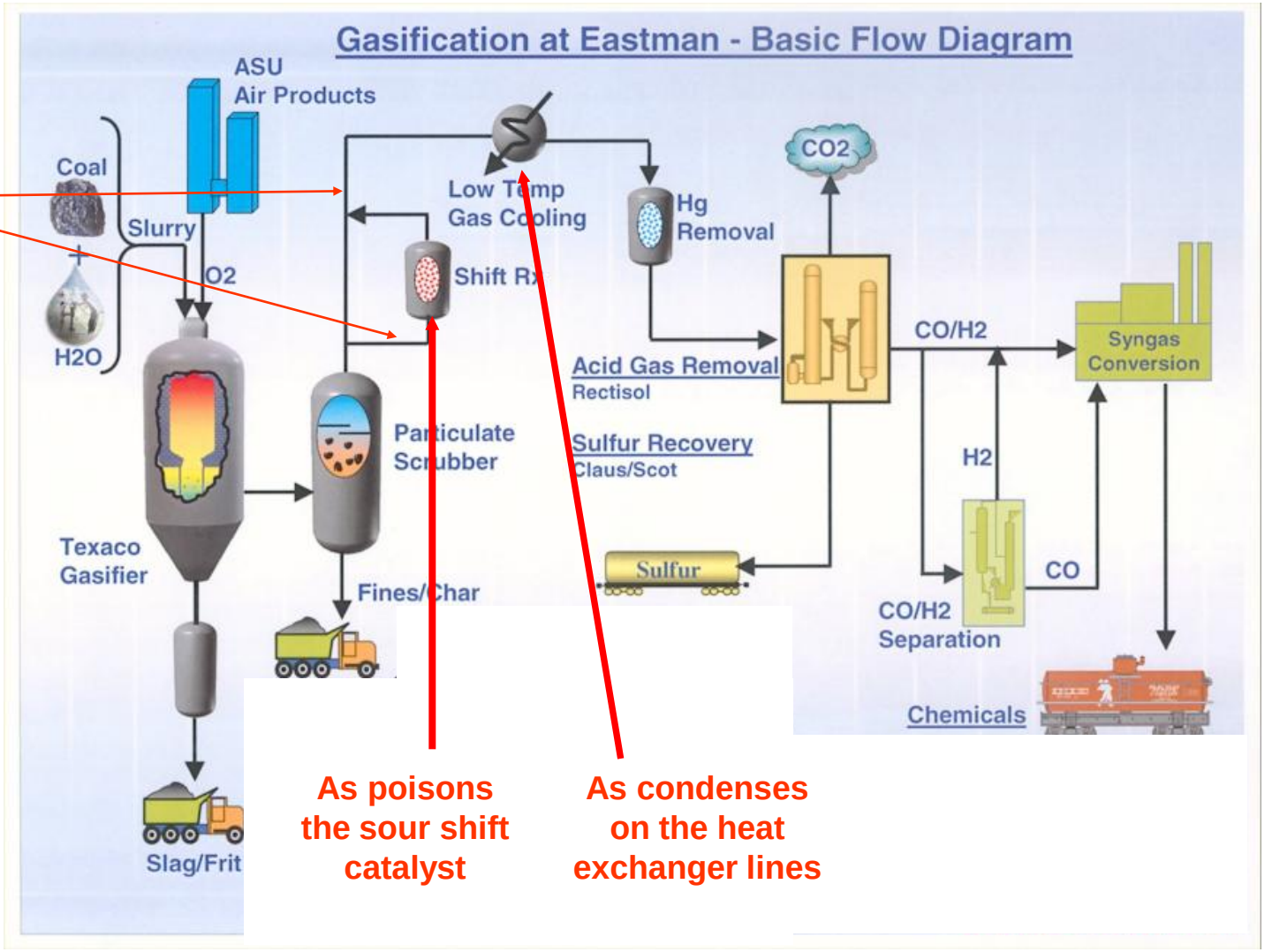


- **In the presence of 4,800 ppmv sulfur, TDA sorbent had 2.89% wt. arsenic absorption capacity**

TDA Research

Need for Removing Arsenic at High Temperature

Potential locations for As sorbent bed



As poisons the sour shift catalyst

As condenses on the heat exchanger lines

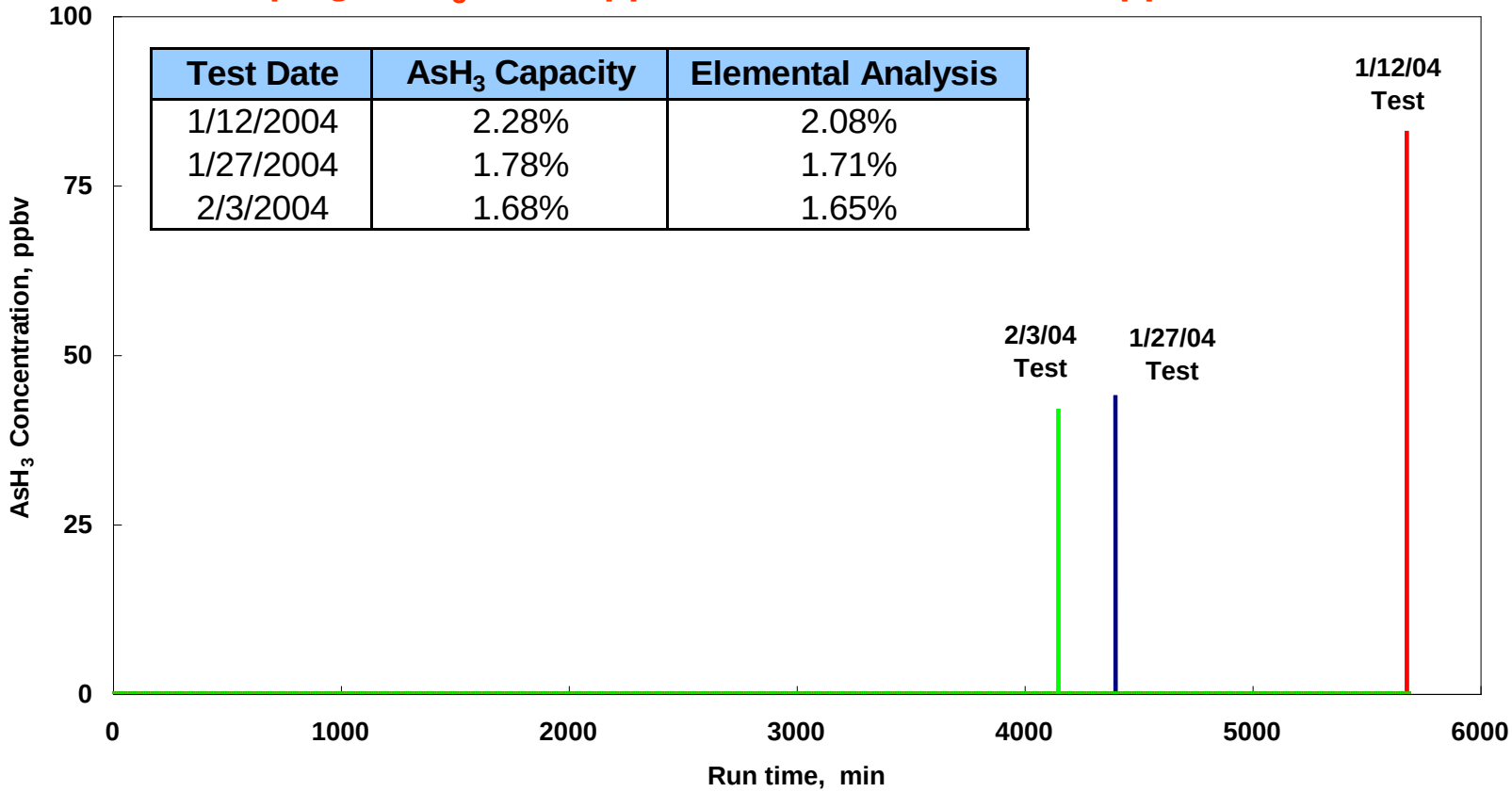
Source: Eastman Chemicals

TDA Research

Repeatability of Results

T= 245°C, P= 500 psig, AsH_3 = 0.66 ppmv, Total Sulfur= 10,000 ppmv, GHSV= 100,000 h^{-1}

Test Date	AsH_3 Capacity	Elemental Analysis
1/12/2004	2.28%	2.08%
1/27/2004	1.78%	1.71%
2/3/2004	1.68%	1.65%



- High arsenic capacity was confirmed by tests under identical conditions
- The experimental results were confirmed by post reaction chemical analysis

TDA Research

Sorbent Scale-up

- **TDA subcontracted Saint Gobain NorPro (NorPro) to scale-up the production of its sorbent**
- **NorPro provided three 10 kg batches of sorbents**
  - Same recipe, different preparation methods
- **A cost estimate of the sorbent is underway**
  - $10-15/lb is expected at large production volumes

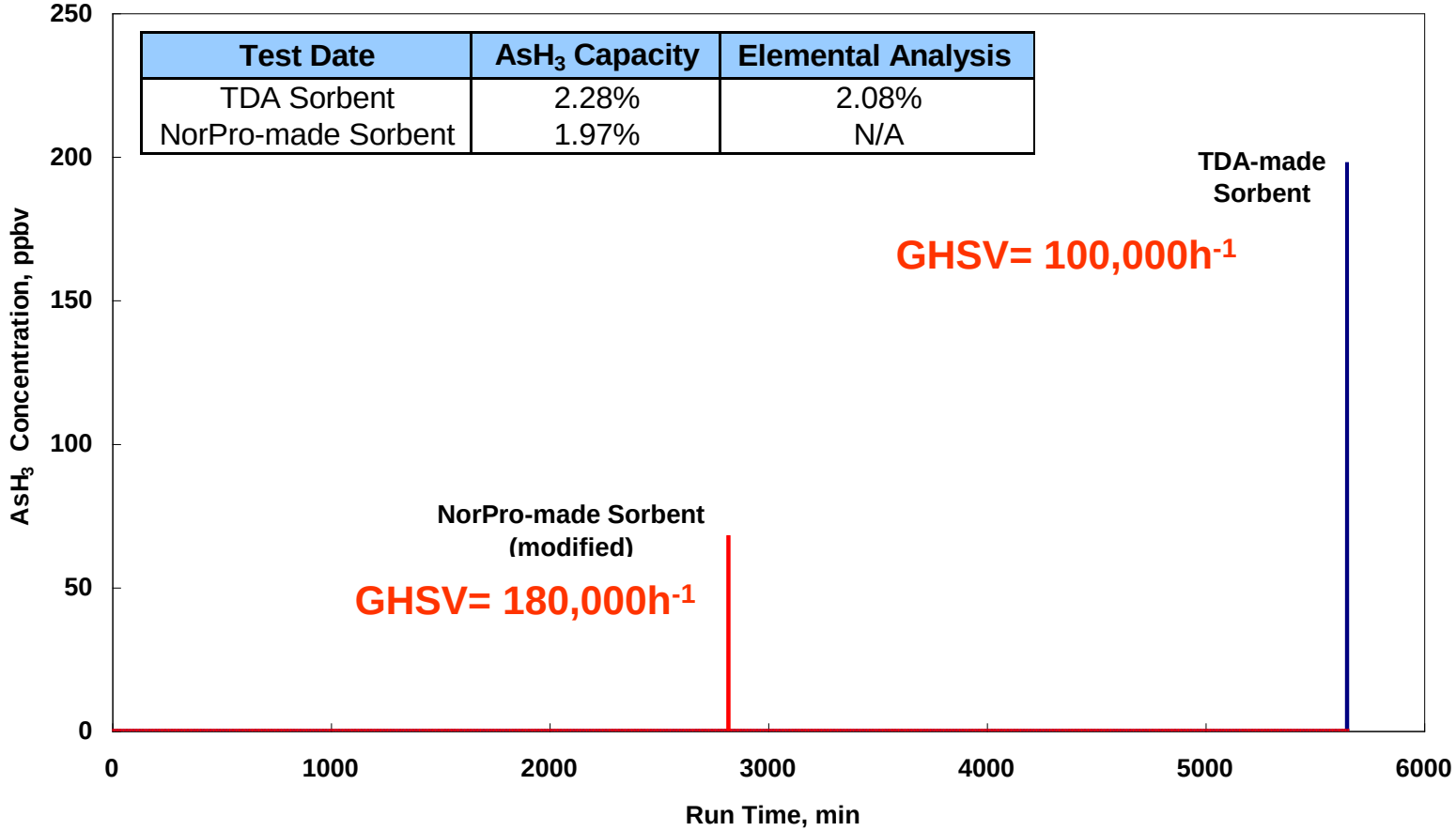
Batch #1 (One-pot formulation)

1/8” cylindrical pellets

Comparing TDA and NorPro-made Sorbents

T= 245°C, P= 500 psig, AsH_3 Inlet Conc.= 0.66 ppmv, Total Sulfur Inlet Conc.= 10,000 ppmv

Test Date	AsH_3 Capacity	Elemental Analysis
TDA Sorbent	2.28%	2.08%
NorPro-made Sorbent	1.97%	N/A

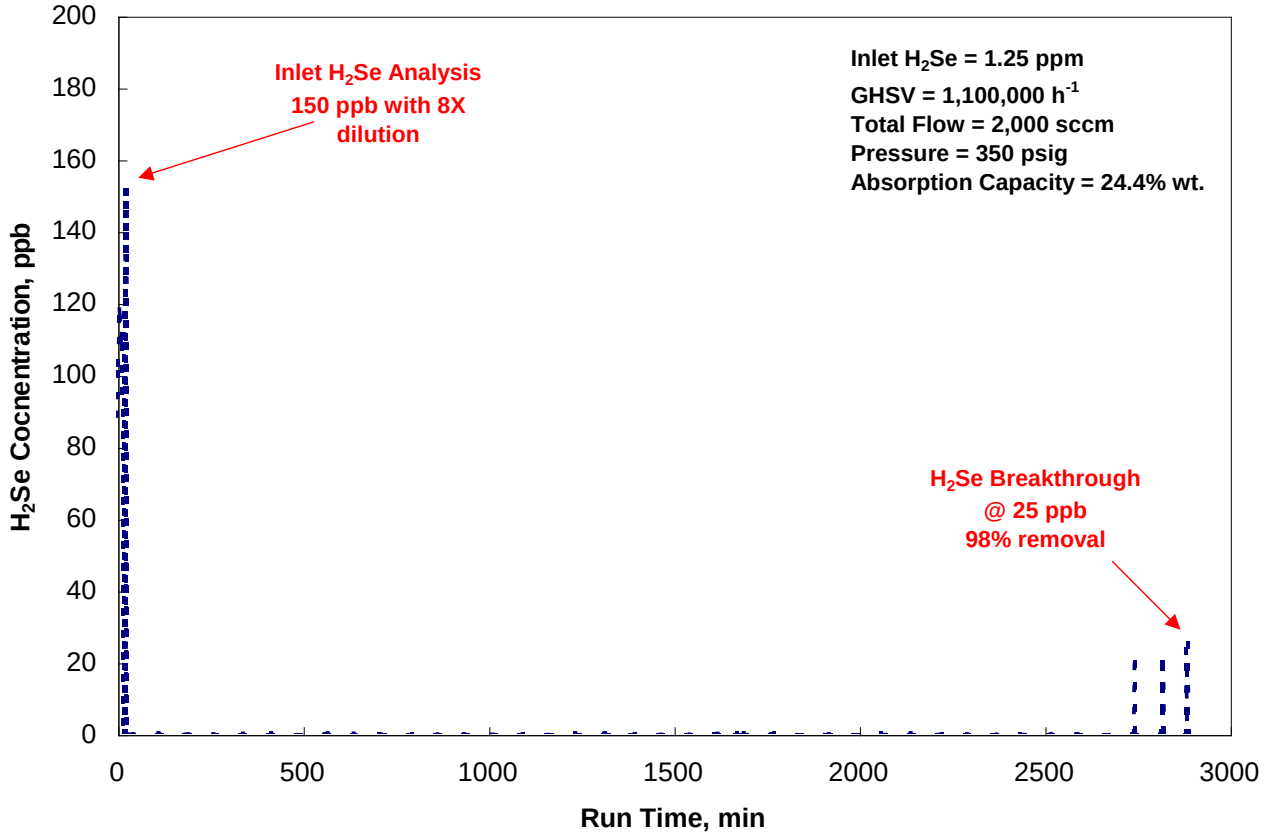


- The sulfur tolerant NorPro-made material has very similar performance capabilities

TDA Research

Selenium Removal Performance

T= 230°C, P= 350 psig, GHSV= 1,200,000 h^{-1}, Inlet H_2Se Conc.= 1.25 ppmv

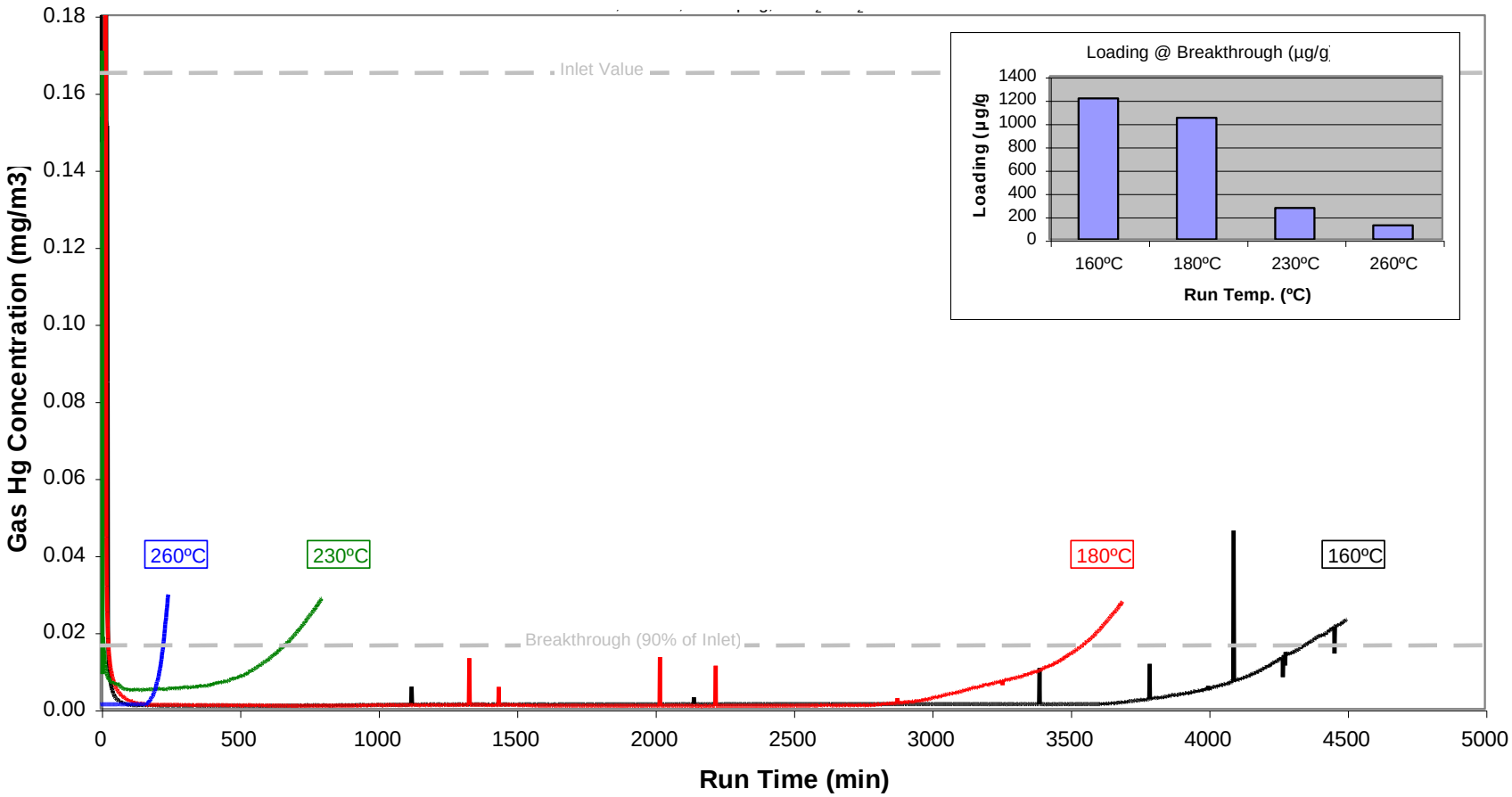


- **Sorbent showed 24.4% wt. capacity for selenium in a sulfur-free reducing gas environment**

TDA Research

Hg Removal Performance

Hg Inlet= 0.17 mg/m^3, P= 5 psig, Simulated CO-rich syngas, GHSV= 68,000 h^{-1}

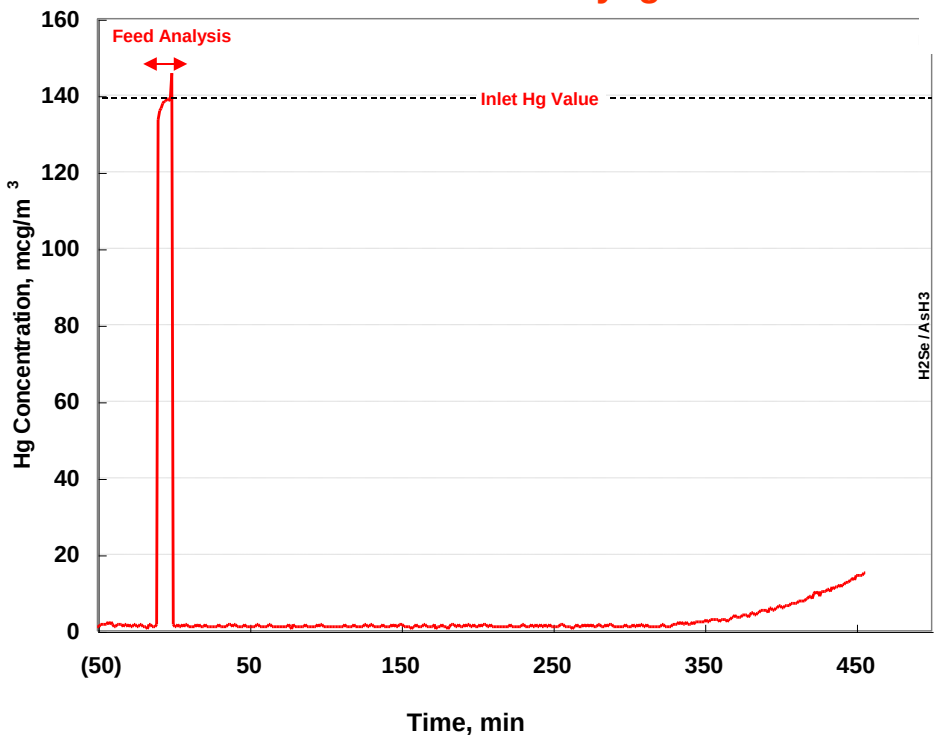


- **Sorbent shows reasonable capacity at 260ºC, while achieving 99% removal efficiency**
- **Hg capacity of the sorbent improves significantly at lower temperature**

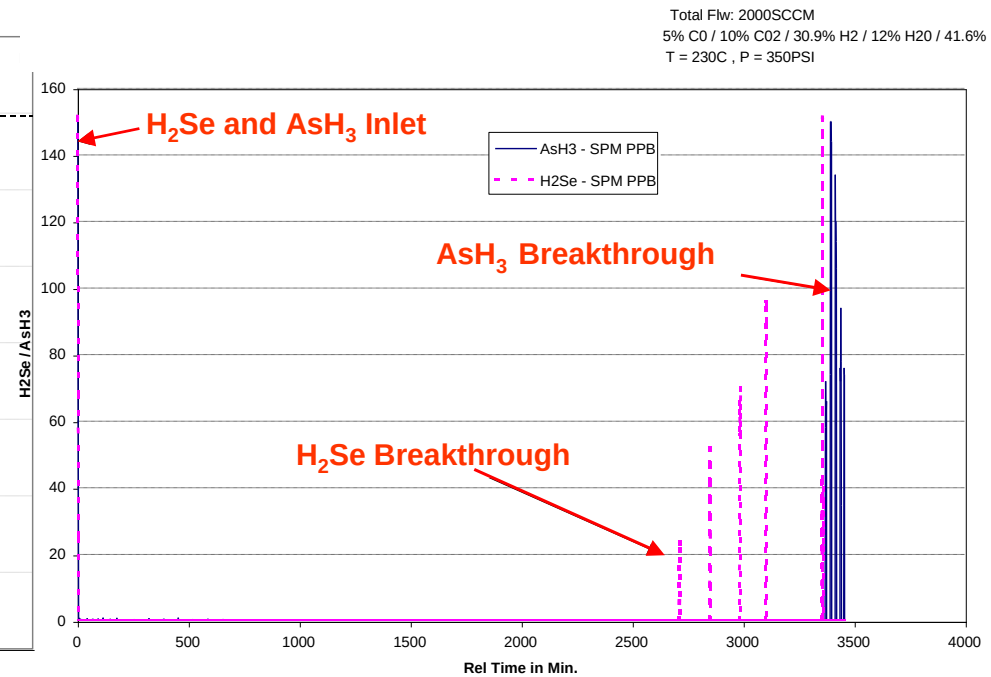
TDA Research

Multi-contaminant Removal

T= 260°C, P= 5 psig, GHSV= 50,000 h^{-1}, Hg Inlet= 140 μg/m^3, AsH_3 Inlet= 0.75 ppmv using sulfur-free simulated syngas



T= 240°C, P= 350 psig, AsH_3 and H_2Se Inlet Conc.= 1.25 ppmv (each), in simulated sulfur-free syngas

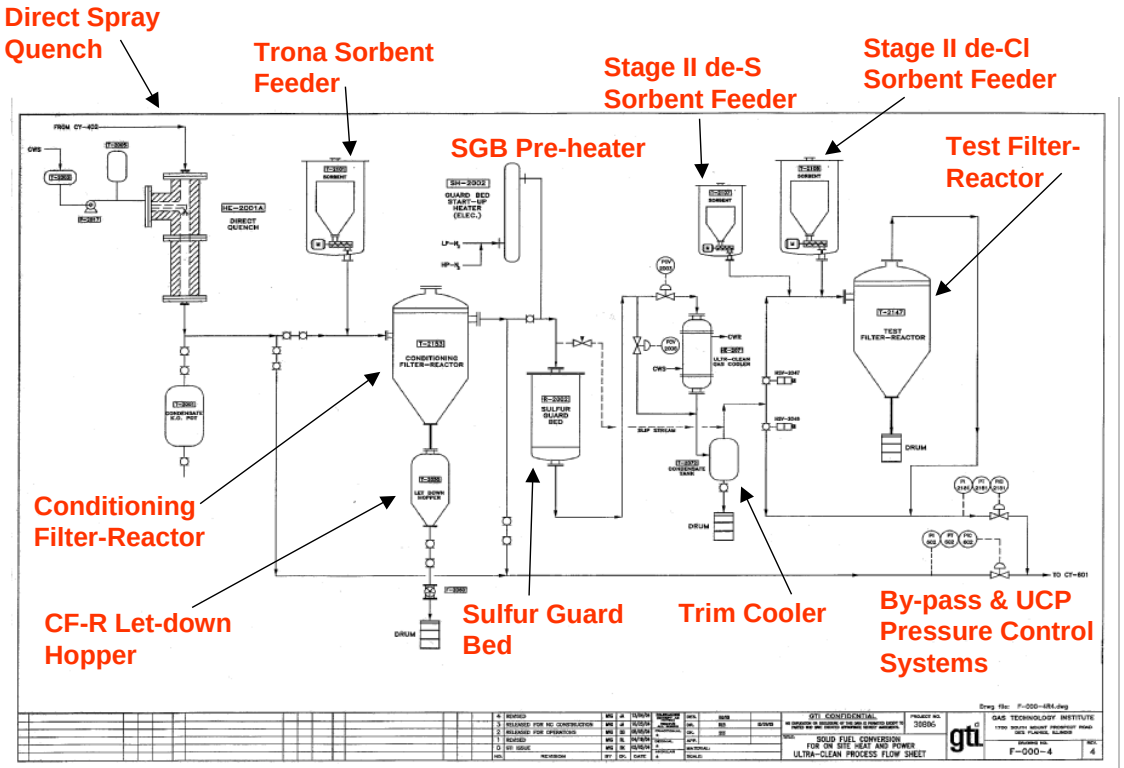


- **We showed that the sorbent could remove Hg in the presence of AsH_3**
  - The absorption capacity of mercury is reduced approximately 20% wt. in presence of arsenic in the gas stream
- **We also showed that sorbent could remove AsH_3 and H_2Se with high capacity**

TDA Research

Demonstration in Ultra-Clean Process

GTI's FlexFuel Facility

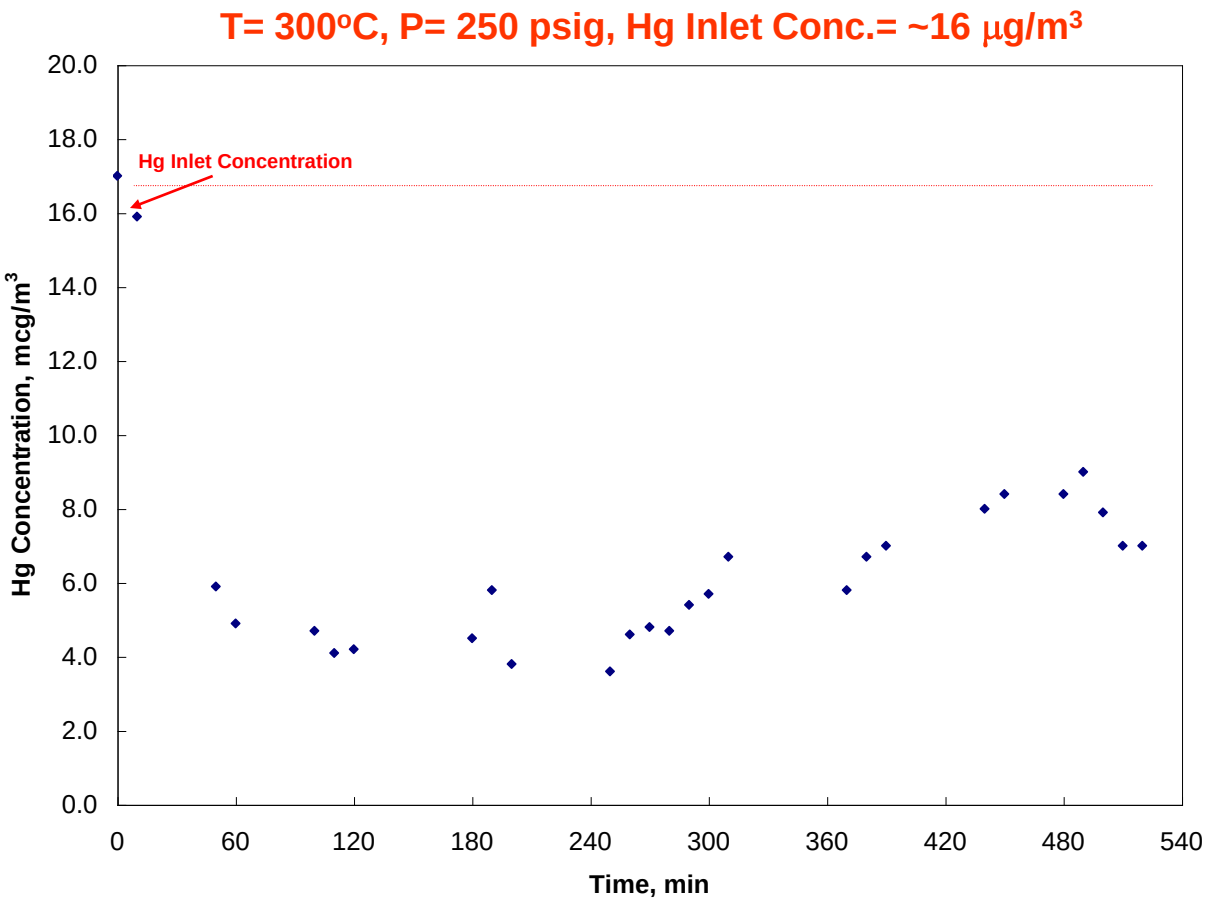


Ultra-Clean Process, Siemens Power Corporation

- **FlexFuel facility can process 10 tpd coal w/air and 20 tpd w/oxygen**
- **Siemens and GTI is jointly demonstrating Siemens' Ultra-Clean Process**
  - Gas clean-up in multi-stage filter reactors
- **TDA's sorbent grinded to the right particle size for injection into Stage II filter**
  - Sorbent is injected with the sulfur and halide sorbents

TDA Research

Preliminary Evaluation Results



- **TDA's sorbent achieved 50-75% Hg removal at 300°C (572°F)**
  - Lower removal efficiency is due to the higher than sorbent ideal operating temperature for the sorbent

TDA Research

Future Work

- **TDA is developing a prototype unit to demonstrate the operation of its multi-contaminant removal system**
  - 10,000 scfh gas processing capacity
- **In collaboration with UNDEERC, we will demonstrate the operation of the multi-contaminant control unit using real coal-derived synthesis gas**
- **We will also supply more sorbents with Siemens/GTI team to be tested in the Ultra-Clean Process if they could raise more funding for future tests**

Acknowledgements

- **Co-authors**
  - Robert Amalfitano, TDA
  - Margarita Dubovik, TDA
- **Authors acknowledge the funding provided for the research**
  - DOE PRDA, Contract No. DE-FC26-05NT42460
  - DOE Phase II SBIR Grant, Contract No. DE-FG03-02ER83551
  - DOE Phase II SBIR Grant, Contract No. DE-FG03-01ER83308
- **Authors thank**
  - Mr. Robert Kornosky, DOE, NETL
  - Dr. Kamalendu Das, DOE, NETL
  - Ms. Elaine Everitt, DOE, NETL
  - Dr. Rachid Slimane, GTI

TDA Research