Syngas Clean-up System to Remove Harmful Contaminants for SOFCs

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TDA Research

TDA Research, Inc.

- **Privately Owned / Began operations in 1987**
- **~13 million revenue in 2009**
- **84 full-time technical staff**
  - Primarily chemists and engineers, more than half with advanced degrees (26 PhDs)

12345-12355 W 52nd Avenue

22,000 ft² offices and labs

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

4663 Table Mountain Drive

27,000 ft² offices and labs

27 fume hoods, Synthetic Chemistry, Catalytic Process Development

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SulfaTrap™ Sorbents

SulfaTreat DO (1.3 ton/day plant at Bakersfield, CA)

SulfaTrap™ sorbents for fuel desulfurization for distributed and transportation fuel cell applications

- TDA has developed and commercialized removal for bulk desulfurization and the removal of organic sulfur species from various hydrocarbons
  - Natural gas, LPG and biogas desulfurization
  - Warm gas and hot reformate gas desulfurization
  - Diesel fuel and logistics fuel desulfurization
- We supply almost every SECA member and other SOFC and PEMFC developers around the world

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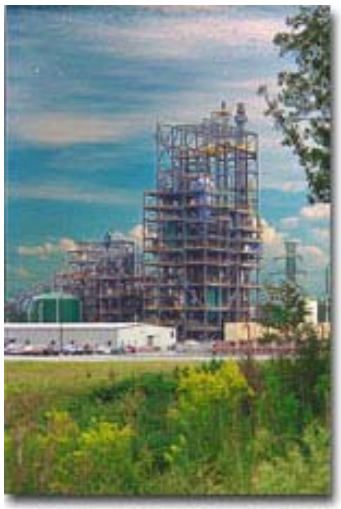
TDA Background In Syngas Clean-up

Trace Contaminant Removal

- With DOE funding, TDA is developing sorbents to remove trace metals in coal-to-chemicals and IGCC plants
- TDA's Hg sorbent is qualified for Siemens' UltraClean™ process
- TDA and Eastman Chemicals are jointly demonstrating a sulfur-tolerant high temperature arsenic removal sorbent



Pre-combustion CO_2 Capture

- Proof-of Concept Demonstrations at Wabash River IGCC Plant
  - Largest single-train, oxy-blown E-Gas™ Gasifier
- National Carbon Capture Center
  - Pilot-scale, air-blown transport gasifier

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Introduction

- **Coal-derived syngas contains a myriad of trace contaminants**
- **In addition to sulfur, As and P have identified as potent poisons for SOFC electrocatalyst**

Typical Metal Contaminants in Coal

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

Bool et al., 1997

- **The concentration of these contaminants vary depending on the coal type and gasification system in place**

Contaminant Concentration for Different Gasifiers

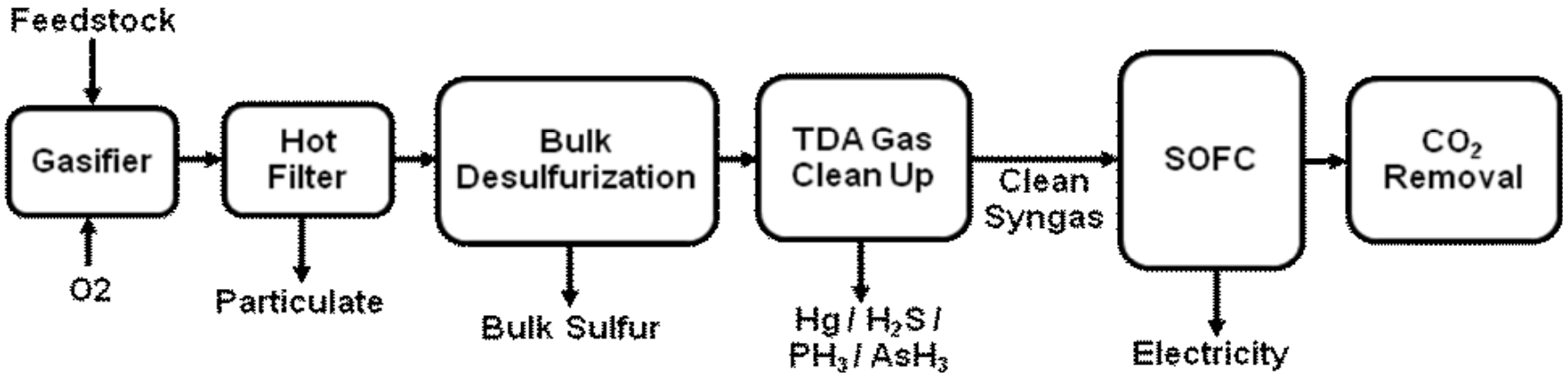
Contaminant	Concentration at the Kingsport facility (ppmv)	UND-EERC
Arsine (AsH_3)	0.15–0.58	0.2
Thiophene		1.6
Chlorine (Cl)		120
Methyl Fluoride (CH_3F)	2.6	
Methyl Chloride (CH_3Cl)	2.01	
Hydrogen Chloride (HCl)	<1	
$Fe(CO)_5$	0.05–5.6	
$Ni(CO)_5$	0.001–0.025	
CH_3SCN	2.1	
Phosphene (PH_3)	1.9	
Antimony (Sb)	0.025	0.07
Cadmium (Cd)		0.01
Chromium (Cr)	<0.025	6.0
Mercury (Hg)	<0.025	0.002
Selenium (Se)	<0.15	0.17
Vanadium (V)	<0.025	
Lead (Pb)		0.26
Zinc (Zn)	9.0	

Synthesis Gas Clean-up Technologies

- The baseline capture technologies uses low temperature processes
  - Eastman Chemicals uses various activated carbon sorbents for Hg and As removal
  - Sulfur is removed with Rectisol
- A major issue with these technologies is that they require to cool the gas below its dew point
  - ~245^{o}C for GE gasifier; ~200^{o}C for catalytic gasifiers
- Warm temperature gas cleaning has major benefits:
  - Improves the efficiency of the power cycle
    - A previous Siemens analysis indicates ~4% efficiency decrease for IGCCs
  - Eliminate the need for any heat exchange equipment
  - Eliminate the difficulties processing the condensate
  - Re-heating and re-humidification of syngas will add to the cost

Project Objective

- **TDA's approach was to use a high temperature chemical absorbent that can remove these contaminants above the dew point of the synthesis gas**



- **The sorbent is operated in an expendable manner**
- **The key contaminants are identified as arsenic, phosphorous and sulfur (and mercury)**
- **In Phase I we carried out carry out proof-of-concept demonstrations at the bench-scale to assess technical and economic viability of the concept**

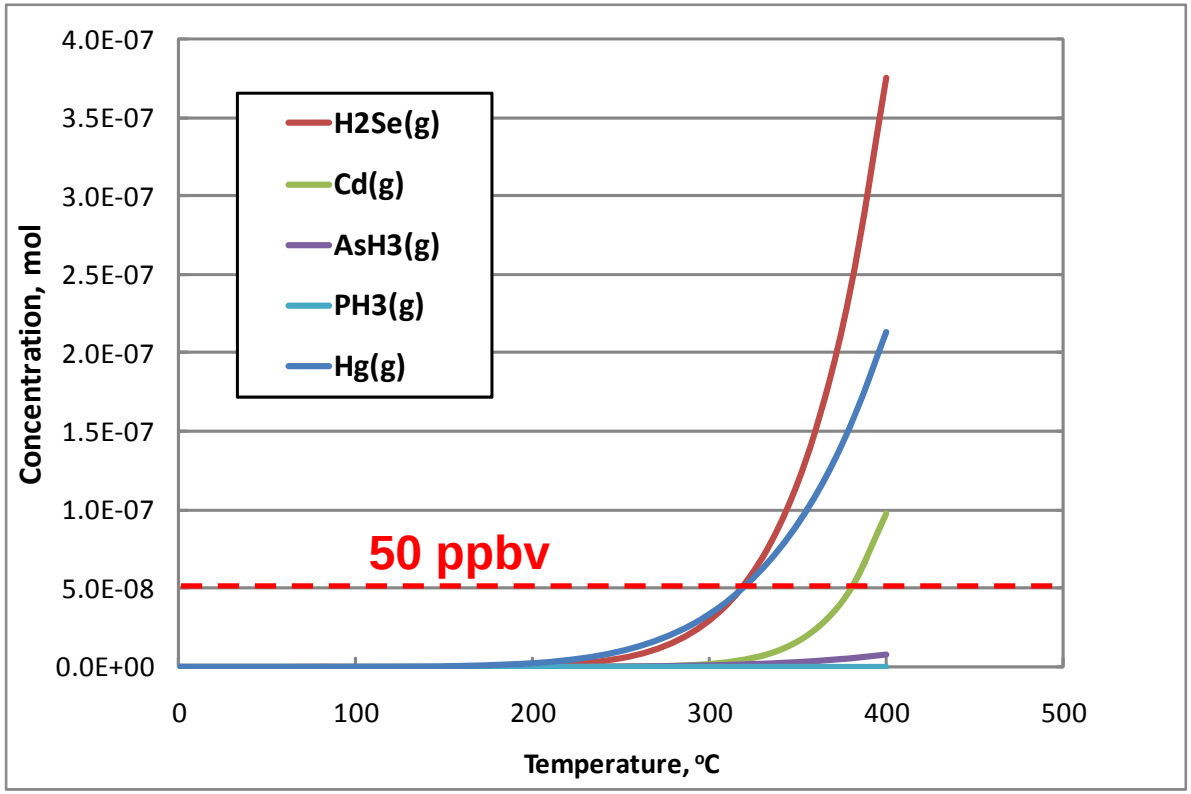
TDA Sorbent

- Sorbent requirements
  - High contaminant absorption capacity
  - Low cost
  - High removal efficiency (99+%)
  - No activity for side reactions
- TDA identified an active phase that can remove both metal hydrides and volatile metals from syngas

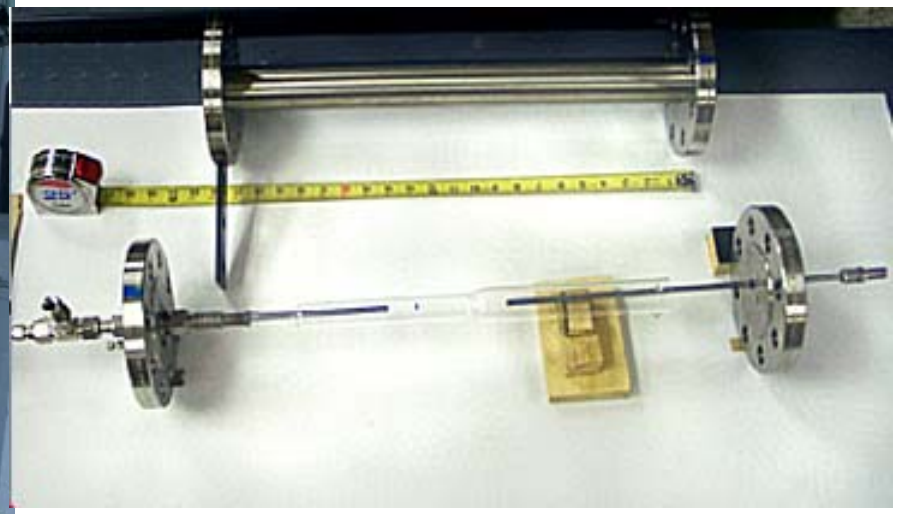
Equilibrium composition of potential contaminants

1 ppmv of each contaminant was added to a representative synthesis gas

Contaminant concentration can be reduced to ppbv levels

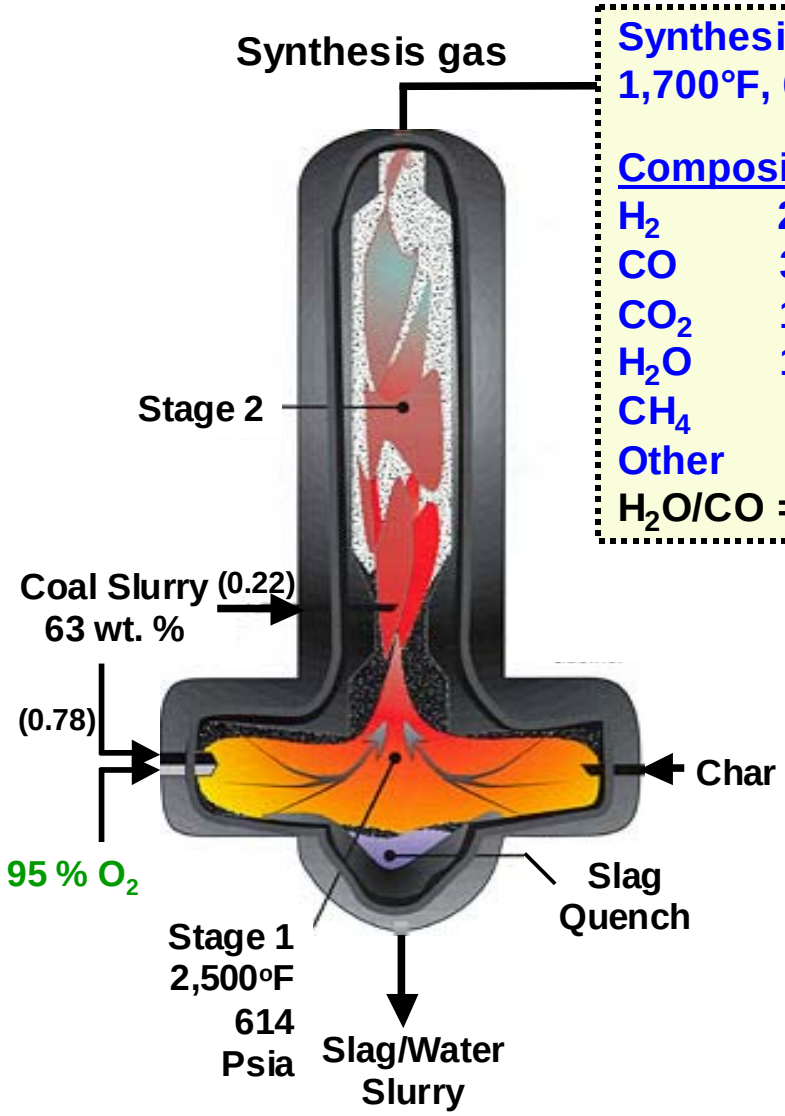


Sorbent Screening



- An automated test units was used for screening and evaluations
  - 0.5 to 25.0 g sorbent tested (sorbent in the form of pellets in selected tests)
- High temperature, high pressure reactors rated for P_{ma} = 900 psig @ 260^{o}C
- On-line analyzers were used to monitor AsH_3 and PH_3 breakthrough
- A chemiluminescence detector was used to monitor sulfur

Test Gas Composition



Synthesis Gas
1,700°F, 614 psia

Composition (Mole%):

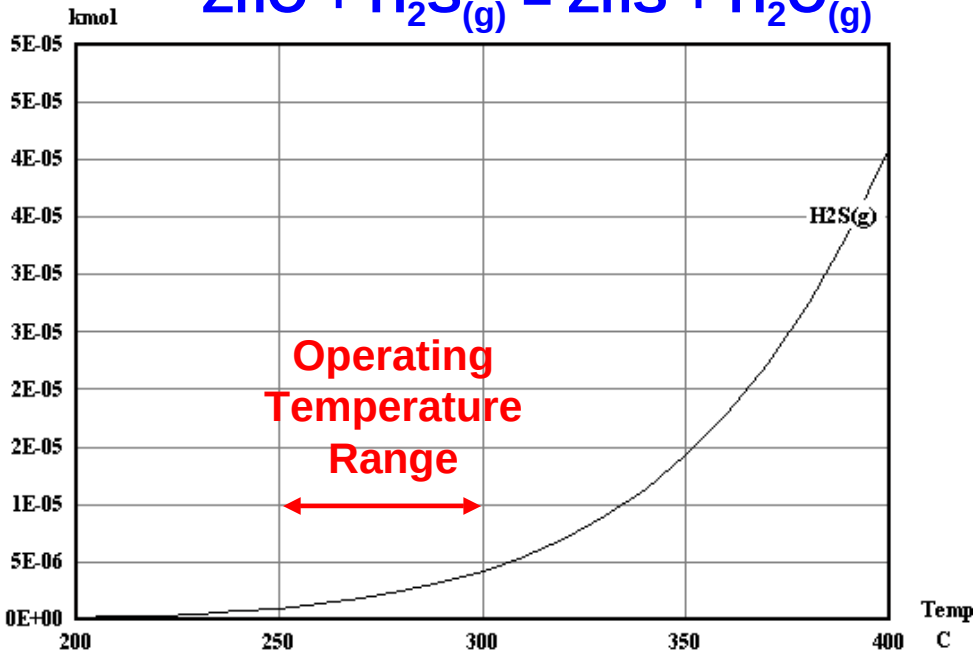
H_2	26%
CO	37%
CO_2	14%
H_2O	15%
CH_4	4%
Other	4%

$H_2O/CO = 0.4$

To Cooler, Acid Gas Removal and

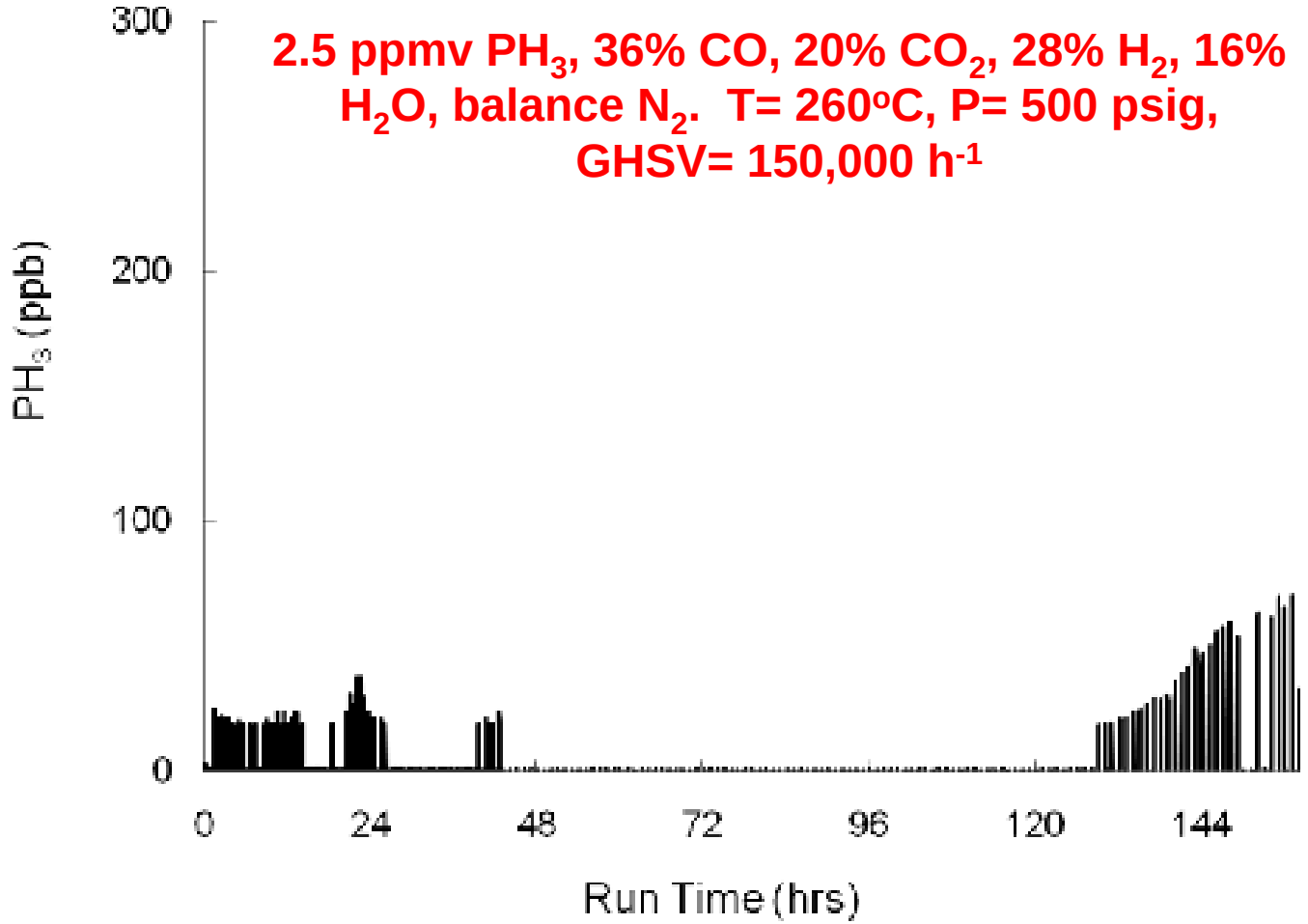
H_2S Equilibrium over ZnO

$ZnO + H_2S_{(g)} = ZnS + H_2O_{(g)}$



PH_3 Removal

2.5 ppmv PH_3, 36% CO, 20% CO_2, 28% H_2, 16% H_2O, balance N_2. T= 260°C, P= 500 psig, GHSV= 150,000 h^{-1}



- **The sorbent also achieved a very high capacity for P in excess of 3% wt. (lb of P removed per lb of sorbent)**
- **The sorbent reduced PH_3 concentrations to single digit ppb levels**

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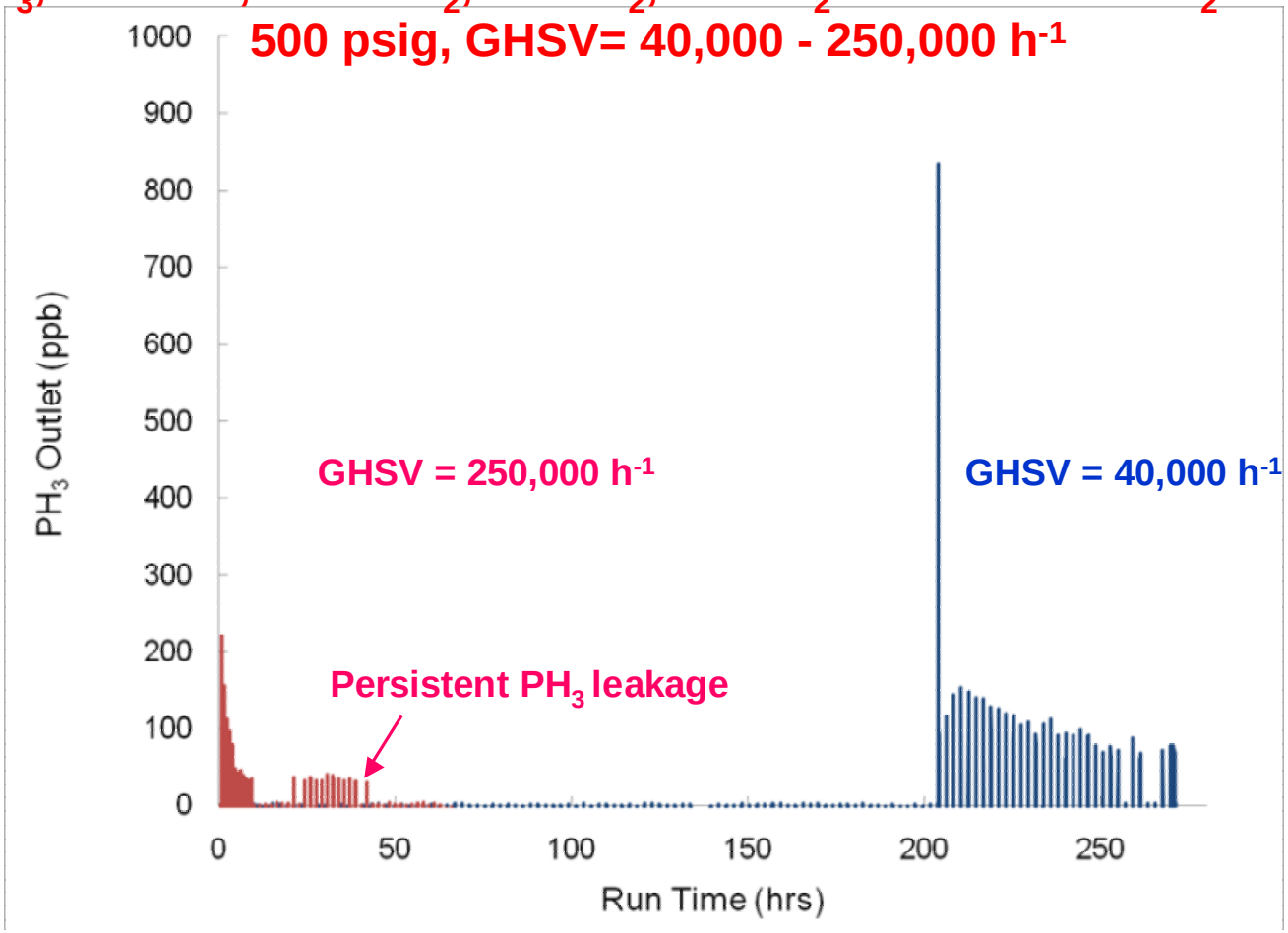
Effect of GHSV

2 ppmv PH_3, 36% CO, 20% CO_2, 28% H_2, 16% H_2O and balance N_2. T= 260°C, P= 500 psig, GHSV= 40,000 - 250,000 h^{-1}



- **Phosphorous capacity at 40,000 h^{-1} (90 miliseconds) exceeded 3.6% wt. and no leakage was detected**

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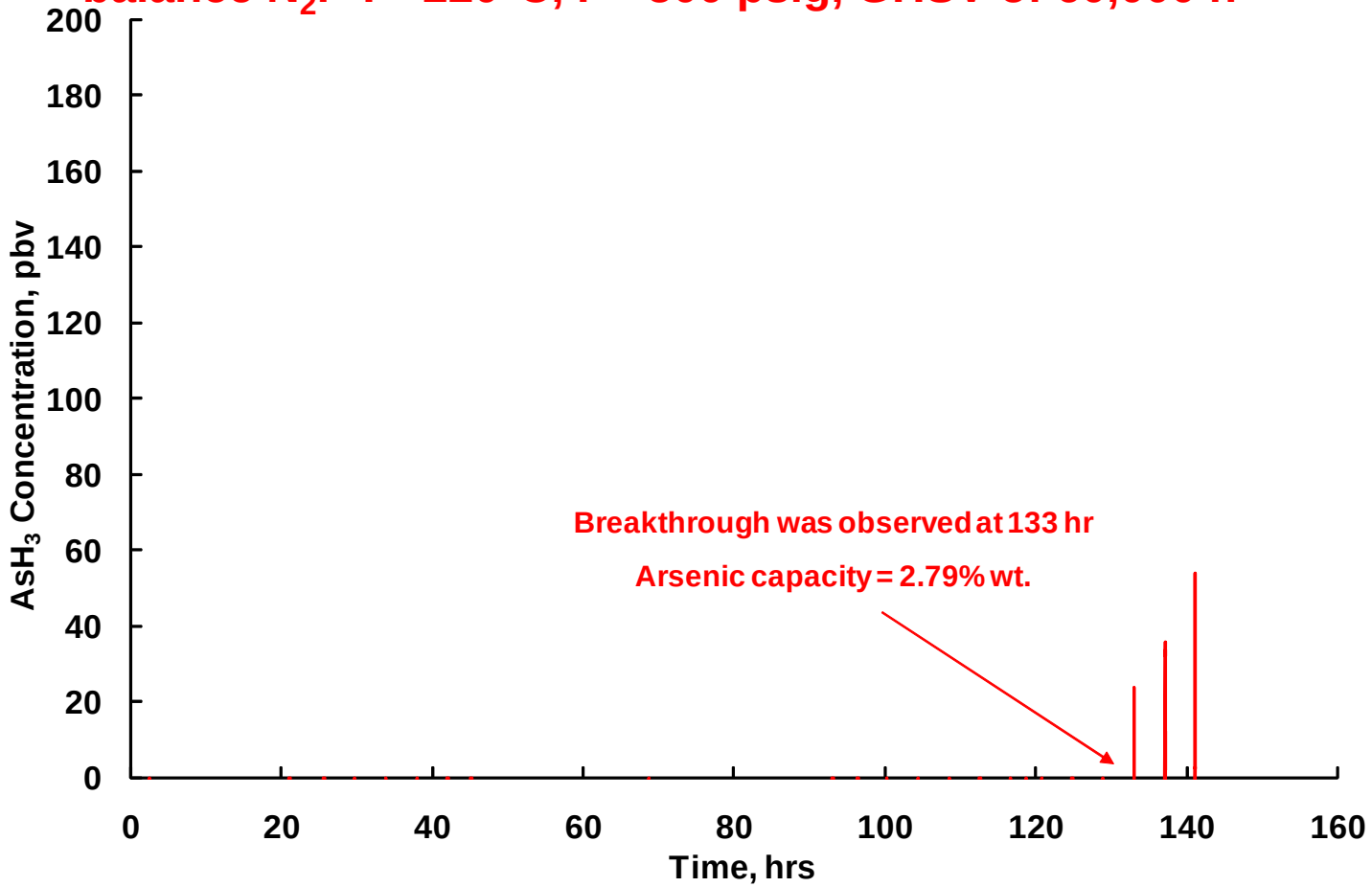
Arsenic Removal

4.6 ppmv AsH_3, 50 ppmv H_2S, 41% CO, 10% CO_2, 29% H_2, 18% H_2O and balance N_2. T= 220°C, P= 500 psig, GHSV of 60,000 h^{-1}



- **TDA MP-carbon achieved 2.79% wt. arsenic capacity (lb of arsenic per lb of sorbent) at 20 ppbv breakthrough**

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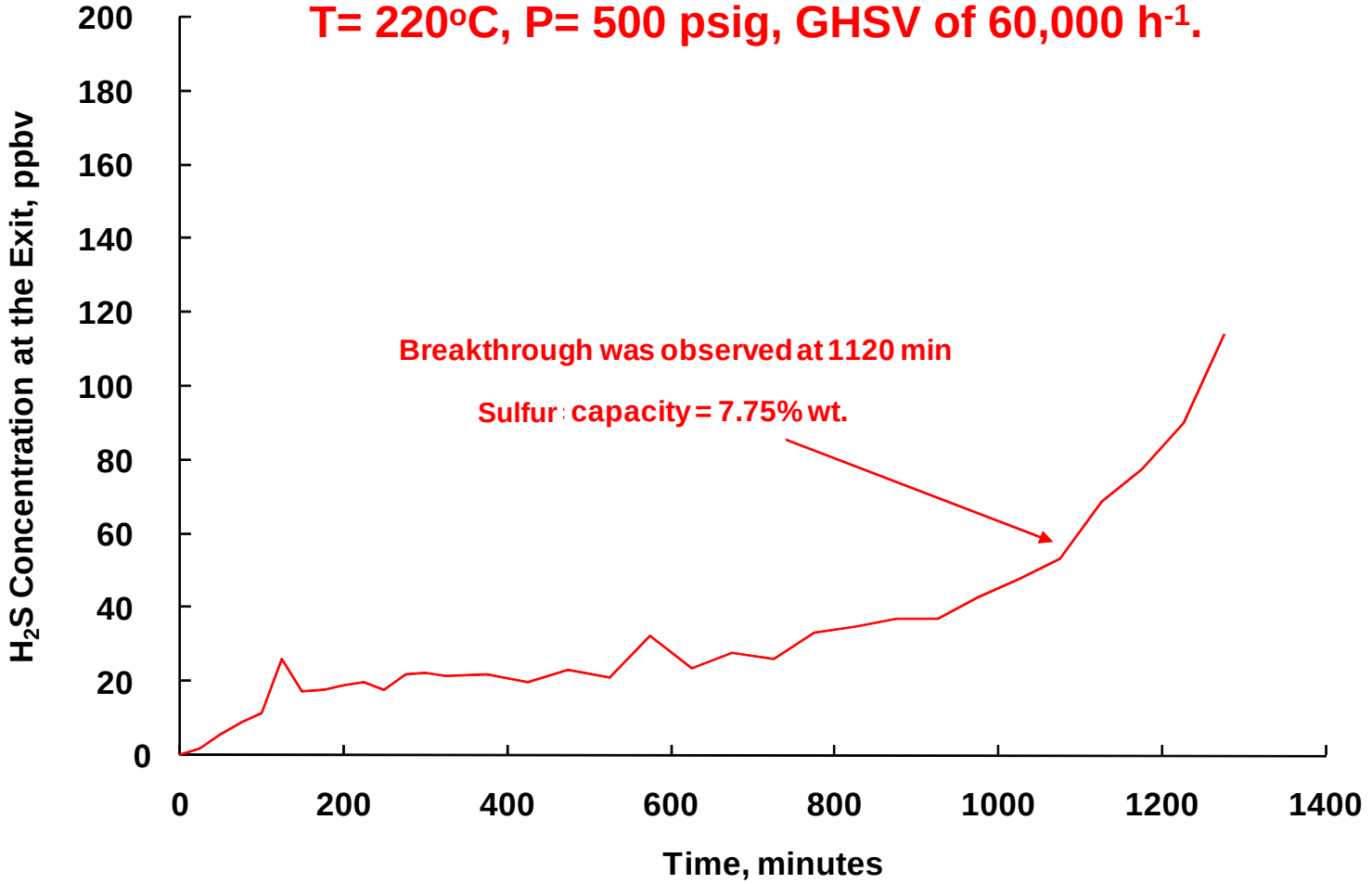
Sulfur Removal Sorbent

50 ppmv H_2S, 41% CO, 10% CO_2, 29% H_2, 18% H_2O and balance N_2.
T= 220°C, P= 500 psig, GHSV of 60,000 h^{-1}.



- **Tested as a polishing sorbent, TDA sorbent achieved 7.75% wt. sulfur capacity (lb of sulfur per lb of sorbent) at 50 ppbv breakthrough**

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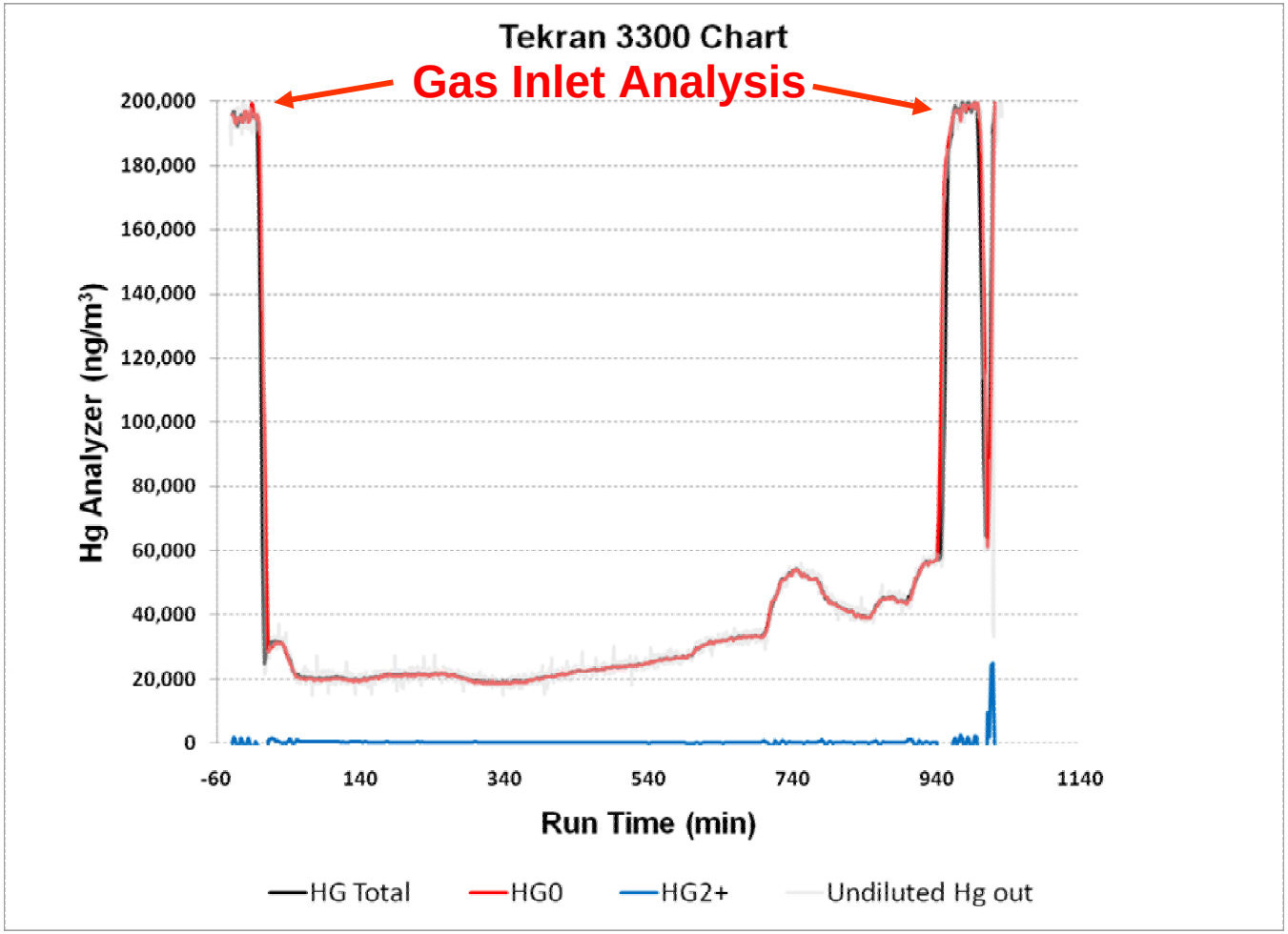
Hg Removal

200 ppbv Hg, 41% CO, 10% CO_2, 29% H_2, 18% H_2O and balance N_2.
T= 230°C, P= 500 psig, GHSV= 60,000 h^{-1}



- **The sorbent also achieved 90% Hg removal at 230°C**

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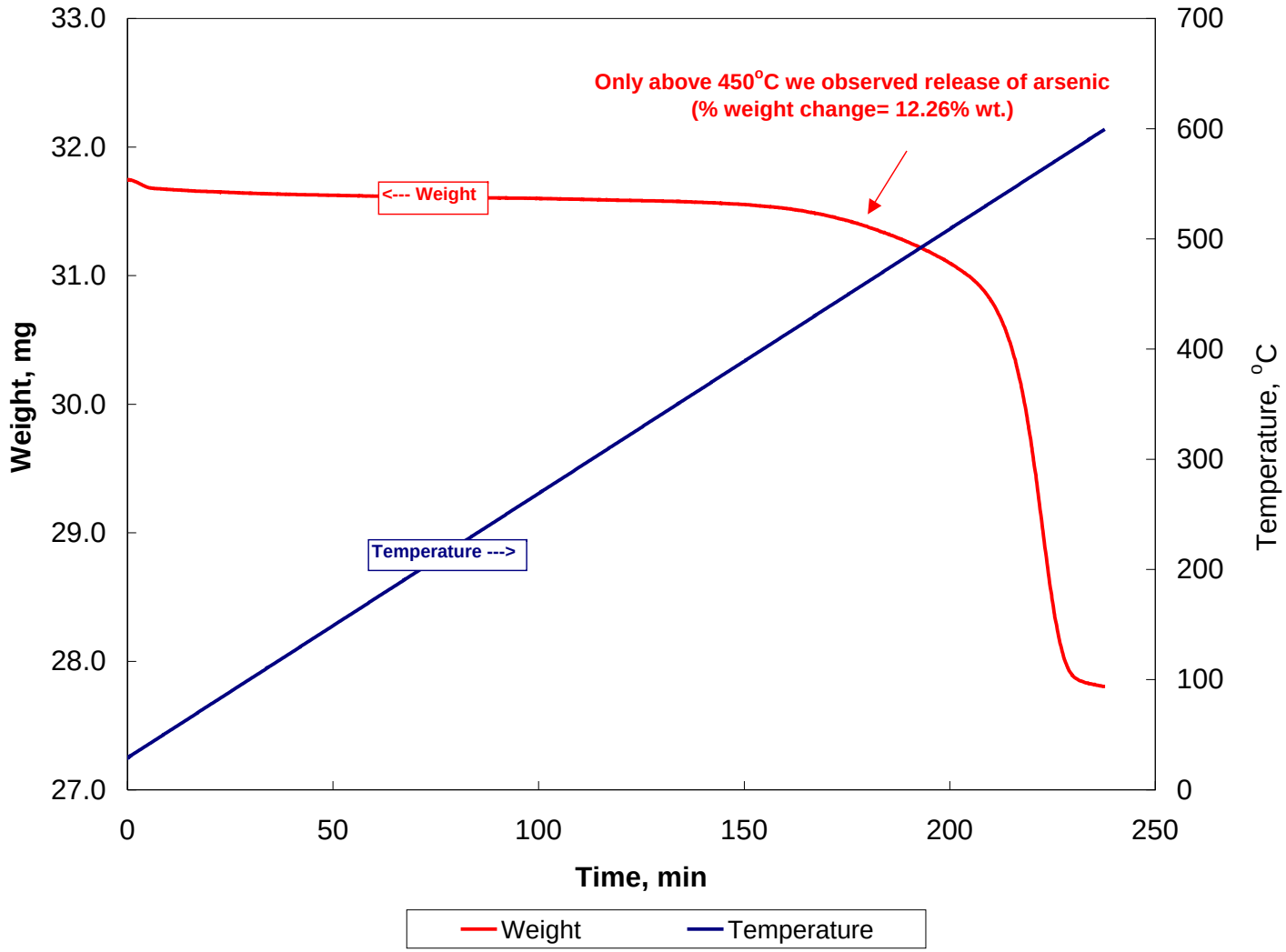
Stability of Absorbed Arsenic



- **The sorbent ties up arsenic strongly with no signs of release below 400°C**

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Engineering and Cost Analysis

- **Sorbent need is estimated based on gas flow rate, contaminant concentration and sorbent capacity**
- **Basis: 100 MW_e**
  - GE gasifier
  - 157,000 lbs per hour of syngas
  - Contaminant concentrations based on published levels at Eastman's Kingsport Facility
- **Sorbent utilization**
  - At projected contaminant concentrations, sorbent still has additional capacity for sulfur and phosphine

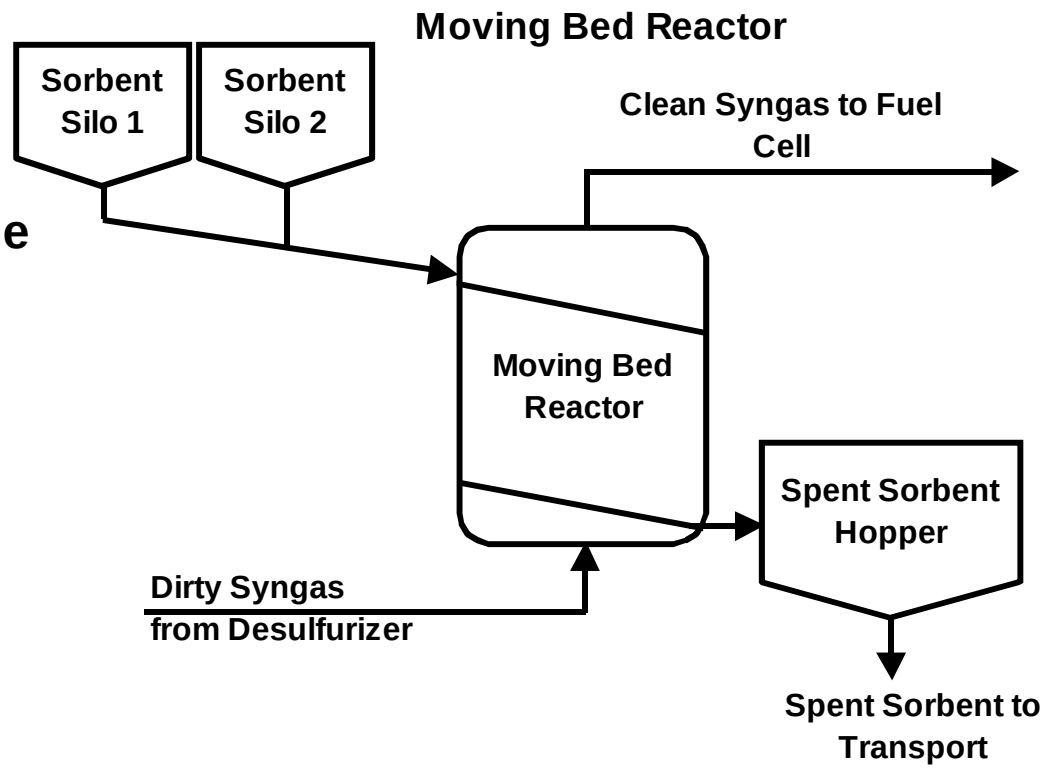
Gas composition Texaco Gasifier, Illinois no. 6 coal	
30.92%	Hydrogen
40.41%	Carbon Monoxide
11.02%	Carbon Dioxide
0.71%	Nitrogen
0.00%	Oxygen
0.10%	Methane
16.84%	Water
100	MWe Output
50%	Efficiency
156,579	lbs/hr Syngas

Contaminant	Concentration
H_2S	3.5 ppmv
PH_3	1.9 ppmv
AsH_3	0.6 ppmv

Contaminant	Sorbent Capacity	Projected Loading
H_2S	7.75%	6.9%
PH_3	7.00%	3.6%
AsH_3	2.79%	2.8%

Reactor Design – Semi-moving Bed

- **Semi moving-bed reactor improves sorbent utilization**
  - **Freshest sorbent is always available at the gas exit**
  - **The sorbent that spends the longest time is removed from the inlet which allows operation at saturation**
- **Operational flexibility**
  - **Different sorbents can be fed at different rates**



- **Sorbent feed rate 138kg/day**
- **Changeover every 3 months**
- **Favorable gas-solid contact time**
  - GHSV= 125 h^{-1} (8 ft x 24 ft reactor)
- **Expected pressure drop of 3.6psi (1/8" pellets)**
- **Parasitic power loss = 13.3 kW (vs. 50 kW in a fixed-bed reactor with annual changeover)**

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Capital Cost Breakdown

DIRECT COSTS SUMMARY (2007 PRICES)			$1,000
	Equipment	Labor	Total
Sorbent Reactor	707.0		707.0
Storage Hoppers	189.4		189.4
Flow Control Feeders	30.0		30.0
Spent Sorbent Hopper	94.7		94.7
Sorbent Mix Hopper	49.5		49.5
Sorbent Flow Piping	38.6		38.6
TOTAL DIRECT COSTS	**1109.2**	**0.0**	**1109.2**
INDIRECT COSTS (Percentage of direct labor)		50%	0.0
TOTAL DIRECT AND INDIRECT COST			**1109.2**
ENGINEERING (percentage of direct costs)		5%	55.5
OVERHEAD & ADMINISTRATION (percentage of direct costs)		8%	88.7
CONTINGENCY		10%	110.9
FEE (percentage of on-site costs)		5%	55.5
TOTAL PLANT COST			**1419.8**
STARTUP COST (percentage of direct costs)		3%	33.3
SPARE PARTS (percentage direct equipment costs)		5%	55.5
INITIAL SORBENT INVENTORY (One Week Usage)			10.7
FACILITIES		20%	221.8
LAND		see note	0.0
WORKING CAPITAL (2 months of annual operating cost)			1148.5
TOTAL CAPITAL REQUIREMENT			**2889.5**

Capital Cost for Purification System = $28.9/kW

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Operating Costs Breakdown with Annualized CAPEX

Operating & Maintenance Costs		$/year	
Operating labor*	$	280,800	3 person shift/$15/hr
Supervising labor*	$	42,120	15% of operating labor
Maintenance labor*	$	154,440	55% of operating labor
Maintenance material*	$	140,400	50% of operating labor
Sorbent replacement cost	$	553,999	
Parasitic Power Cost			
Disposal, $500/ton	$	25,182	
Overhead*	$	95,472	20% of direct labor cost
Taxes, insurance and Admins	$	115,580	4% of Total Capital Cost
Total O&M	$	1,407,992	
Capital recovery, 20%	$	577,899	
Annual Operating Costs	$	1,985,891	
Cost of Clean Syngas	**$**	**3.19**	**per ton**

- **Annualized Cost for Purification = $1,985,000/year**
- **Cost of Removal of Contaminants = $3.19 per ton of syngas treated ($29.96 per pound of contaminant)**
- **Impact on COE = $0.0023/kWh**
  - **<3% of COE (at $0.0753/kWh) - <1.8% of COE @ 500 MW capacity**

Acknowledgements

- The funding provided by DOE is greatly acknowledged
- DOE Project Monitor – Joe Stoffa