Desulfurization of Refinery Off-Gases for Hydrogen Production

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Introduction

- Petroleum refining is 2nd largest industrial consumer of energy in U.S contributing
  - 3% of toxic emissions
  - 17% greenhouse gas emissions, and
  - 10% of total manufacturing energy use

- Mostly due to flaring off-gases from various process units
  - Crude distillation
  - Cracking
  - Hydro-treating

H_2 Production from Off-Gases

- Off-gases from various refinery unit operations can be converted into valuable chemicals such as hydrogen
- Refinery off-gases contain large concentrations of sulfur and other impurities such as arsenic that must be removed
- Sulfur and Arsenic are potent poisons for the catalysts used in the conversion of refinery off-gas to H_2
- Traditionally, hydrodesulfurization (HDS) is used for deep desulfurization
  - Two-step process - hydrogenation of sulfur compounds and subsequent removal of H_2S with an expendable chemical absorbent
  - For higher sulfur levels cost of HDS is very high and also results in hydrogenation of olefins
- High capacity sorbents are needed that can remove sulfur (both H_2S and organic sulfur species) and arsenic directly by adsorption from refinery off-gases

SulfaTrap™ Series Sorbents

- **High selectivity to all sulfur species (mercaptans, sulfides, thiophenes, etc)**
- **High capacity**
  - Expendable sorbent achieves over 27% wt. capacity (lb of sulfur per lb of sorbent)
  - Regenerable sorbent achieves over 0.4% wt. breakthrough capacity
- **High sulfur removal efficiency**
  - Reduce sulfur levels to less than 5 ppbv
- **Regenerable operation**
  - Demonstrated stable capacity for over 20 cycles
  - Oxidizing (e.g. air), reducing (e.g., H_2 or natural gas) or inert gases (e.g., N_2) can be used for regeneration
- **Low cost**
- **Tolerance to off- gas contaminants**
  - Moisture, heavy hydrocarbons (unsaturated and aromatics), CO_2
- **Easy disposal**
  - No flammability, toxicity or pyrophorocity
  - No acetylide formation (copper and silver free)

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Field Demonstrations with SulfaTrap™ Sorbents

- **Several field demonstrations were successfully completed with partners including Siemens Power Corp., Delphi, Logan Energy, GTI, FuelCell Energy, Versa Power, Gaz de France, GTT, Precision Combustion since 2004**

2.2 L sorbent bed provided 1 year continuous operation


TDA's 100 kWe Desulfurizer at GTT, Milano, Italy

- In 2007, TDA produced and delivered 1,500 lb of SulfaTrap™-R series sorbents in-house
  - **In 2008, we already had a 780 lb order; this is expected to grow up to 20,000 lb**

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Refinery Off-Gas Composition

Typical Refinery Off-gas (ROG) Composition*

Gas	Target % vol.
C1	25.5
H2	47
C2	10
C3	5
N2	2.7
C3=	0.9
C2=	4.8
C4	2.2
C4=	0.6
iC5	0.6
C6	0.05
CO2	0.6
C5=	0.05
Total	100

sulfur compound	ppmv
Methyl Mercaptan	44.3
Ethyl Mercaptan	17.5
i-Propyl Mercaptan	5.7
DiMethyl Sulfide	5.5
Hydrogen Sulfide	50
Total	123

* dry basis

- We tested the sorbents in the typical ROG stream at two different moisture levels; 2000 ppmv and saturated (7% vol. H_2O at 5 psig)

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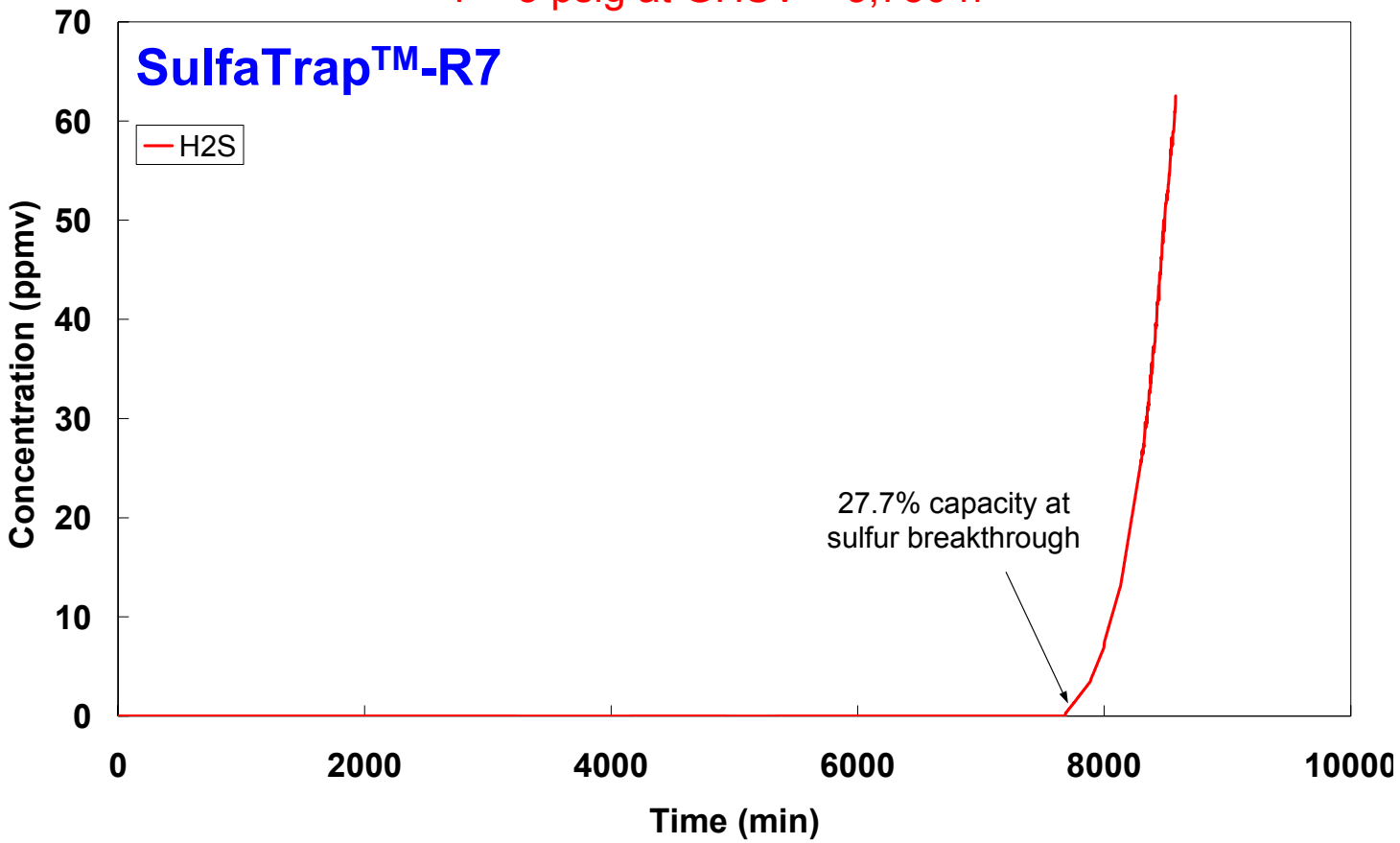
Expendable – H_2S Sorbent

ROG containing 400 ppmv H_2S, 6% ethylene and sat. H_2O at T= 45°C,
P= 5 psig at GHSV = 3,750 h^{-1}



- The sorbent achieved 27.7% wt. sulfur capacity for H_2S at 1 ppmv breakthrough and ~28.9% wt. at 10 ppmv in a ROG stream containing 7% H_2O

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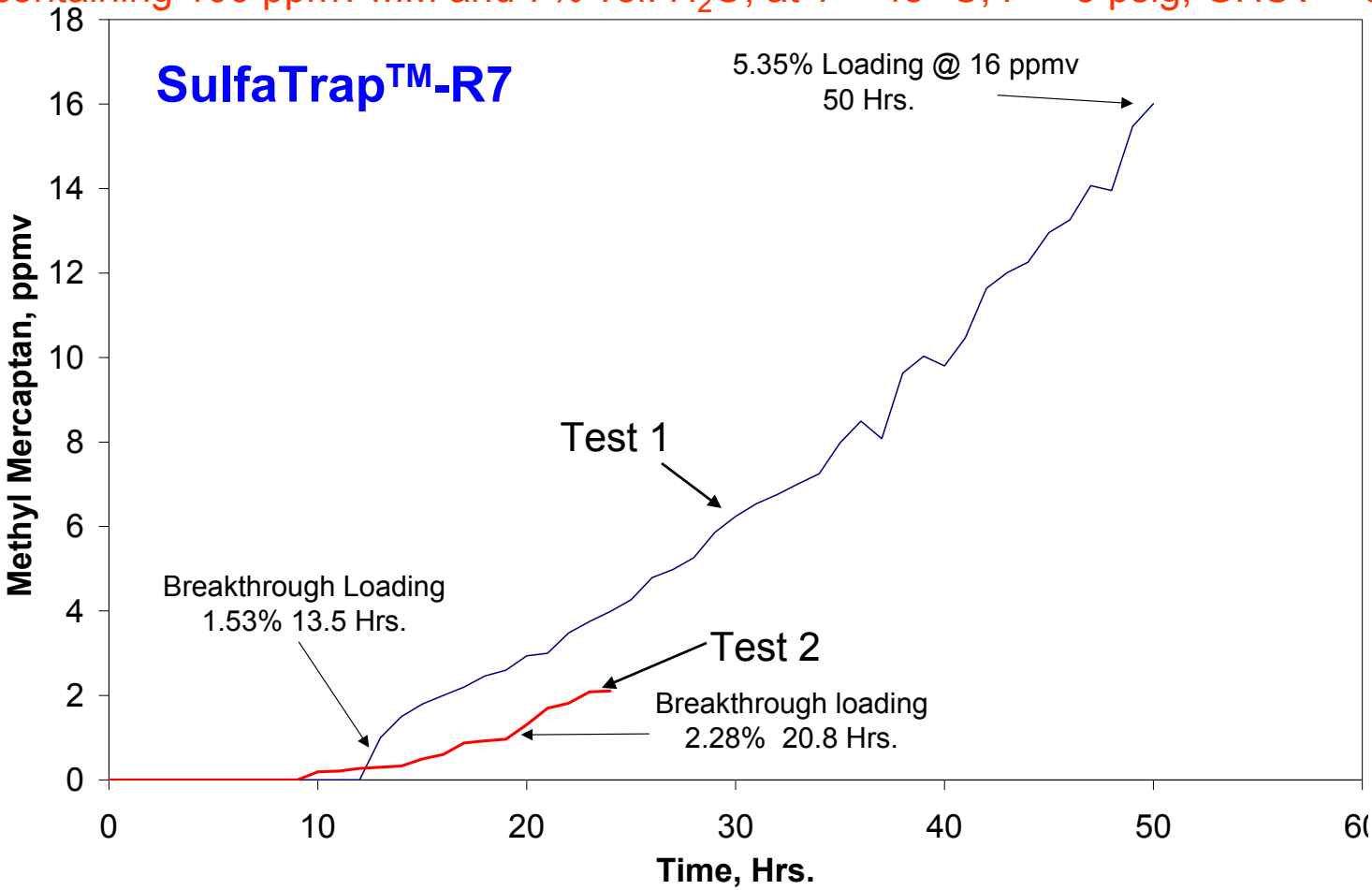
Expendable – Methyl Mercaptan Sorbent

ROG containing 100 ppmv MM and 7% vol. H_2O, at T = 45 ºC, P = 5 psig, GHSV = 6,000 h^{-1}



- The sorbent achieved over 1.53% wt. sulfur capacity for methyl mercaptan at 1 ppmv breakthrough and ~5.35% wt. at 16 ppmv in a ROG stream containing 7% H_2O

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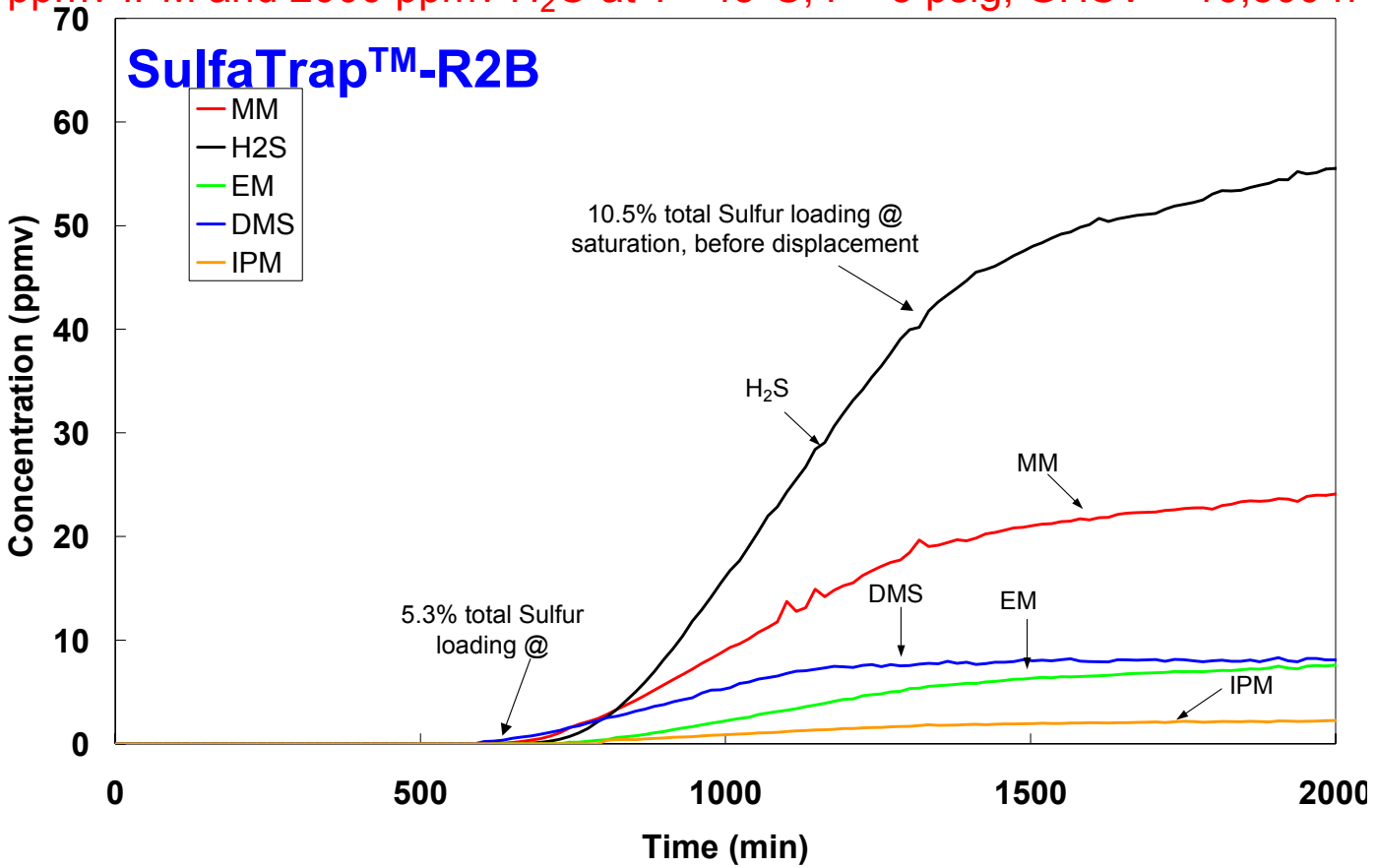
Expendable – Organic Sulfur Sorbent

ROG containing 50 ppmv H_2S, 44.7 ppmv MM, 17.5 ppmv EM, 5.5 ppmv DMS, 5.7 ppmv IPM and 2000 ppmv H_2O at T= 45°C, P= 5 psig, GHSV = 16,500 h^{-1}



- High sulfur adsorption capacity of 5.3% wt. at breakthrough and 10.3% wt. at saturation for organic sulfur compounds
- The order of breakthrough is: DMS < MM < H_2S < EM <IPM

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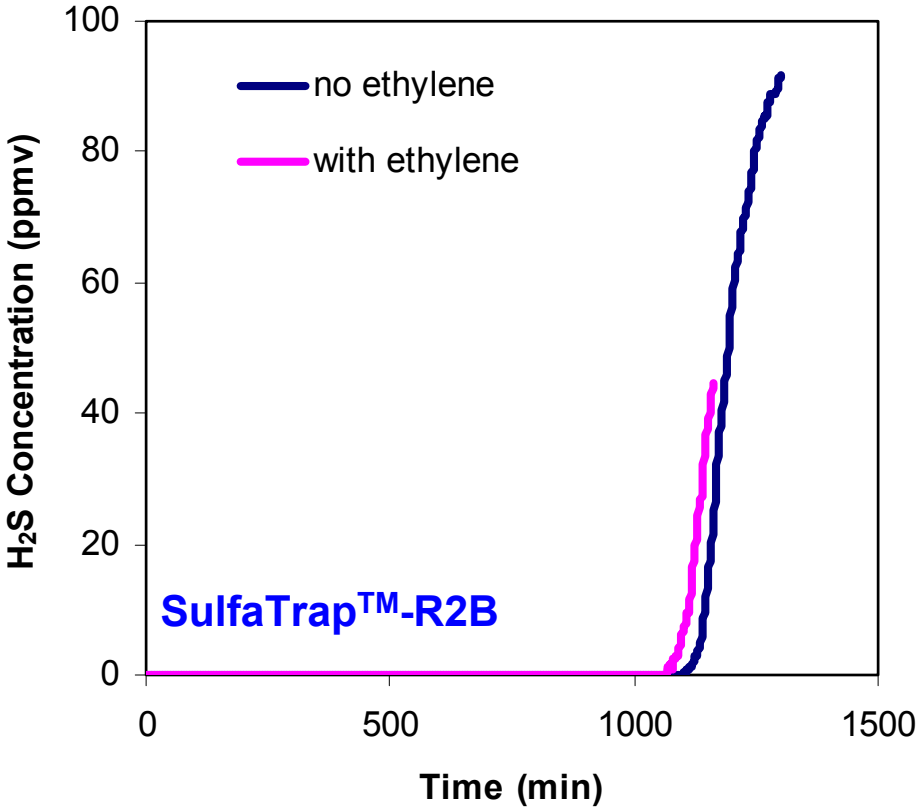
No Impact of Olefins on Performance

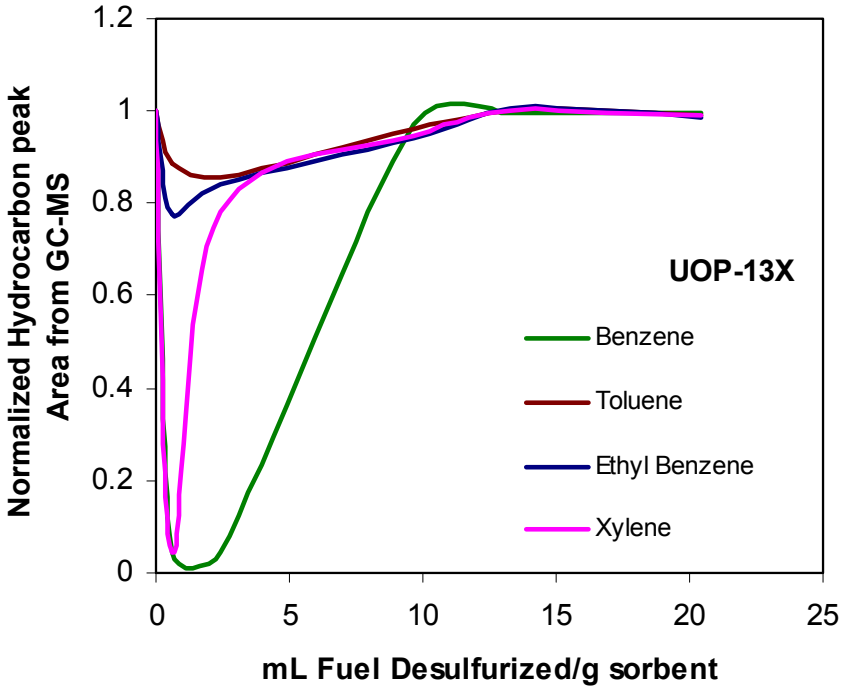
ROG containing 400 ppmv H_2S and 7% vol. H_2O
at T= 45°C, P= 5 psig at GHSV = 3,750 h^{-1}

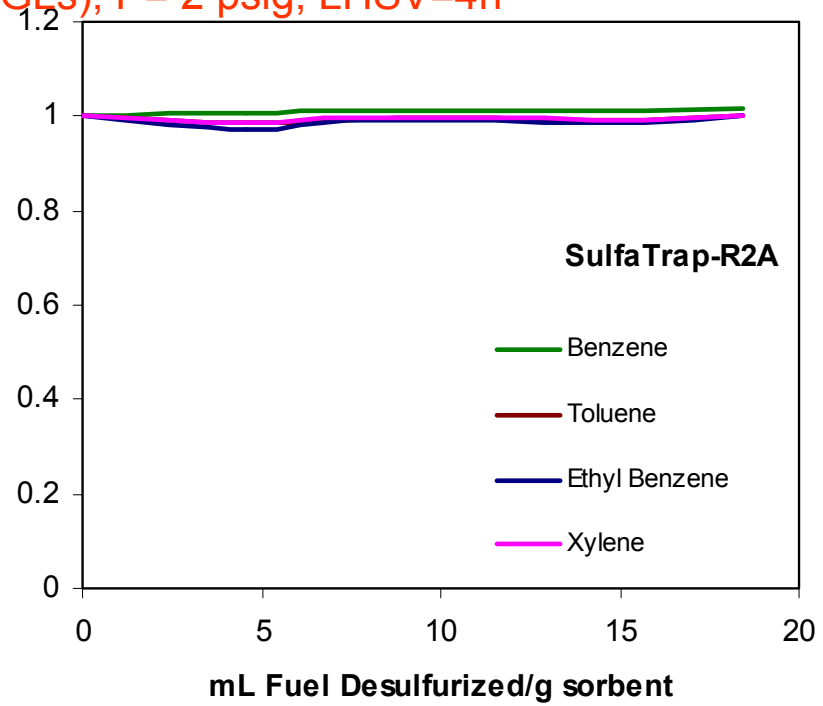


- Sorbent was able to maintain performance in the presence of olefins (6%) and high levels of moisture (~7% vol.)

Effect of Aromatics

T=40°C, DMS Conc.= 75 ppmw S, NPM=1,020 ppmw S in Natural Gas Liquids (NGLs), P= 2 psig, LHSV=4h^{-1}





UOP-13X Sorbent

- **The adsorption of aromatic hydrocarbons was evident with the UOP-13X sorbent**
  - competitive adsorption between aromatics and sulfur

TDA SulfaTrap™-R2A Sorbent

- **No hydrocarbon adsorption was observed with the SulfaTrap™-R2A**
  - Highly selective sulfur adsorption

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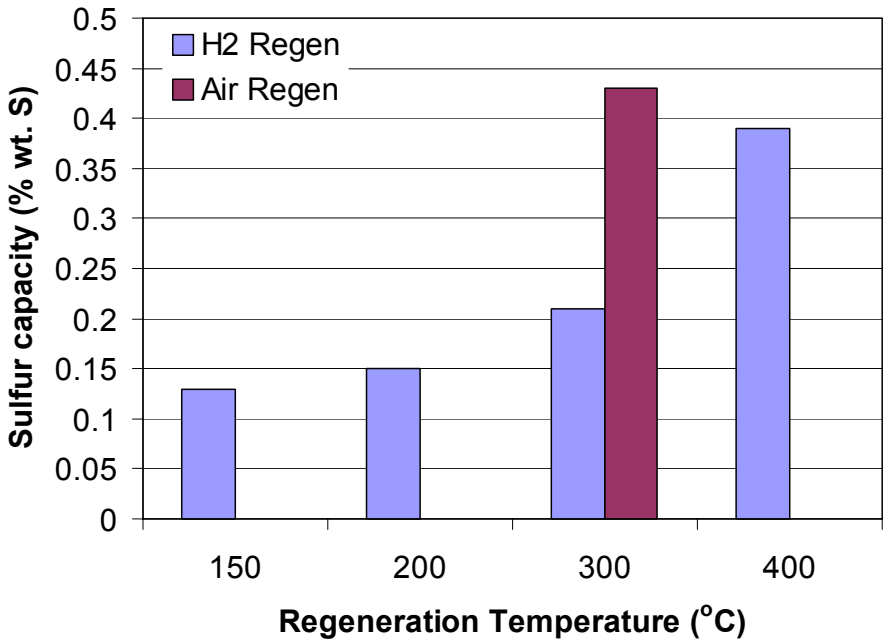
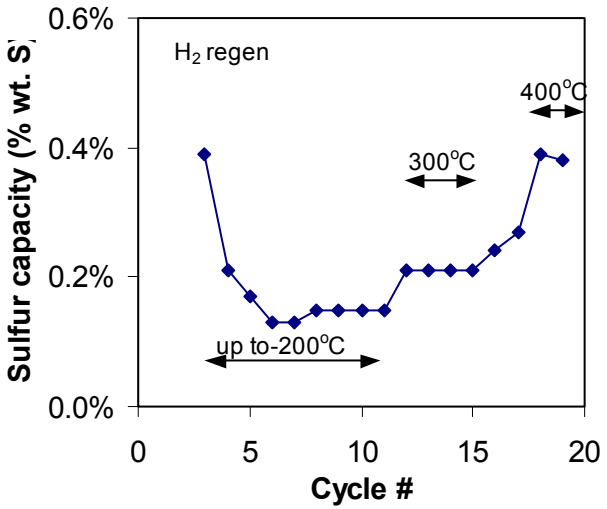
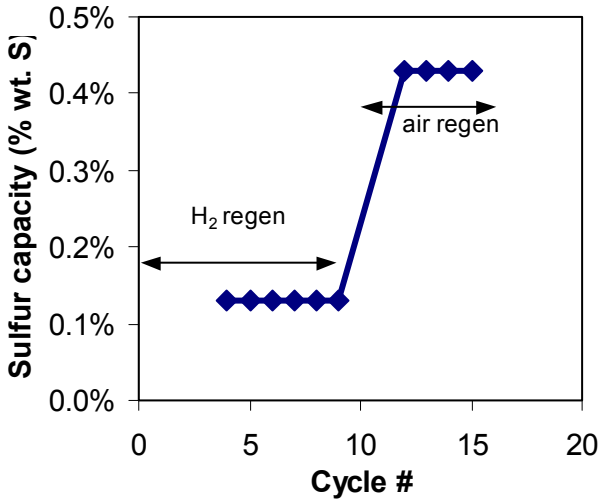
Regenerable Sorbent Performance

Cycling data in ROG containing 1000 ppmv H_2S, and 7% vol. H_2O at T= 45°C, P= 5 psig at GHSV = 7,500 h^{-1}

SulfaTrap™-R2C







- Sorbent achieved a stable sulfur adsorption capacity of 0.4% wt. at 1 ppmv H_2S breakthrough in H_2 regeneration at 400°C
- Higher capacities are possible with air regeneration at lower temperatures (0.43% wt. at 300°C)

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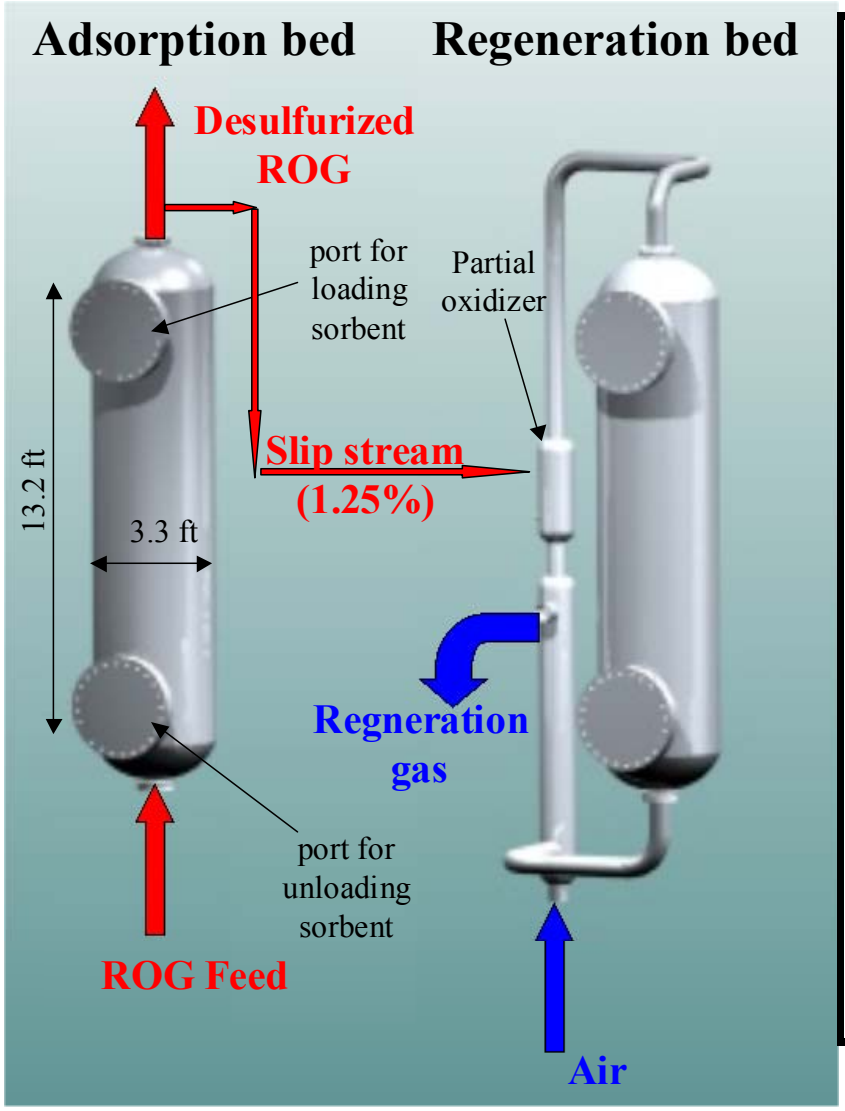
System Design



Basis	
H_2 produced	5.00 MMSCFD
ROG feed	3.02 MMSCFD
Regenerable Sorbent	
Half-cycle time	12 hr
Sulfur capacity	0.4% wt. S
Sorbent life (replacement)	365 cycles
Sorbent needed per bed	2.3 tons
Sorbent bed volume	114 cu ft
Reactor Sizing	
L/D	4
Diameter	3.3 ft
Height	13.2 ft
Overall System Dimensions	
Footprint	6' x 12'
Maximum Height	20'

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System Analysis

Desulfurization Cost Analysis

Total Sorbent Requirement per year			
Sorbent amount		4.52	tons
Sorbent Volume		228	cu ft
	$/year		
Sorbent replacement cost	$ 248,745		
per lb Sorbent Cost		$ 25.00	
Regeneration heat cost	$ 54,910		
Total O&M	$ 433,746		
Capital recovery, 20%	$ 45,188		
Annual Operating Costs	$ 478,934		
Cost of Sulfur Removal			
per MMSCF of ROG	$ 435.11		
per kg of H_2 produced	$ 0.10		
per kg sulfur	$ 72.52		

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Cost of H_2 from ROG

			ROG Cost	
Feed Cost	$	882,230	**$/MMBTU**	**1**
Annual Desulfurizer Operating Cost	$	478,934	**Processing Cost**	
Cost for Reforming and H_2 separation	$	1,067,625	**$/MMBTU**	**1.8**
Total Cost	$	2,428,789		
Cost of ROG processing	**$**	**2,207**	$/MMSCF	
	$	**2.75**	$/MMBTU	
Cost of H_2 recovered from ROG	**$**	**0.52**	$/kg	
	$	**4.09**	$/MMBTU	
Desulfurization Cost	**$**	**0.81**	$/MMBTU	
		19.7%	of H_2 Cost	
		5.6%	of H_2 RSP	

- **Desulfurization cost for TDA's SulfaTrap™ sorbent is only 5.6% of current required selling price (RSP) of H_2**

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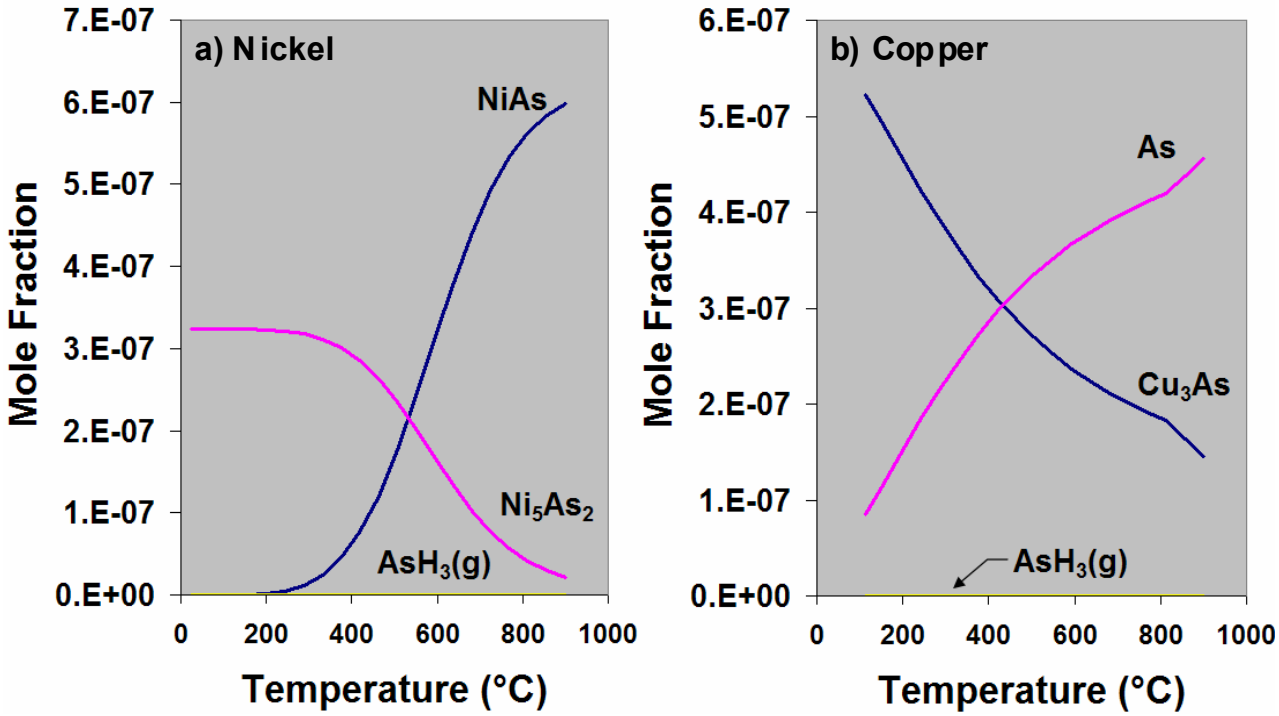
Arsenic Poisoning

Concentrations of As-containing species at equilibrium



- As poisons the metal catalysts used in hydrogen production
- One of the main contributors to the arsenic is the delayed coker off gas
- High temperature delayed coking process also produces a large amount of volatile metals, which will convert into respective hydrides in the presence of hydrogen (e.g., arsenic hydride, hydrogen selenide)

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TDA's Arsenic sorbents

- TDA has previously developed a high temperature arsenic sorbent to work as a guard bed in coal-to-chemicals plants and successfully carried out various demonstrations

TDA sorbent is qualified for Siemens' UltraClean™ Process at GTI's 10 ton/day FlexFuel Gasification Facility (Plains, IL)

Eastman Chemicals coal-to-chemicals plant Kingsport, TN

TDA demonstrated its gas cleaning technology with Southern Company at PSDF Facility, Wilsonville, AL

- We modified the high temperature sorbent to suit the low temperature (20-60°C) refinery off-gas – H_2 production application

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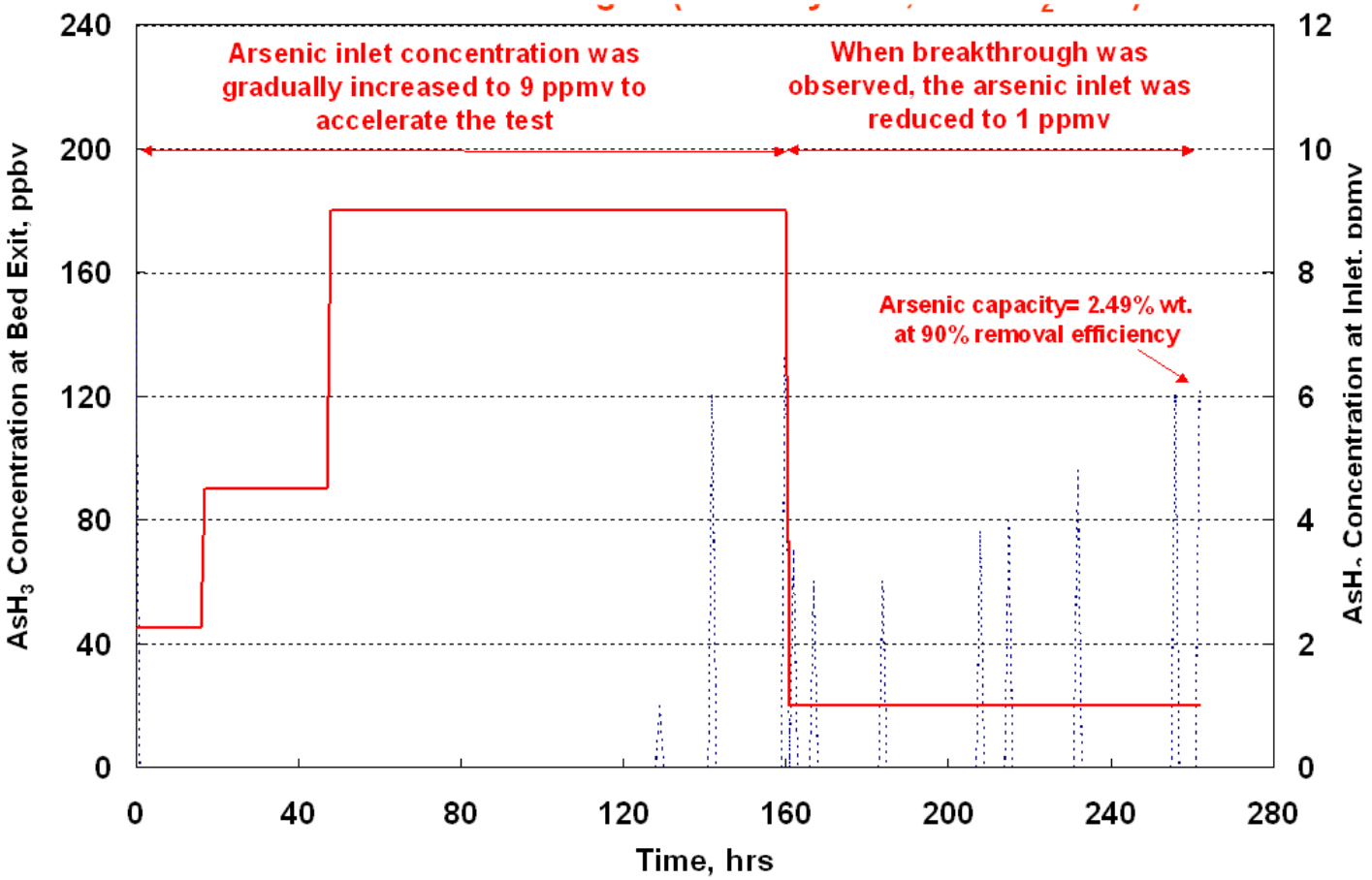
Non-Cu Arsenic Sorbent

ROG containing Arsenic and 7% vol. H_2O at T= 45°C, P= 5 psig at GHSV = 3,750 h^{-1}



- **Non-Cu based Arsenic sorbent achieved 2.5% wt. As capacity in a refinery off-gas stream**

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Conclusions

- SulfaTrap™ sorbents can achieve up to 5.3% wt. sulfur capacity for the organic sulfur species and up to 27% wt. for hydrogen sulfide (H2S)
- 20 consecutive adsorption/regeneration cycles with a stable 0.4% wt. sulfur breakthrough capacity
- TDA has developed a sorbent for low temperature (45°C) removal of arsenic (i.e., arsenic hydride or commonly referred to as arsine)
- Like the sulfur, arsenic is a potent poison for the nickel-based reforming and Cu-based water-gas-shift (WGS) catalysts.