RNG WORKS

THE COALITION FOR RENEWABLE NATURAL GAS

Hydrogen Sulfide Removal From Biogas & Landfill Gas

Basics of H2s & Commercial Removal Technologies

Guild Associates, Inc.
5750 Shier Rings Road
Dublin, OH 43016
Phone: (614) 798-8215
Fax: (614) 798-1972

Agenda

Hydrogen Sulfide Removal From Biogas and Landfill Gas

Basics of H_2S and Commercial Removal Technologies

Presented By

Guild Associates, Inc.

01 Basics of Hydrogen Sulfide

- What is it, where does it originate?
- What is the impact of H2S, What are the regulations?

02 Commercial Options for H2S Removal

- Integral with CO2 Removal (Molecular Gate™, Water Wash)
- Regenerative Media Systems
- Replaceable Media Systems

03 Deep Dive: Controlling the Process Parameters to Enhance Replaceable Media system

Basics of Hydrogen Sulfide

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- What is it, where does it originate?
- What is the impact of H_2S
- What are the regulations?

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Basics of Hydrogen Sulfide

What Is Hydrogen Sulfide?

- Colorless Gas that is an Irritant and Dangerous Asphyxiant
  - Characteristically a "rotten egg" smell
  - Can be detected in concentrations as low as 0.1-1.5 ppm
- Irritant and asphyxiant
  - NIOSH PEL (Permissible Exposure Level): 10 ppm
  - NIOSH IDLH (Immediately Dangerous to Life and Health): 100 ppm
- Flammable in a wide range of concentrations
  - Explosion Level in air 4% - 44% v/v
  - Heavier than air – tends to collect in low-lying area

Basics of Hydrogen Sulfide

Sources of Hydrogen Sulfide

- Municipal Solid Waste Landfills
  - Waste Water Treatment Plant sludge
  - Pulp & paper mill wastes
  - Gypsum/drywall
    - Alone and as part of Construction and Demolition waste streams
    - Construction and Demolition fines (small particles)
    - Major Storm event (hurricanes, tornado) debris can change landfill characteristics quickly
- Agricultural Digesters
  - Feed for Livestock influences H_2S Content in Manure
  - Rendering waste

Basics of Hydrogen Sulfide

H2S impact on Downstream Equipment

- Detrimental to metallic components
- Causes Deposits on Valves
- H_2S combustion in Flare or Thermal Oxidizer leads to SO_2 formation
  - Air Permits of the Biogas Site affected by SO_2 Emissions
  - 100 TPY (tons per year) of SO_2 results in Major Source Status for Air Permitting by local EPA

Commercial Options for H_2S Removal

H_2S Process Selection Design Considerations

- Total Biogas flow
  - Current flow, anticipated peak flow, and minimum flow
  - Project flow 20 years outward
- H_2S concentration projection at the noted flows
- Requirements for treated gas and waste gas
  - Flaring of waste gas – Air Permit
  - RNG Pipeline standard, CNG Vehicle Fuel requirement
- Feed gas pressure and anticipated system pressure drop
  - Design feed blower to deliver at needed pressure
  - How much drop should I expect to see across the treatment system?
- Feed gas temperature requirement
- Available equipment footprint at site
- Scalability – grow with anticipated biogas flow?.

Commercial Options for H_2S Removal

Equipment Options for Commercial H_2S Removal

- Integral with CO_2 Removal (Molecular Gate™, Water Wash)
- Regenerative Media Systems
- Replaceable Media Systems

Commercial Options for H_2S Removal

Molecular Gate™ Pressure Swing Adsorption by Guild Associates

- H_2S removed with CO_2, siloxanes, VOCs and water
- Media is regenerated using vacuum compression
- Media lasts the life of equipment (20+ years)
- H_2S is combusted in the TOX/Flare with other contaminants
- Field proven for feed gas of 7000 PPM reduced to pipeline standards
- Requires air permits for H_2S combustion

Commercial Options for H_2S Removal

Water Wash CO_2 Removal Technology

- H_2S removed with CO_2 in water wash tower
- CO_2 is released to atmosphere/burned in TOX
- Media lasts the life of equipment (20+ years)
- H_2S accumulates in water, needs to be treated and replaced

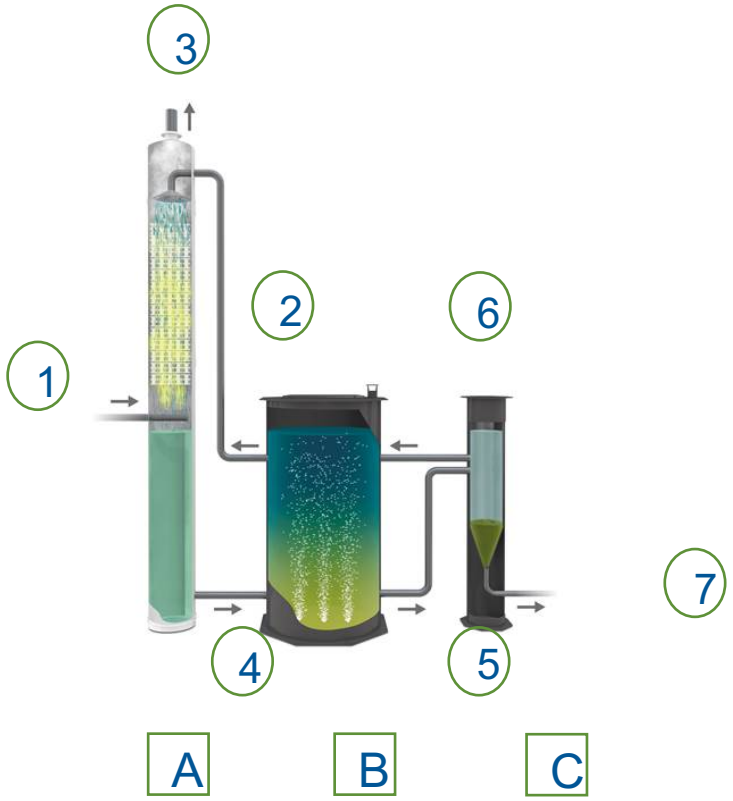
Commercial Options for H_2S Removal

Regenerative Media Systems

- Wet scrubber application for feed biogas
- Liquid is regenerated by various methods
- "Caustic" solution – chelated iron, hydroxide, bicarbonate …
- Solution can be recovered and recycled
- Chemical process requires monitoring
- Biological regeneration is an option

Commercial Options for H_2S Removal

Example of Regenerative Process



A. Absorber/contactor
B. Reactor
C. Settling

1. Raw (sour) LFG
2. Wash solution
3. Treated (sweet) LFG
4. High-sulfur liquid
5. Concentrated-sulfur liquid
6. Recovered wash solution
7. Elemental sulfur paste

Commercial Options for H_2S Removal

Replaceable Media Systems – Activated Carbon Media

Feed gas passes through a vessel of Activated Carbon

- Media adsorbs H_2S in pores of media
- Media tends to adsorb other non-target chemicals, reducing H_2S capacity
- Spent media can typically be disposed in landfills, can possibly be classified as Hazardous
- Elemental sulfur is "fixed" and doesn't leach back into waste
- Media generally removes about 25% of its weight in H_2S

Commercial Options for H_2S Removal

Replaceable Media Systems – Catalytic Reaction Media

Feed gas passes through a vessel of Catalytic Reactive Media

- Feed gas fed through media
- Sequential chemical reaction enabled by media
  - First with water, then oxygen
  - Results in elemental sulfur deposited on media
- Iron Sponge media prone to agglomerating particles into large bricks, resulting in less capacity, higher removal costs, higher pressure drops
- BSR-050 from Guild Associates not susceptible to bricking
- Media capacity typically 10-15% for Iron Sponge, 120% for BSR-050
- Spent media can typically be disposed in landfills

Controlling Process Parameters to Enhance Replaceable Media Systems

Problem Statement and Objectives

Problem:

- H_2S Removal is problematic, expensive and unpredictable

Objectives:

- Maximize utilization of H_2S scavenger media to reduce cost and logistics burdens associated with natural gas purification
- Relationships between $[O_2]$, $[H_2O]$, $[H_2S]$ and temperature on media performance

Controlling Process Parameters to Enhance Replaceable Media Systems

Basics of Media Reaction Chemistry

H_2S Reaction Chemistry

$M\text{-}O + H_2S \rightarrow M\text{-}S + H_2O$

$M\text{-}S + \frac{1}{2} O_2 \rightarrow M\text{-}O + S$

Two Reactions:

- Metal sulfide formation – very fast
- Site regeneration – slower and must be balanced

Reaction is Catalytic

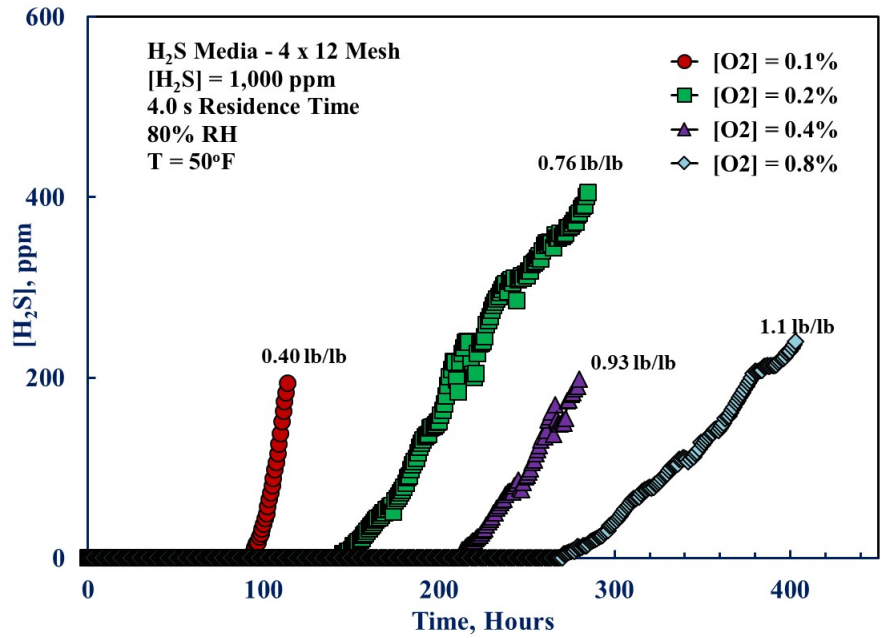
- O_2 necessary for reaction
- Reaction slows then terminates as elemental sulfur blocks reaction sites

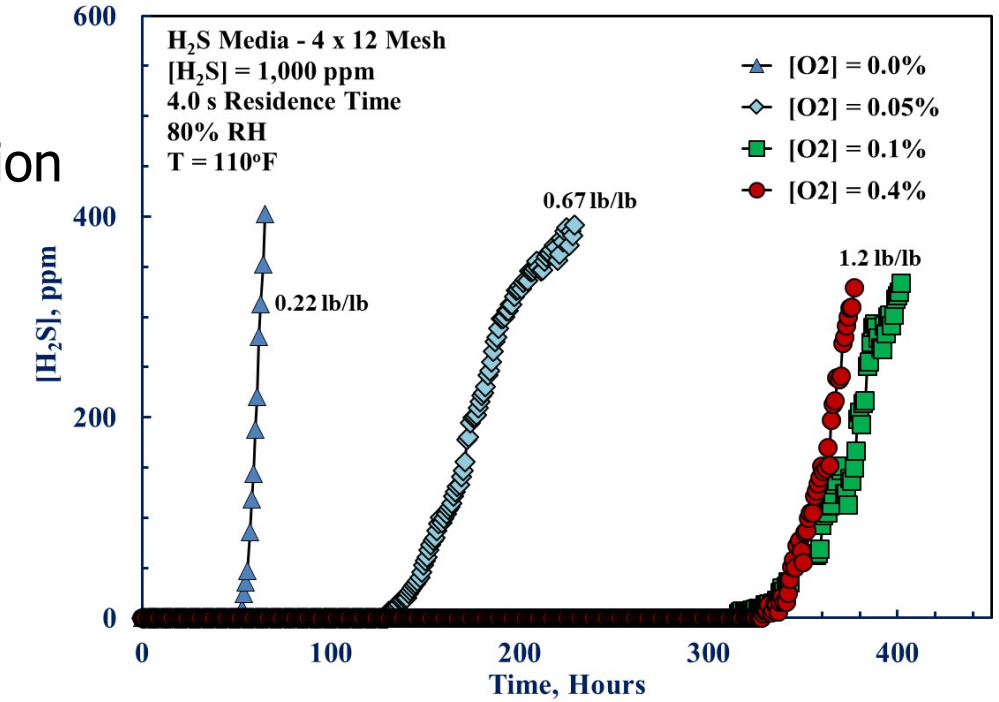
BSR-050 H2S Media

Controlling Process Parameters to Enhance Replaceable Media Systems

Effects of [O_2] and Temperature

- More O_2 required at lower T to maximize capacity
- Operation at increased T allows for operation at lower O_2





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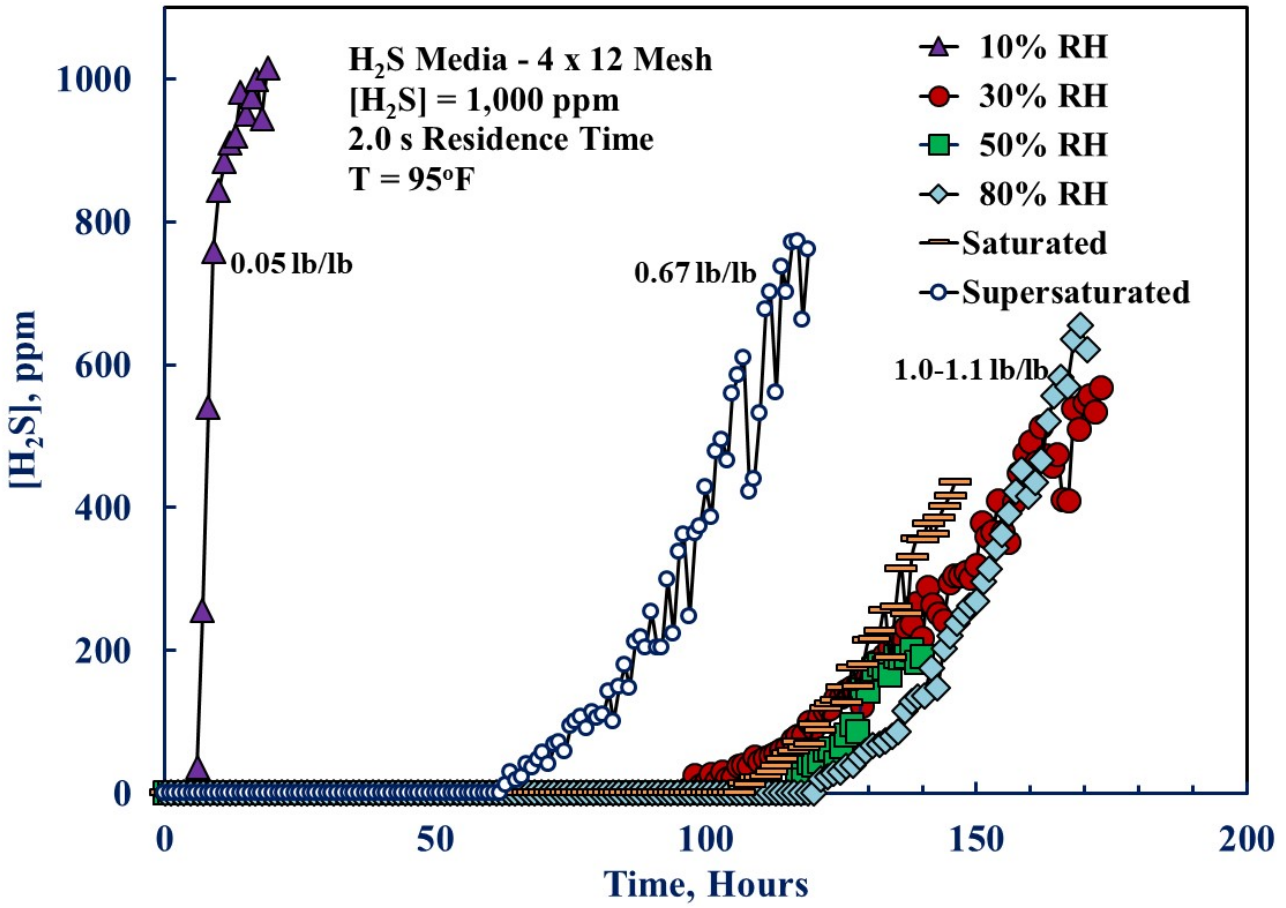
Controlling Process Parameters to Enhance Replaceable Media Systems

Effects of [H_2O]

H_2O is necessary for the reaction to proceed – active site is a hydrated metal oxide/hydroxide

- Fill pores of media with water, preventing H_2S from accessing active sites within media – leading to decreased capacity
- Force reaction to external surface, leading to "bricking" and clumping of media
- Drying media does not return capacity – media is "eggshelled" with sulfur and/or iron sulfide



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Controlling Process Parameters to Enhance Replaceable Media Systems

Effects of [H_2O] – Case Study

Spent media removed from vessel
where water had significantly condensed
H_2S removal capacity = 0.78 lb/lb

Spent media in vessel from process
where water condensation was minimized
H_2S removal capacity = 1.15 lb/lb

Controlling Process Parameters to Enhance Replaceable Media Systems

Summary of Temperature, O_2 and H_2O

Temperature, [H_2O], [O_2] and [H_2S] in the process stream will impact H_2S removal capability of media

- Higher temperatures required for optimal operation when [O_2] is low
- Prolonged periods of water condensation in bed detrimental to performance
  - Reduced H_2S removal capacity
  - "Bricking"

Thank You!

Please Contact Guild Associates should you have questions!

Guild Associates, Inc.

www.GuildAssociates.com
H2S@GuildAssociates.com
614-798-8215

Guild Associates, Inc.
5750 Shier Rings Road
Dublin, OH 43016
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Fax: (614) 798-1972