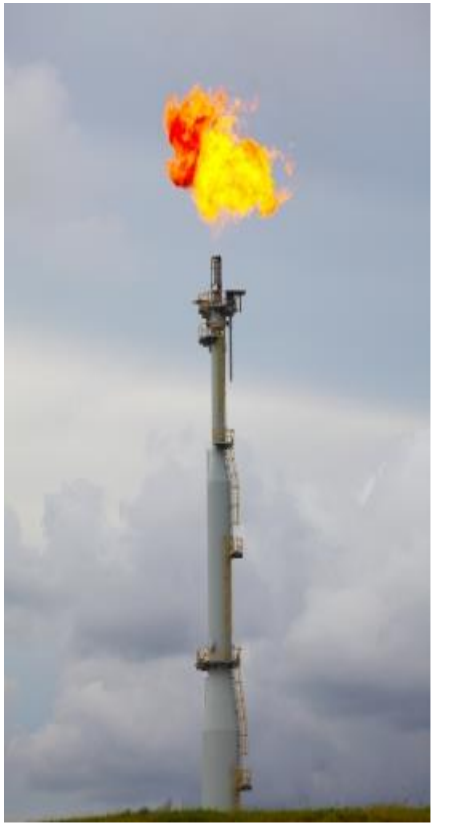
Characteristics of Sour Flare Gas Streams that Impact H_2S Treatment Technologies

*Darshan Sachde, PhD (presenter)**
Kenneth E. McIntush, P.E.
Darryl L. Mamrosh, P.E.
Carrie Beitler
Trimeric Corporation

** darshan.sachde@trimeric.com*

Topics

- Introduction
- Design Basis Selection
- Amine Treating of Refinery Flare Gas
- Caustic Scrubbing of Flare Gas
- Solid H_2S Scavengers for Flare Gas
- Liquid H_2S Scavengers for Flare Gas (In summary only)
- Conclusions



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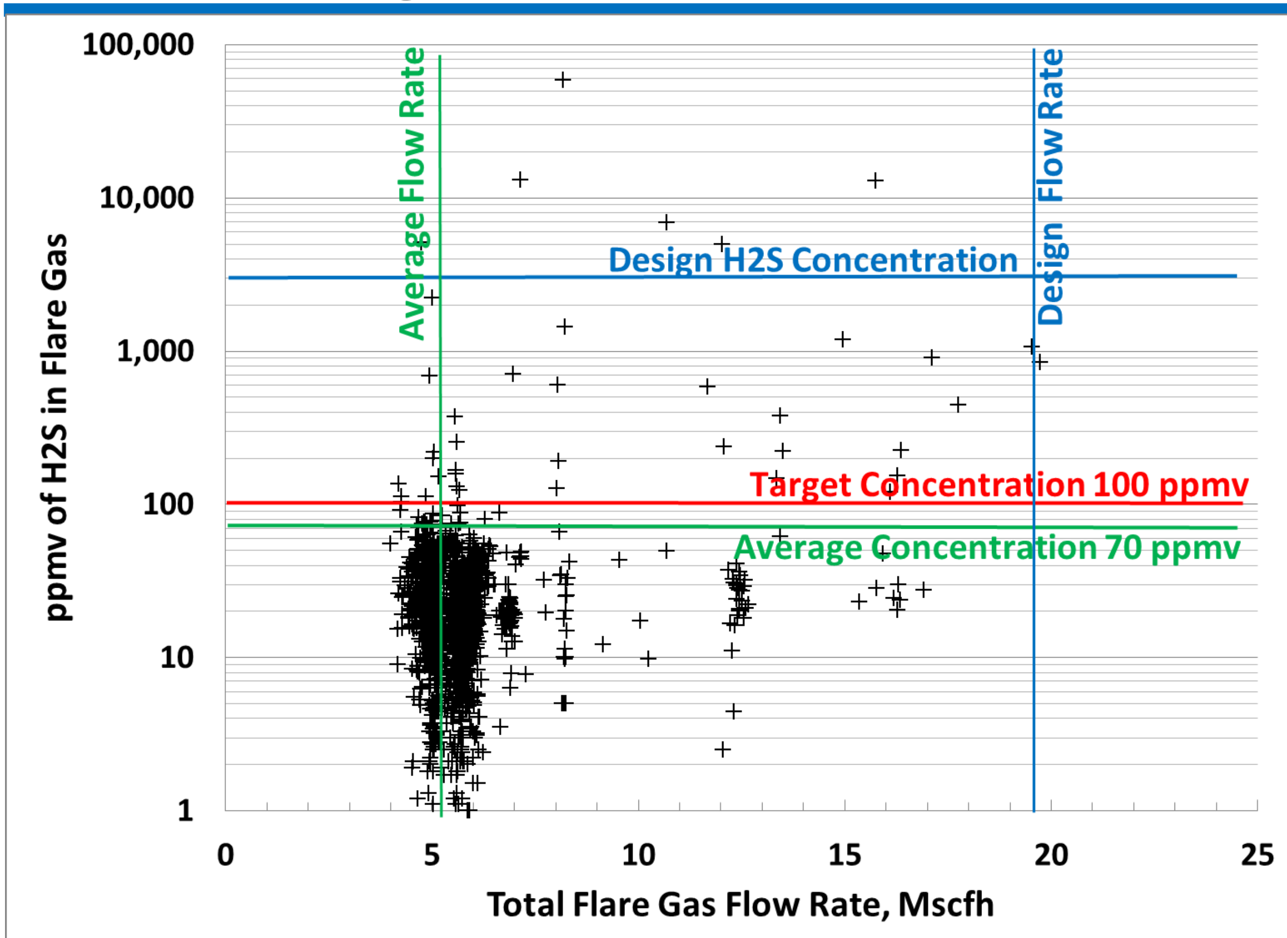
Introduction

- Based on paper with same title. See Trimeric website (www.trimeric.com/publications).
- H_2S removal technology selection based on:
  - Sulfur load (lb/day of S, or LTPD of S)
  - Gas impurities (CO_2, O_2, H_2, etc.)
  - Water content
  - Operating temperature, pressure, and flow rate
- Critical to develop sound design basis
- Covers characteristics that impact: amine, caustic, solid scavengers, and liquid scavengers

Design Basis Selection

- Understand important regulatory drivers:
  - NSPS Ja limit of ~160 ppmv H_2S
  - Develop design limit (e.g., 100 ppmv H_2S)
  - Eliminate excursions, if permit allows
- Review historical flare gas data due to varying conditions over time
- Average data gives typical operating expenses
- Maximum rates used to size and cost equipment

Example Flow and H_2S Variability (flare gas before treatment)



- Entire range of gas flow used since high H_2S at high flows (limiting design)
- Gas treated even if < 100 ppmv H_2S
- Some high H_2S points allowed by permit

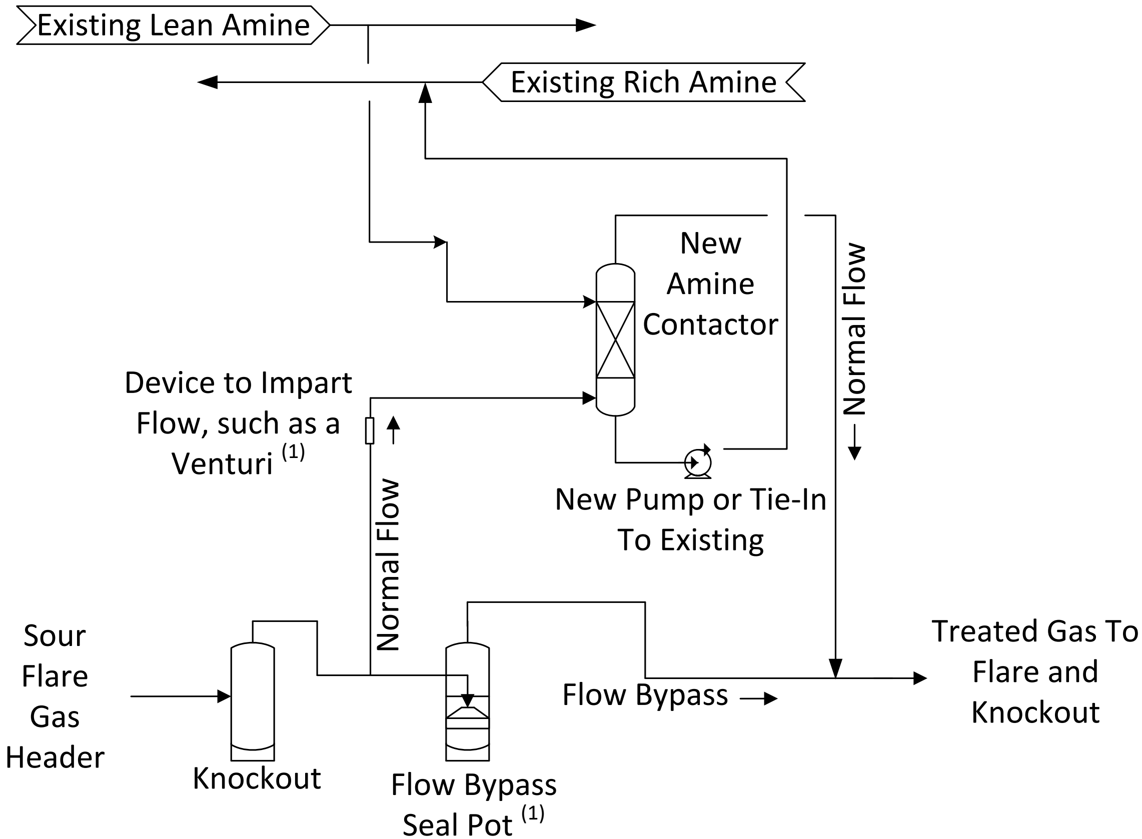
Other Key Characteristics for Design Basis

- Sulfur load: impacts operating costs
- Operating temperature and pressure:
  - Temperatures track ambient (long pipe w/o heat trace or insulation)
  - Pressures generally low (inches WC to a few psig)
- Composition/variability of other gas components

Amine Treating of Flare Gas

- Amine treating common for H_2S removal in refineries
- Dedicated amine unit not economic for flare gas w/ low sulfur load
- Consider new standalone, low dP, amine contactor tied to existing amine circuit
- Determine load capacity of existing amine unit

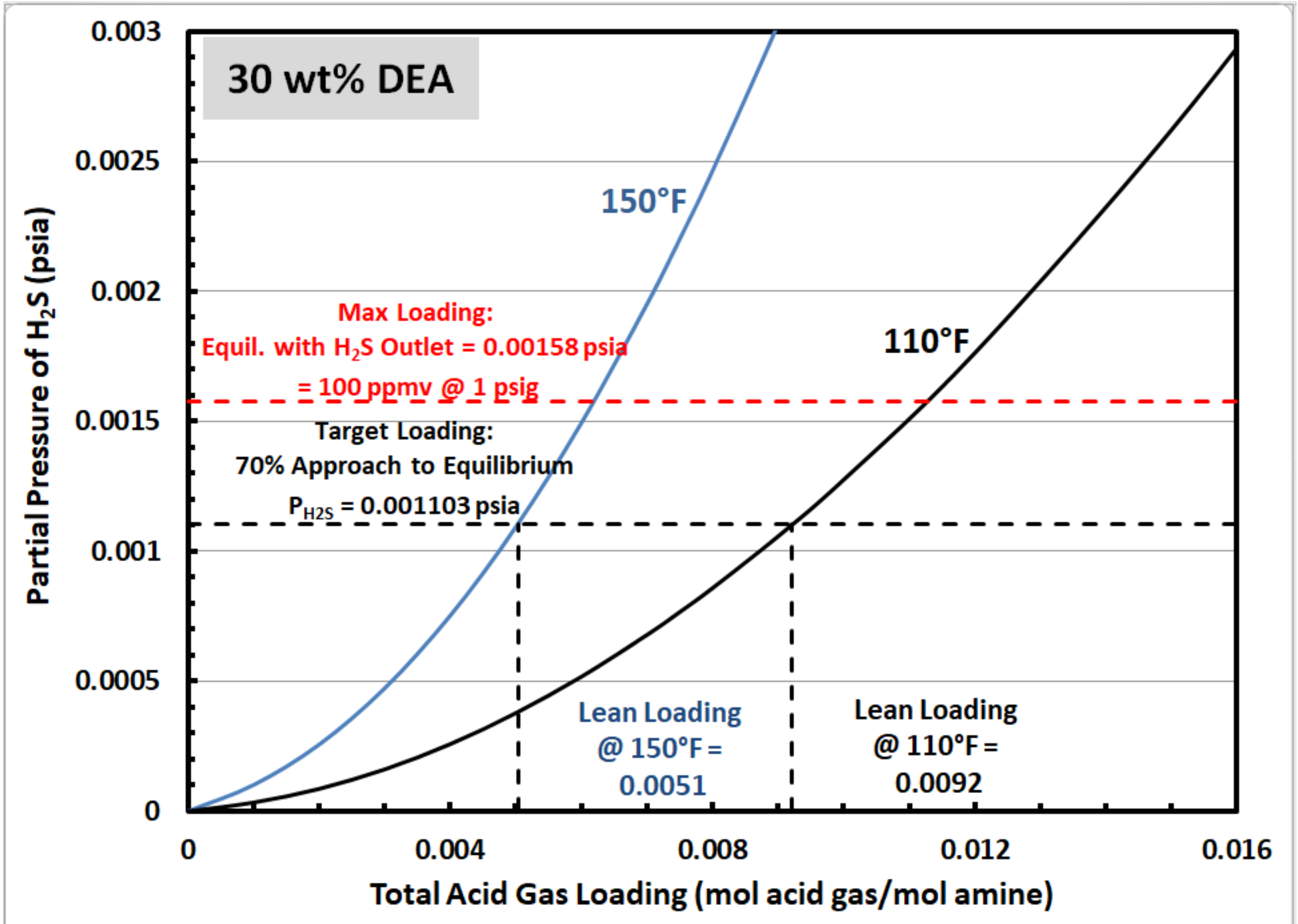
Example New Amine Contactor



Note 1: Either a device to impart flow (Venturi) or a liquid seal pot would be needed to force normal flow through the new amine contactor.

- Simple process
- No chemicals to purchase or dispose of
- Familiar process to operators
- Consider contaminants, VLE for treat ability

Example VLE for H_2S Treat



Caustic Scrubbing of Flare Gas

- NaOH scrubs H_2S and CO_2 from gas:

$$NaOH + H_2S \rightarrow NaHS + H_2O \quad (1)$$

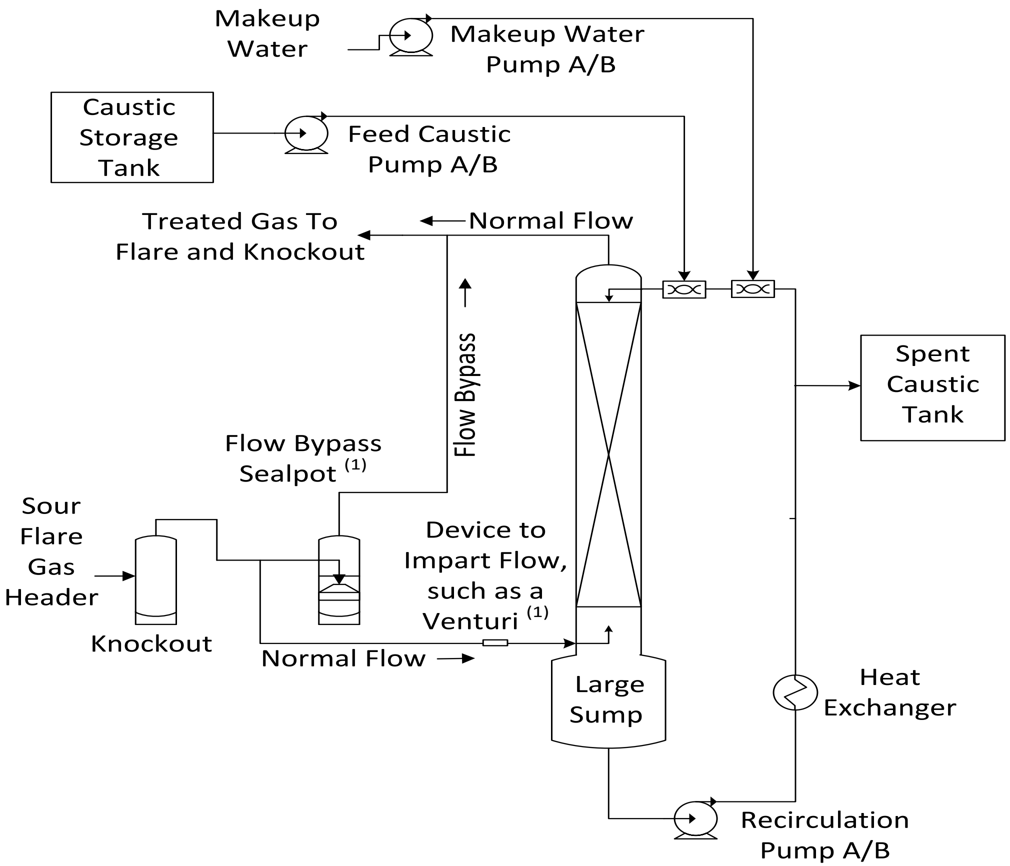
$$NaHS + NaOH \rightarrow Na_2S + H_2O \quad (2)$$

$$NaOH + CO_2 \rightarrow NaHCO_3 \quad (3)$$

$$NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O \quad (4)$$

- Packed/trayed towers used
- Concerns with caustic scrubbing:
  - Waste of caustic (due to CO_2 or high pH)
  - Salts precipitation
  - Blowdown volume and characteristics

Example Caustic Scrubber



Note 1: Either a device to impart flow (Venturi) or a liquid seal pot would be needed for force normal flow through the caustic scrubber.

- Inexpensive chemical
- Caustic often already present at refinery
- Simple process
- Automated chemical addition
- Many equipment variations

Important Gas Characteristics for Caustic Scrubbing

- Operating temperature and pressure:
  - High temperatures limit H_2S removal and result in special materials of construction
  - Low temperatures can result in salt precipitation
  - High pH used to achieve treat at low operating pressures of flare gas

Important Gas Characteristics for Caustic Scrubbing

- Other gas constituents:
  - CO_2 removal not needed and wastes caustic
  - Some organic sulfur, NH_3, and aromatics absorbed
- Refinery factors:
  - Consider pipe lengths between scrubber and existing tankage
  - Available dP dictates type of equipment used

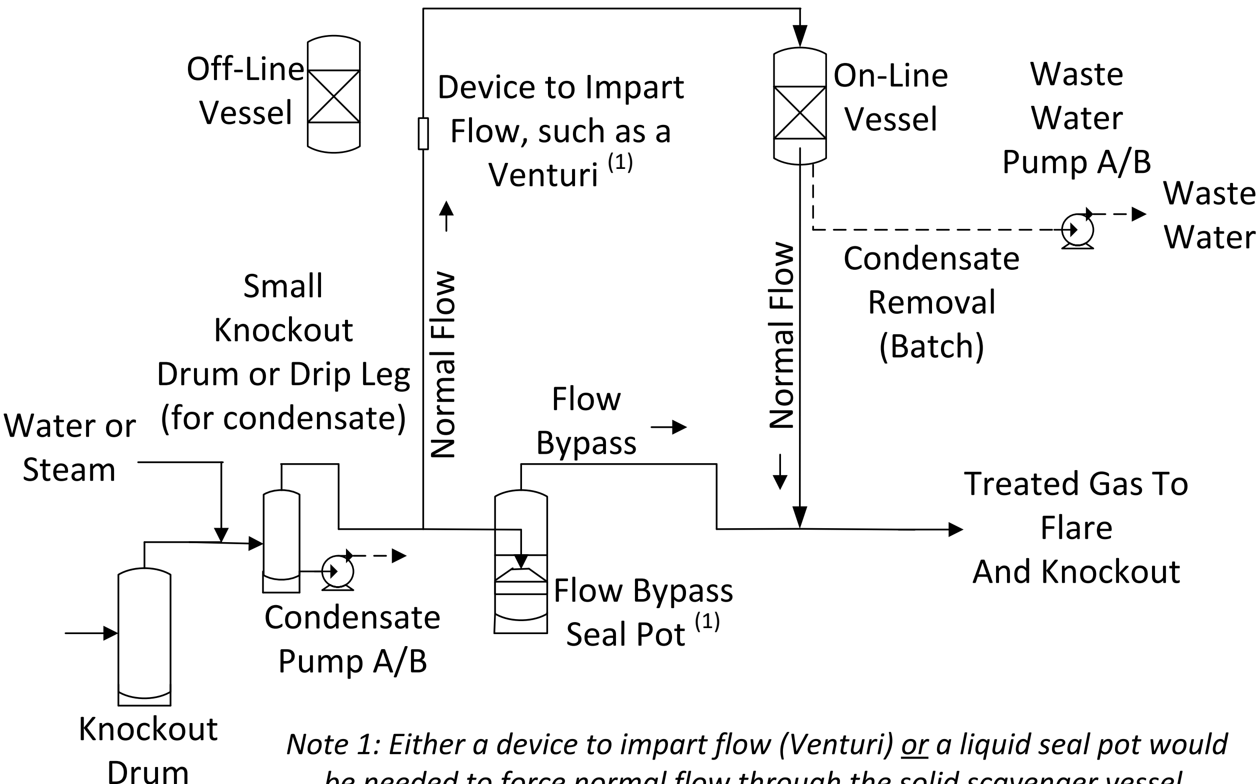
Solid Scavenging of Flare Gas

- Non-regenerable solids react with H_2S
- Iron oxide is a common scavenger material
- Desired reaction:

$$3\ H_2S + H_2O + Fe_2O_3 \rightarrow Fe_2S_3 + 4\ H_2O \qquad (5)$$

- Iron oxide is granular solid or supported on inert, non-flammable substrate
- Two vessels commonly used (one operating, one spare)

Example Solid Scavenger System



Note 1: Either a device to impart flow (Venturi) or a liquid seal pot would be needed to force normal flow through the solid scavenger vessel.

- Simple process
- Low operator attention
- Media change-out
- Nonhazardous media (unless hazardous gas component adsorbed)

Important Gas Characteristics for Solid Scavenging

- Sulfur load: usually used below ~0.4 LTPD due to high cost of scavenger material
- Operating temperature and pressure:
  - Media performance decreases below 45-50F
  - Temperatures up to 200F extend life of media
  - No significant impact of operating pressure (vessel size changed to give same residence time regardless of pressure)

Important Gas Characteristics for Solid Scavenging

- Other gas constituents:
  - Saturate gas with water to extend iron-oxide life
  - One vendor cannot guarantee removal with >10 % H_2; another claims no effect / has high H_2 refinery application in operation
  - Oxygen speeds up reaction and increases capacity, but may complicate media removal
  - High H_2S & O_2 give high H_2S heat of reaction
- Refinery factors: very low pressure drop can be achieved

Liquid Scavenging of Flare Gas

- Different liquid H_2S scavengers available
- Triazine commonly used
- Triazine makes water-soluble products w/ H_2S, if not over spent
- Spent solution typically 100% liquid (solids form if over spent)
- Loadings range from 0.5 lb/gal to 2-3 lb/gal
- Direct injection is common (batch also possible)

Important Gas Characteristics for Liquid Scavenging

- Sulfur load: used < 0.1 LTPD due to high chemical cost

- Operating temperature and pressure:
  - Temperatures of 60-120F typical
  - Low T = slow kinetics
  - High T = decompose
  - H_2S removal difficult at low P

Important Gas Characteristics for Liquid Scavenging

- Other gas constituents:
  - Water addition if gas not saturated
  - Triazine reacts selectively with H_2S
- Refinery Factors:
  - Flow changes impact removal with direct injection
  - Atomizing agent important
  - Odor and WWTP issues (biocide)

Summary Tables

	Typical Sulfur Load	Other Flare Gas Components	Temp. Impacts	Operating Pressure Impact	Other Factors
Amine	**All**: Economics Favored at High Loads	**O_2**: Degrade amine	**High T**: Limits Treat	**Low P**: Limits Treat	Piping runs for amine.
Caustic	**All**: Economics Favored at Low (0.1 – 1 LTPD)	**CO_2, other S**: Consume Caustic **NH_3**: Odor	**High T**: Limits Treat, Materials issues **Low T**: Salts	Negligible	Piping/tanks for caustic.
Solid Scavengers	**Low:** < 0.4 LTPD	**O_2:** Heat-up **H_2:** Performance **H_2O:** Saturated Gas Recommended	45 – 200 F recommended for performance	Negligible	Limited piping, simple system.
Liquid Scavengers	**Low:** < 0.1 LTPD	**H_2O:** Saturated Gas Recommended	**Typical**: 60 – 120 F **High T**: Degrade **Low T**: Slow Kinetics	**Low P**: Limits Treat	Easy to Implement (Direct Injection).

Conclusions

- Typical sulfur loads: 0.1 LTPD to much greater
- Impact of operating temperature, pressure, and other gas constituents varies greatly
- Need to establish representative design basis over wide range of conditions
- Factors give refiners better sense of flare gas information needed to select H_2S treating system

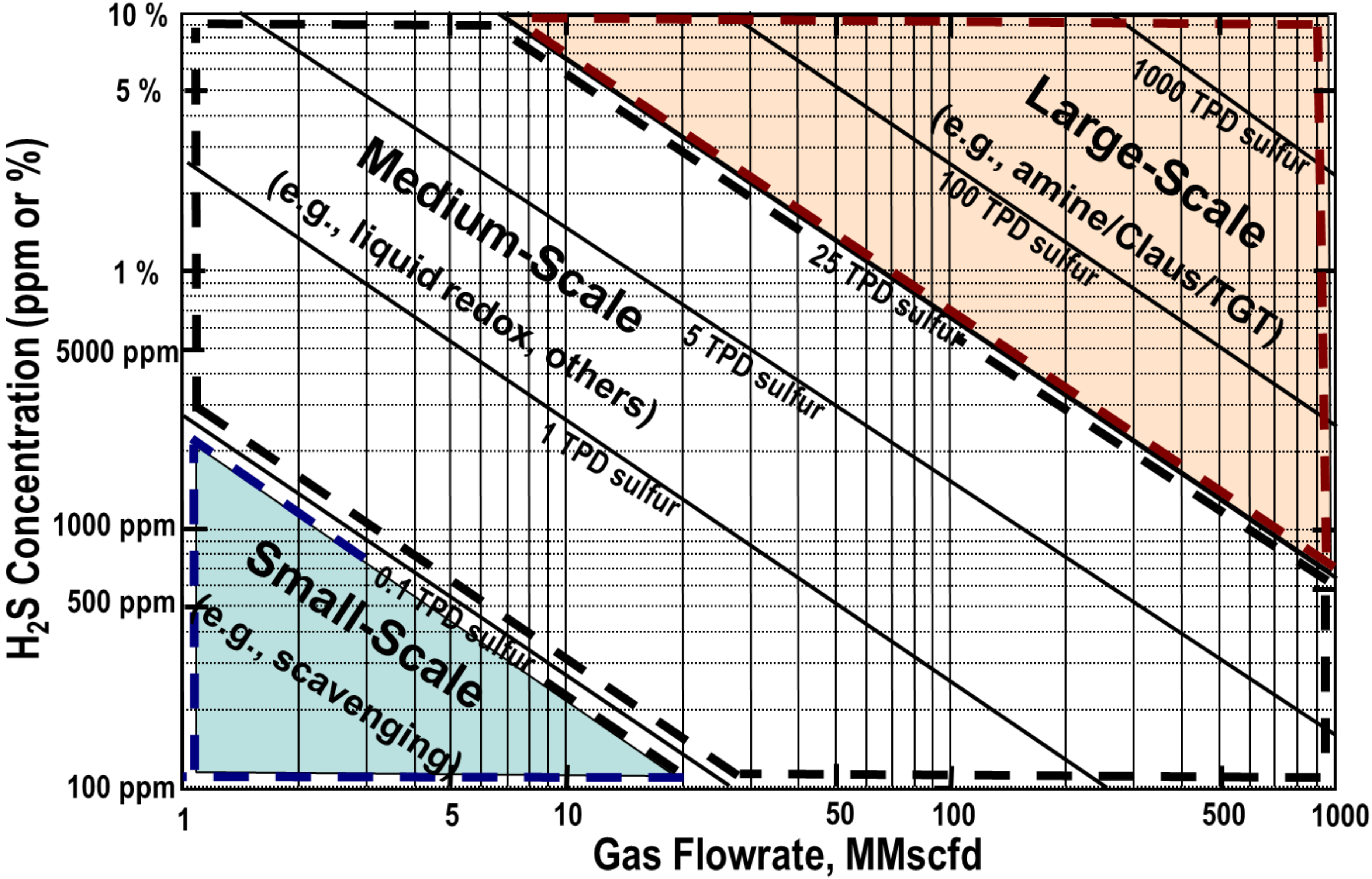
Questions

Thank you

- Contact Information:
  - darshan.sachde@trimeric.com
  - www.trimeric.com

Background on H_2S Removal & Sulfur Recovery Niches

- Technology niches for H_2S removal
  - Large-scale niche – over ~20 LTPD of sulfur (amine/Claus/TGT process common)
  - Medium-scale niche – ~0.1 to ~20 LTPD sulfur (amine/Claus, liquid redox, other regenerable liquid chemical processes common)
  - Small-scale niche – less than ~0.1 LTPD sulfur (nonregenerable liquid or solid chemicals common)
- Size refers to amount of sulfur, not gas rate
- Niches assume new build and continuous operation (temporary or standby service favors nonregenerables)



Niches are guidelines only; technologies should be evaluated on a case-by-case basis because feed gas conditions, treatment goals, and other parameters can impact technology selection.