GPA MIDSTREAM ASSOCIATION

100TH ANNIVERSARY

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Sulfur Storage and Handling

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2021 GPA Midstream Convention

Sour Gas and Sulfur Symposium

September 29, 2021

Presentation Overview

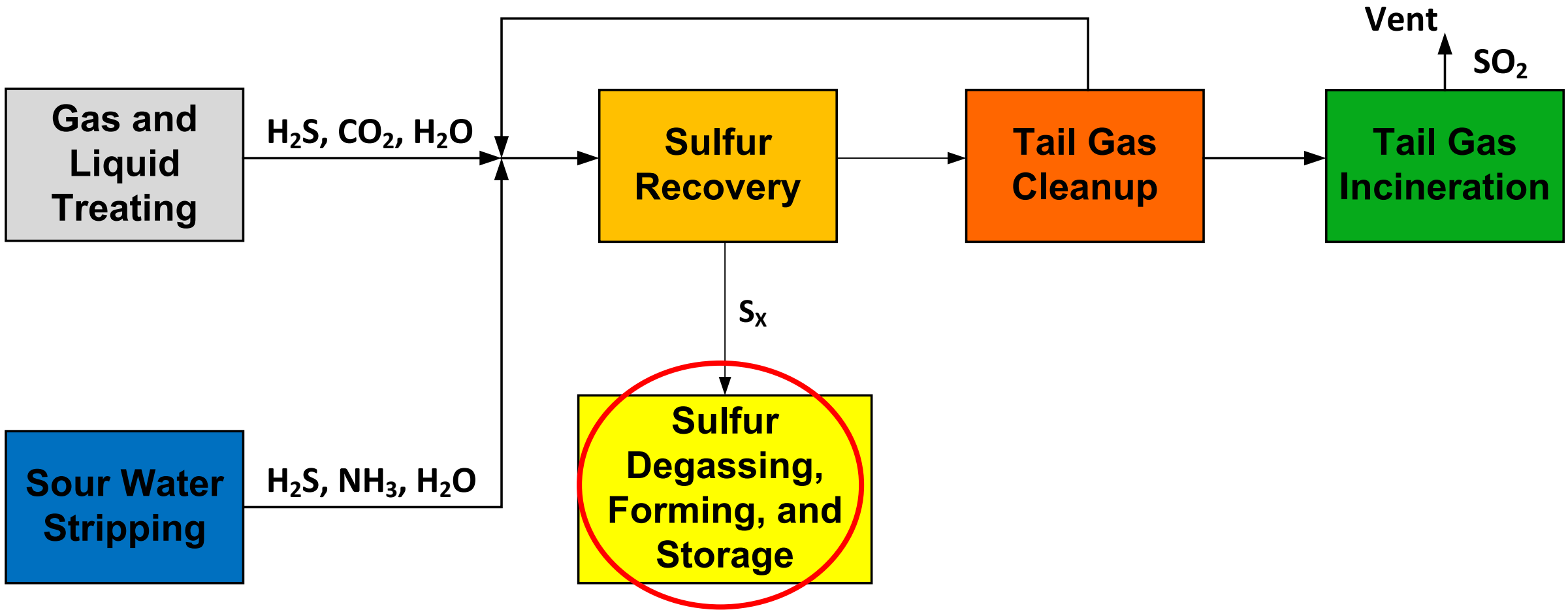
- Overview of Sulfur Handling and Storage
- Properties of Molten Sulfur
- Design and Safety
  - Sulfur Storage and Handling Systems
- Sulfur Degassing
- Summary

Overview of Sulfur Handling and Storage

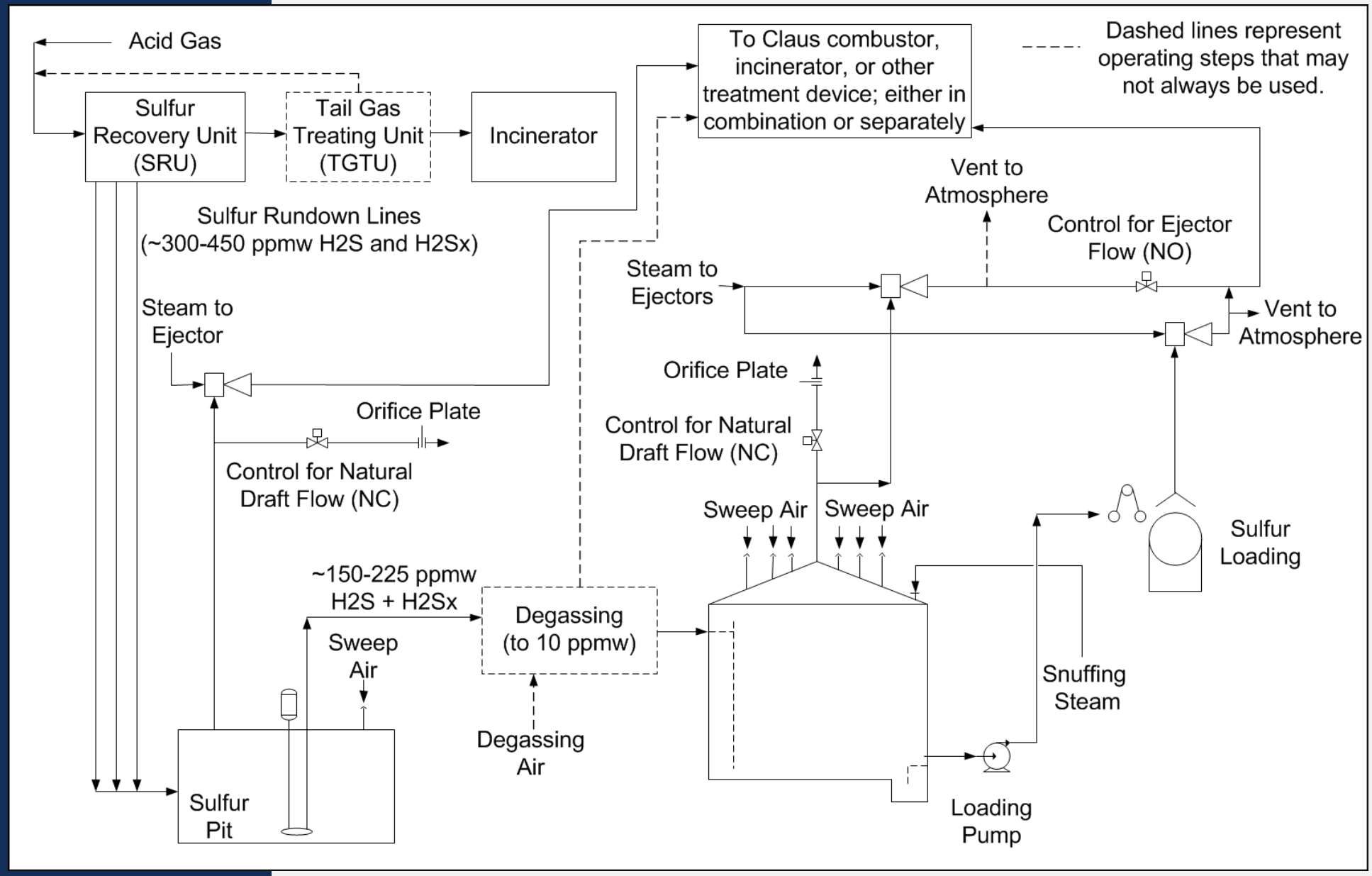
Overview of Sulfur Handling and Storage

- Goal: Safe storage and handling of sulfur
  - Maintain molten sulfur conditions to:
    - Minimize/limit emissions & exposure to H_2S, SO_2
    - Prevent fire/explosive conditions in vapor space
    - Allow reliable transport and loading of sulfur (prevent plugging, freezing, etc.)
  - Incorporate knowledge into system design and operations

Sulfur Recovery Schematic



Generic Molten Sulfur Handling Process



Hazards of Sulfur Handling and Storage

- Molten Sulfur from SRU contains residual H_2S
  - ~300 - 450 ppmw H_2S (H_2S + H_2S_x) leaving SRU
- SO_2 forms when sulfur is exposed to O_2:
  - Air sweep in storage (pits, tanks)
  - Degassing can *increase* SO_2
- H_2S & SO_2 Hazards
  - Toxic (potentially lethal)
  - Fires, explosions, even pyrophoric (FeS)
  - Corrosive in presence of water
- Sulfur properties create narrow operating windows

Sulfur Properties

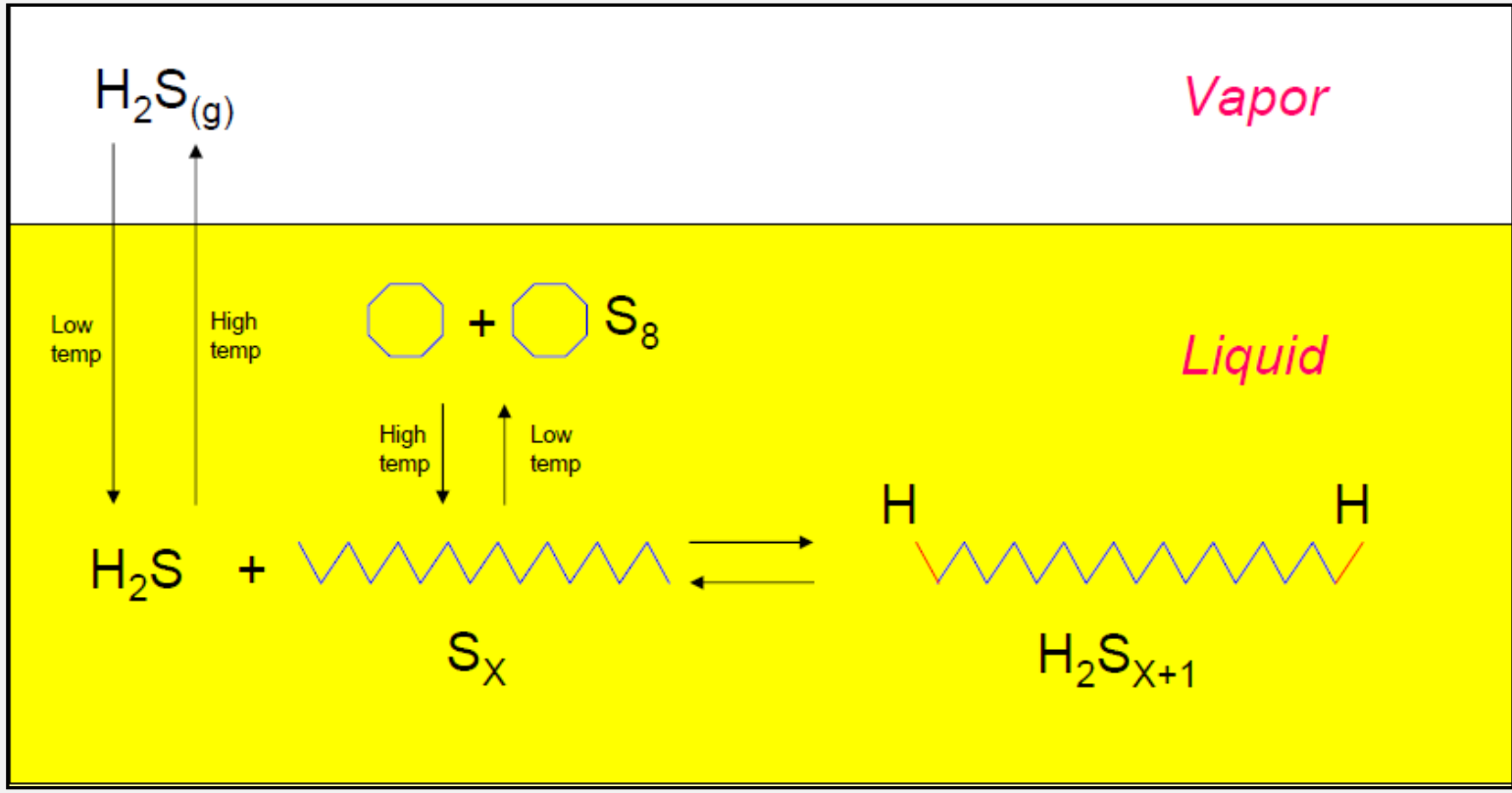
Impacts on Sulfur Handling

Sulfur Property or Characteristic	Impact/Hazard
Viscosity	Difficulty pumping/handling
H_2S Solubility	EHS Risks, explosions, impact on other properties
Melting/Freezing Point	Plugging Equipment, Expansion/rupture of pipes upon re-heat
Flash Point	Fire in presence of ignition source
Autoignition T	Spontaneous combustion in air
Electrical Insulator	Static discharge/ignition/explosions

- Properties are a function of operating conditions
  - Especially **temperature**

Composition of "Sulfur"

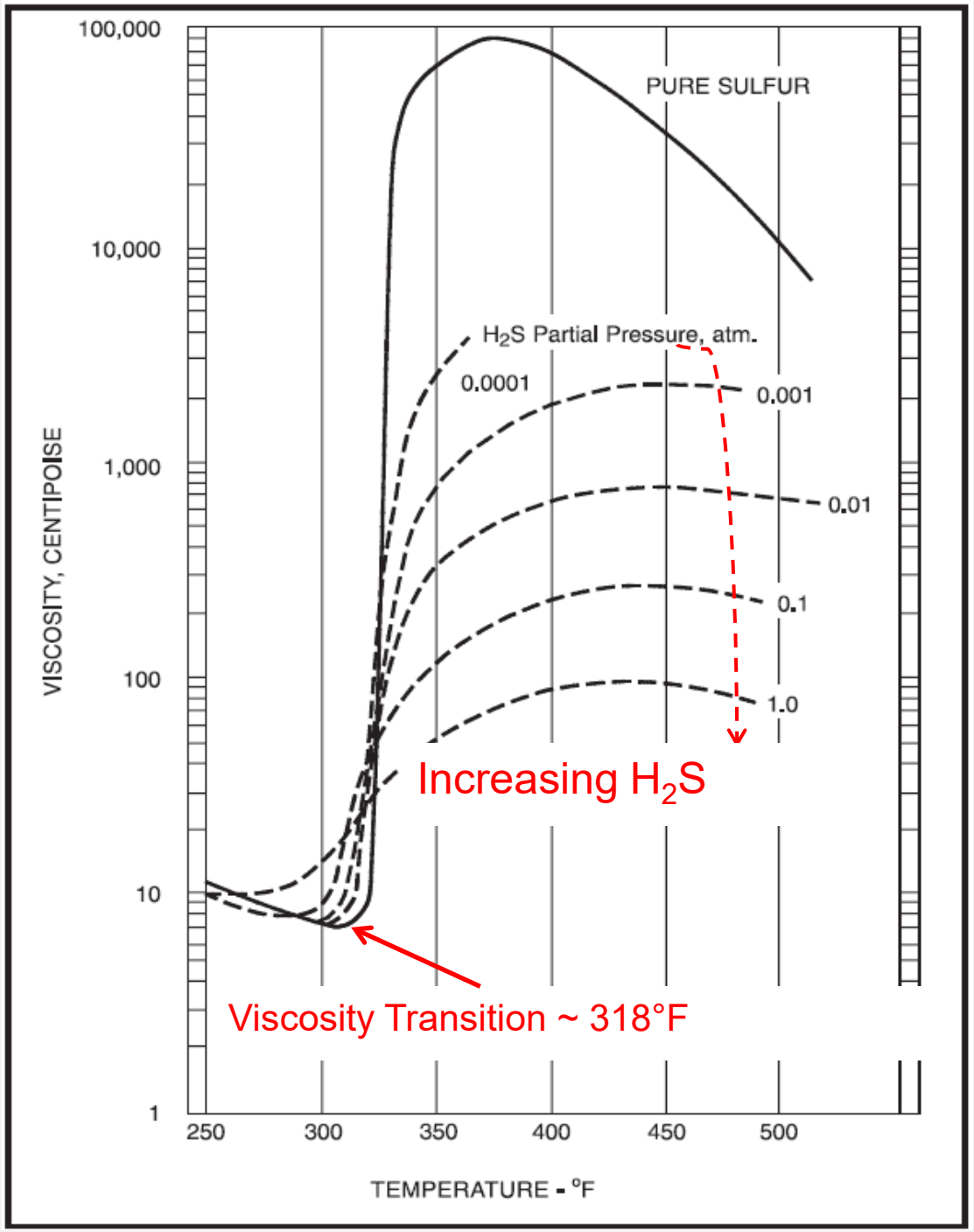
- Sulfur present as S_8 rings and S_x polymeric chains
- H_2S present as dissolved H_2S and H_2S_x
- Composition is a function of operating conditions
  - Especially **temperature**



Source: 2007 LRGCC Fundamentals

Unusual Properties of Sulfur

- Viscosity:
  - Non-monotonic with temperature (see figure)
- H_2S Solubility:
  - Total H_2S solubility ***increases*** with temperature (H_2S_x forms)

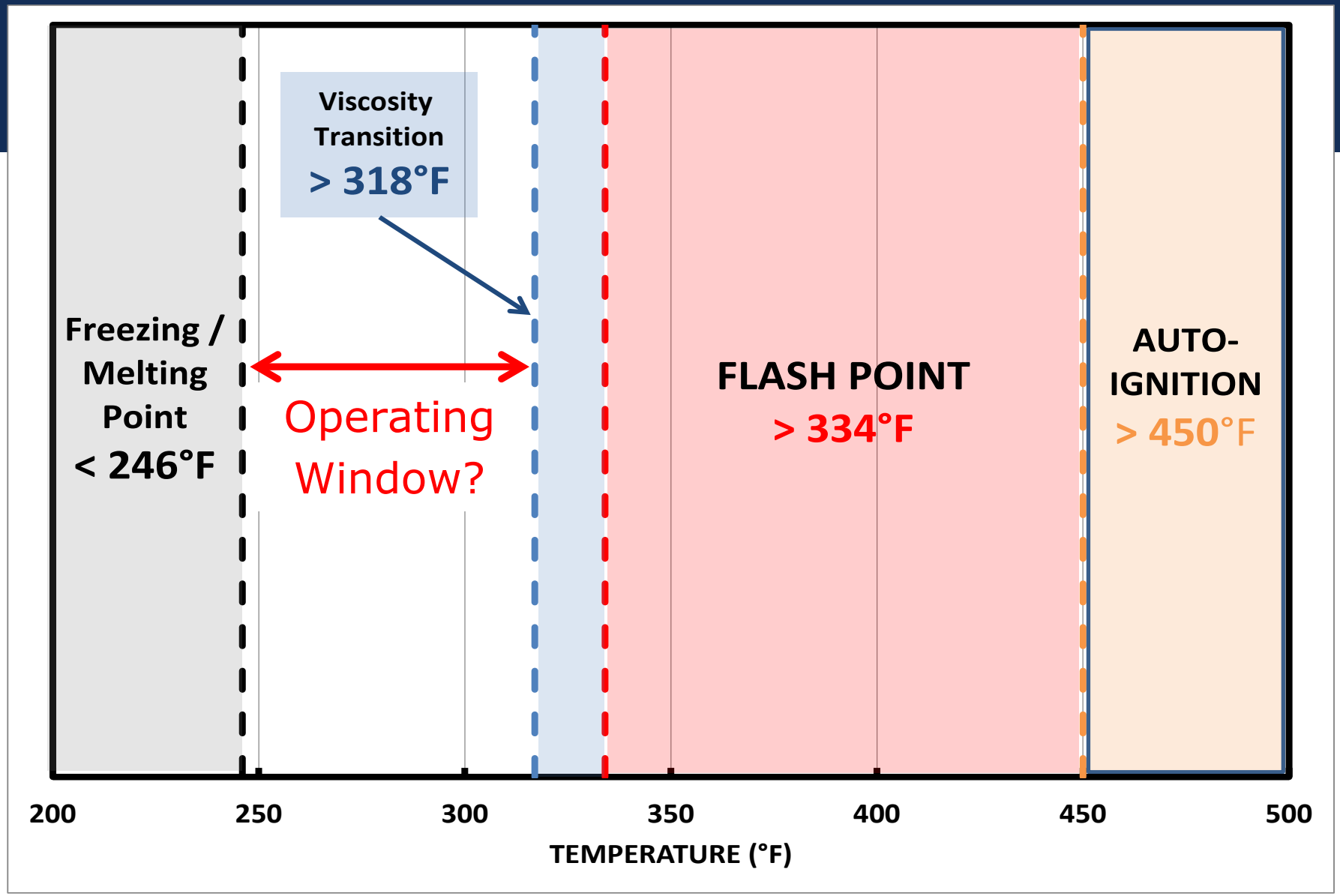


Source: GPSA Databook 13th Edition

Property Values Vary

Property or Characteristic	Range	Explanation
Melting/Freezing Point	Low: 238°F High: 246°F	<u>Different Sulfur Crystals</u>: Low Value = π-Sulfur High Value = Monoclinic (β) Sulfur
Flash Point	Low: 334°F High: 405°F	Different Experimental Methods Different Data Sources
Autoignition T	Low: 450°F High: 511°F	Different Experimental Methods Different Data Sources

- When in Doubt – Choose Conservatively

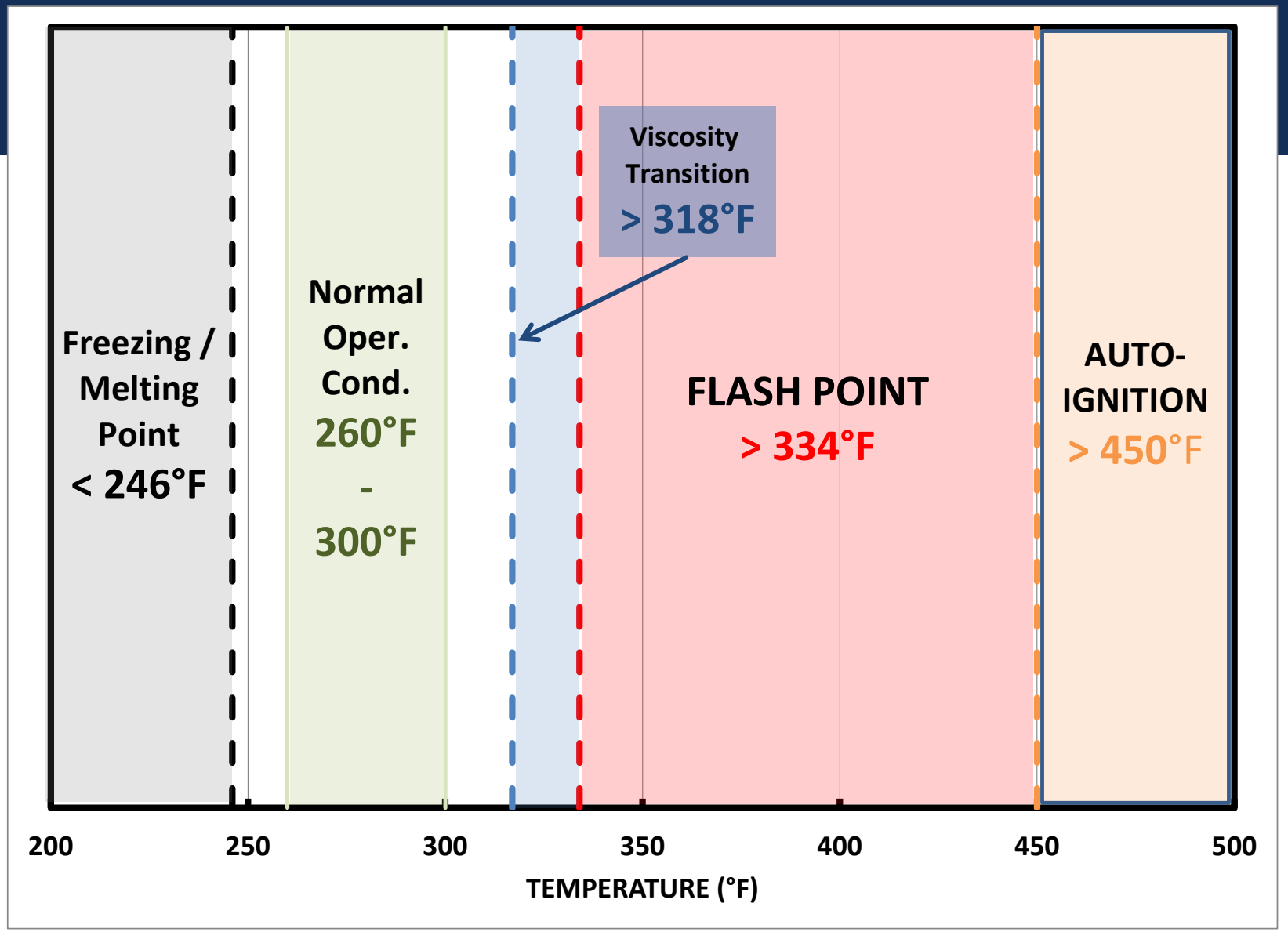

Viscosity Transition
> 318°F
Freezing / Melting Point
< 246°F
Operating Window?
FLASH POINT
> 334°F
AUTO-IGNITION
> 450°F
200
250
300
350
400
450
500
TEMPERATURE (°F)

Other Temperature Concerns

- Higher T = Higher Sulfur Vapor Pressure
- NFPA 655
  - Above 309°F, deflagration vents and other requirements
- Sulfur Pit Fires below Flash Point[1]:
  - Refiner observed persistent fires in pit
  - Tank Operating T = 315 - 320°F
  - Many changes to reduce static discharge, etc. (no luck)
  - Fires only eliminated when operating T reduced to < 300°F

1: Brimstone 2014: "Molten Sulfur Reliability Issues and Solutions"

- Lesson: Warmer is only better to a point

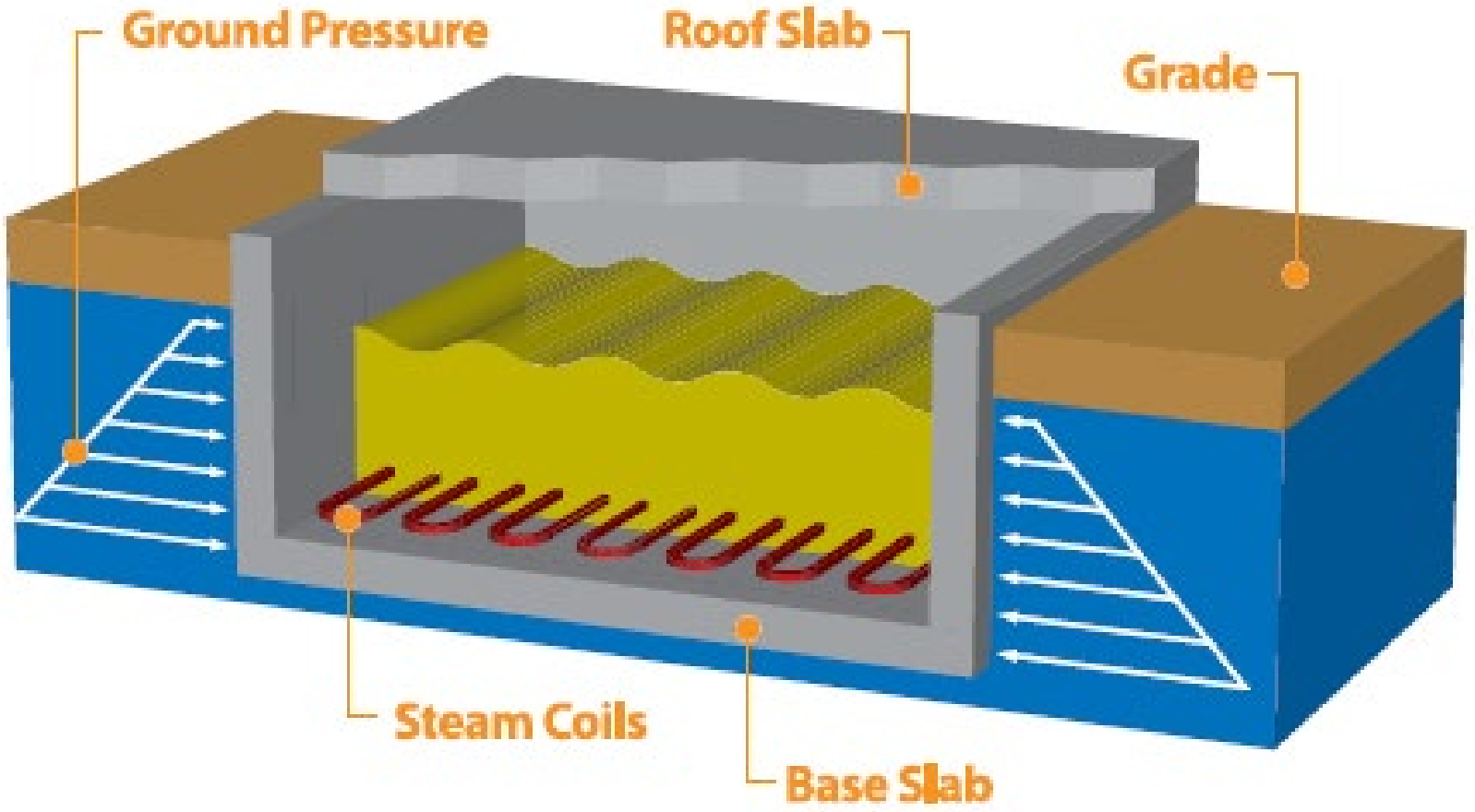

Freezing / Melting Point
< 246°F
Normal Oper. Cond.
260°F
-
300°F
Viscosity Transition
> 318°F
FLASH POINT
> 334°F
AUTO-IGNITION
> 450°F
200
250
300
350
400
450
500
TEMPERATURE (°F)

Design and Safety

Sulfur Collection: Sulfur Pits and Vessels

- Gravity drain sulfur from sulfur recovery unit (SRU)
  - Storage will be below grade – sloped rundown to storage
  - Sulfur sealing device to prevent process gas from entering storage
- Storage Capacity should account for worst case shipping scenario
  - Typical: 1 – 5 days production
  - Preferred: 5 – 10 days production
  - Capacity can be split with above-ground storage tank
- A collection “header” with limited surge capacity is an alternative

Molten Sulfur Pit



Sulfur Collection: Sulfur Pits and Vessels

Sulfur Pit

- In-ground concrete structure
- Operates at slight vacuum
- Air sweep
  - Maintain pit headspace below 25% LEL of H_2S @ design T
- Challenges:
  - Water intrusion
  - Corrosion

Collection Vessel

- Steel vessel in concrete sump
- Can be a pressure vessel
  - Withstand deflagrations
  - No sweep system
- Challenges:
  - Typically less capacity than pits

Molten Sulfur Tank

- Above-Ground Carbon Steel Tank
  - Buffer Storage Capacity for Loading
  - API-650 Tank Specification
- Key Design Elements:
  - Common: Internal heating with steam coils
    - Multiple parallel coils (redundancy)
  - Newer / better: External heating via ControTrace Panels
    - No risk of internal steam leaks (corrosion, etc.)
  - All attachments to tank: Heat-traced/insulated
  - Headspace sweep system to prevent explosions (covered later)

ControTrace Panels

Molten Sulfur Tank Sweep

- Goal: Headspace < 25% of LEL for H_2S (3 vol % H_2S @ 330°F)
- If tank headspace stagnant:

Total H_2S in Sulfur	Temperature	H_2S in Vapor Space	Notes
ppmw H_2S +H_2S_x	F	vol%	
300	300	29.7	> LEL for H_2S
300	280	40.5	> LEL for H_2S
150	300	14	> LEL for H_2S
150	280	20.4	> LEL for H_2S
50	300	4.3	> LEL for H_2S
50	280	6.9	> LEL for H_2S
10	300	0.7	Degassed Sulfur. Lethal H_2S levels.
10	280	1.4	Degassed Sulfur, > 25% of LEL of H_2S

Source: 2000 LRGCC Fundamentals

Sweep Air vs. Inert Purge

	Air	Inert
Flammability	Introduces O_2 = risk for ignition.	No air present.
Explosion Risk	Adequate sweep air (H_2S < 25% of LEL) should mitigate risk.	FeS formation in reducing environment. **Exposure to Air = Pyrophoric**
Tank Pressure	Slight vacuum. Limit H_2S venting.	Cannot be exposed to ambient air. Operates under positive pressure.
Cost	Readily available. Some cost if heated.	Tie into existing system or add new source of inert gas.

Both are used, but air is best practice

Molten Sulfur Piping

- Vapor Piping:
  - Ejector should be high point of system if possible
  - Gravity drain back to source (tank/pit) or to vapor destination (e.g., incinerator)
  - Steam-jacketed or Contro-traced
- Liquid Sulfur Piping:
  - Avoid elbows and tees (Flanged crosses allow rodding of pipe)
  - Tank external piping: Steam-jacketed or Contro-Traced
  - Tank-internal piping: Heated

Molten Sulfur Loading

https://www.opwglobal.com/products/

- Key Design Features:
  - Vapor recovery
  - Grounding to prevent discharge
  - Limit sulfur velocity & free-fall distance
  - Jacketing/heating of lines
  - Measurement: Coriolis, weigh scales

Sulfur Degassing

How do you degas sulfur?

- Mechanisms and Principles of Degassing:
  - Convert H_2S_x to H_2S (dissolved) – shift equilibrium
    - Low T favors decomposition of H_2S_x
    - Oxygen – mass transfer of oxygen to liquid phase
    - Catalysts (liquid or solid)
  - H_2S evolution to gas phase
  - Remove gas phase H_2S to maintain driving force
  - Good surface to bulk mixing of sulfur (e.g., mechanical agitation of sulfur)

- Goal: Total H_2S in molten S $\leq$ 10 ppmw

Degassing Technologies

Technology	Features					
	Sparge Gas	**Elevated Pressure?**	**Catalyst**	**Agitation**	**External or In-Pit**	**Field Experience**
Shell Process	Air	Yes (external), No (In-pit)	None	Sparging	Both	300+ Applications
Fluor D'GAASS	Air	Yes	None	Contactor	External	100+ Applications
Hyspec Process	Air	No	Liquid	Mechanical + Sparging	External	20+ years
Aquisulf/SNEA	None	No	Liquid	Mechanical	In-Pit	80+ Applications
CSI ICOn	Steam, Air, N_2, Claus tail gas	No	Solid	Sparging	External	Recent Commercial
Exxon/Worley Parsons	Air	No	Liquid	Sparging	In-Pit	Significant

Others: Sandvik DG, Siirtec Nigi, B&V MAG, BP Amoco

Other Considerations

- Integration and Operation Challenges
  - Vent gas handling – corrosive, prone to plugging, EHS risks (SO_2)
  - Pit modifications (often not possible) or plot space nearby pit
  - Continuous degassing vs. intermittent sulfur transfer
  - Contingency if degassing is OOS
- Safety Considerations
  - Generates additional SO_2
  - H_2S can still accumulate to dangerous levels

Summary

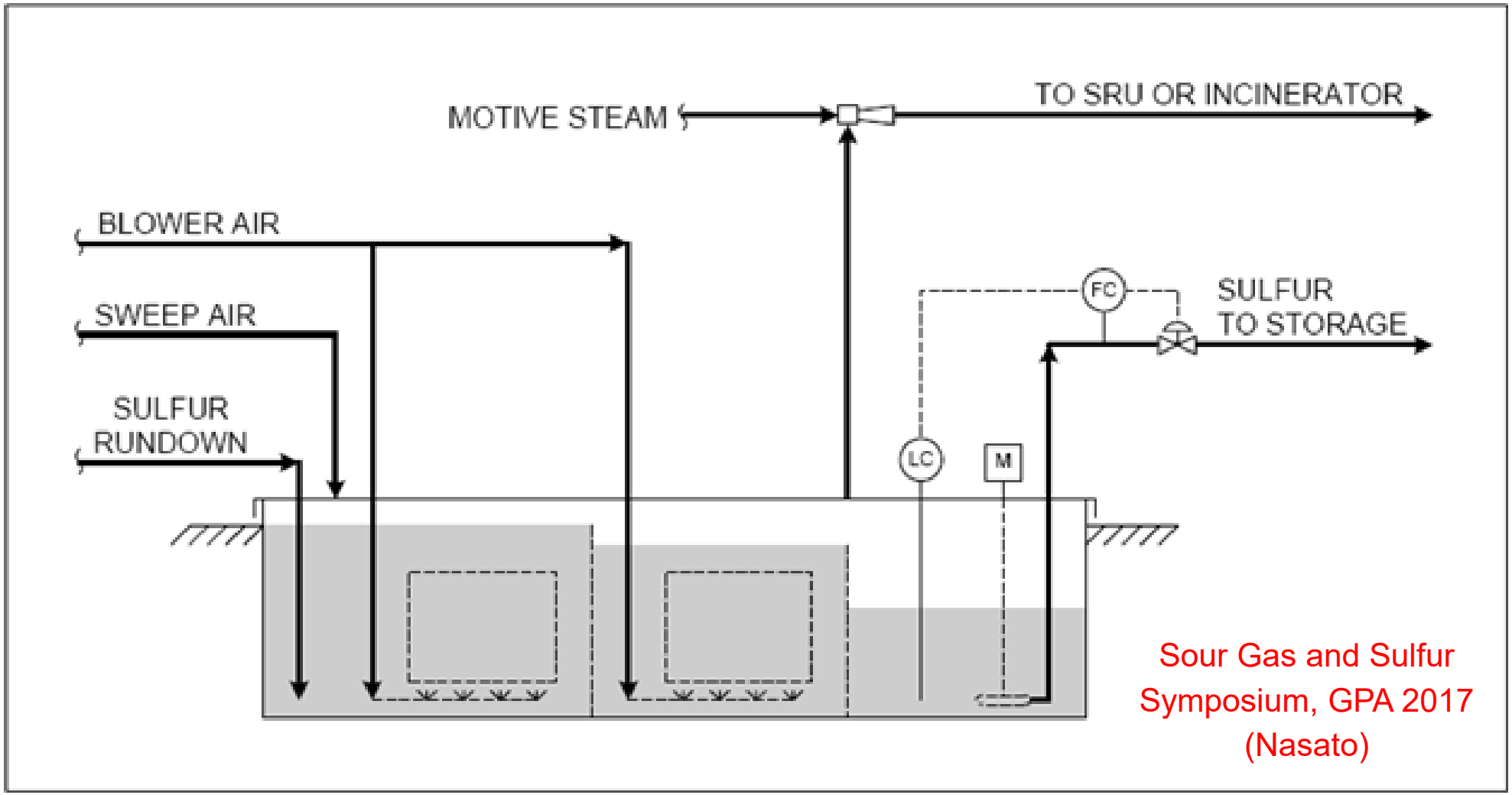
Summary

- Molten sulfur properties present unique challenges for storage and handling
- Many design and safety features needed
  - More than one approach is used in industry
  - Design and safe operations will be site specific
- Sulfur degassing technology provides EHS benefits
  - Lots of innovation and options
  - Degassing is not a silver bullet for safety
  - Entire sulfur production & handling process, from SRU to sulfur product, should be considered
- Other topics to consider:
  - Sulfur loading (train, truck, barge)
  - Sulfur prilling, forming, etc.
  - Sulfur product quality
  - Each area is as specialized as those covered in this talk

Questions?

Degassing Technologies: In-pit Air Sparging

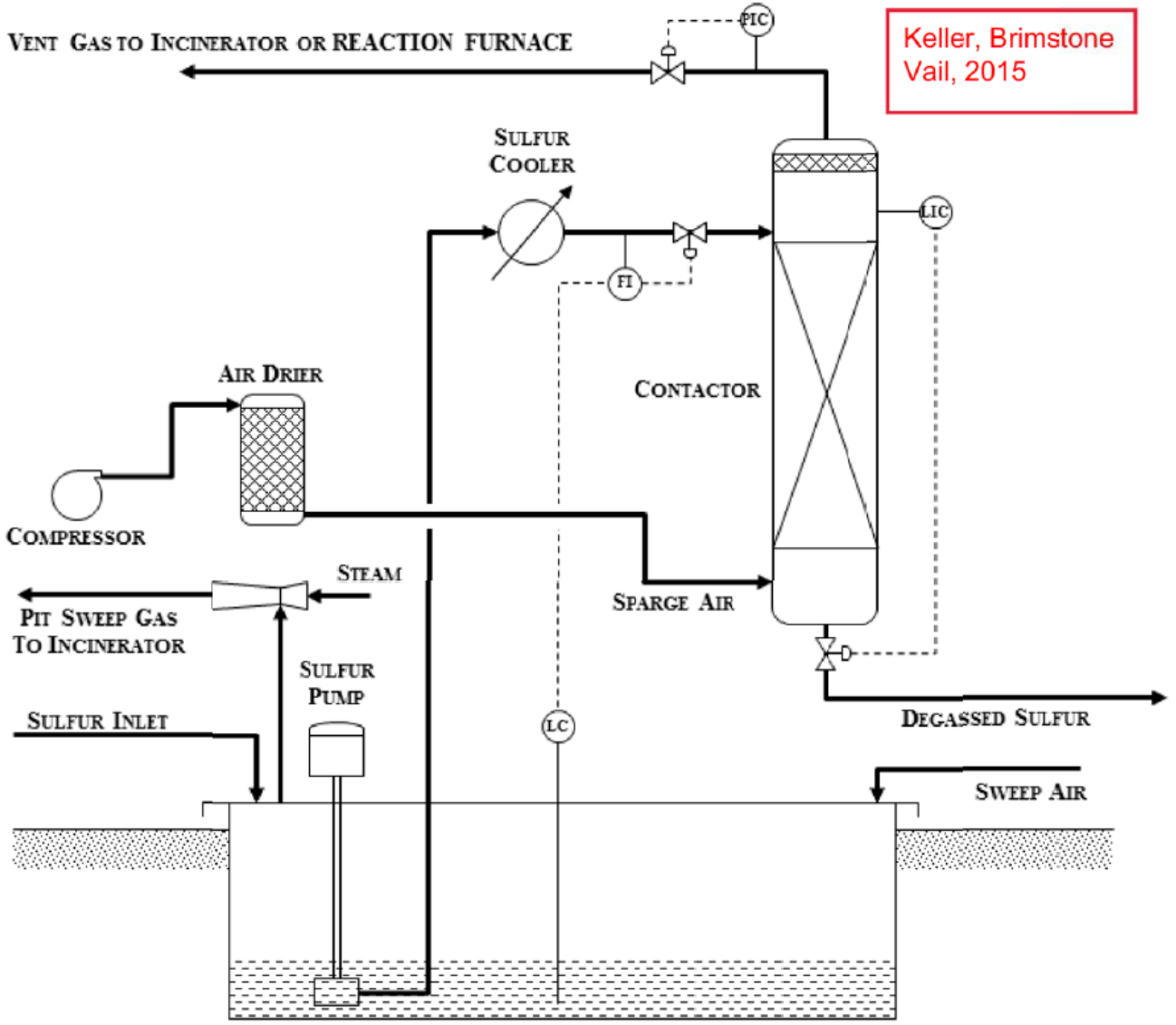
Shell Process



Sour Gas and Sulfur Symposium, GPA 2017 (Nasato)

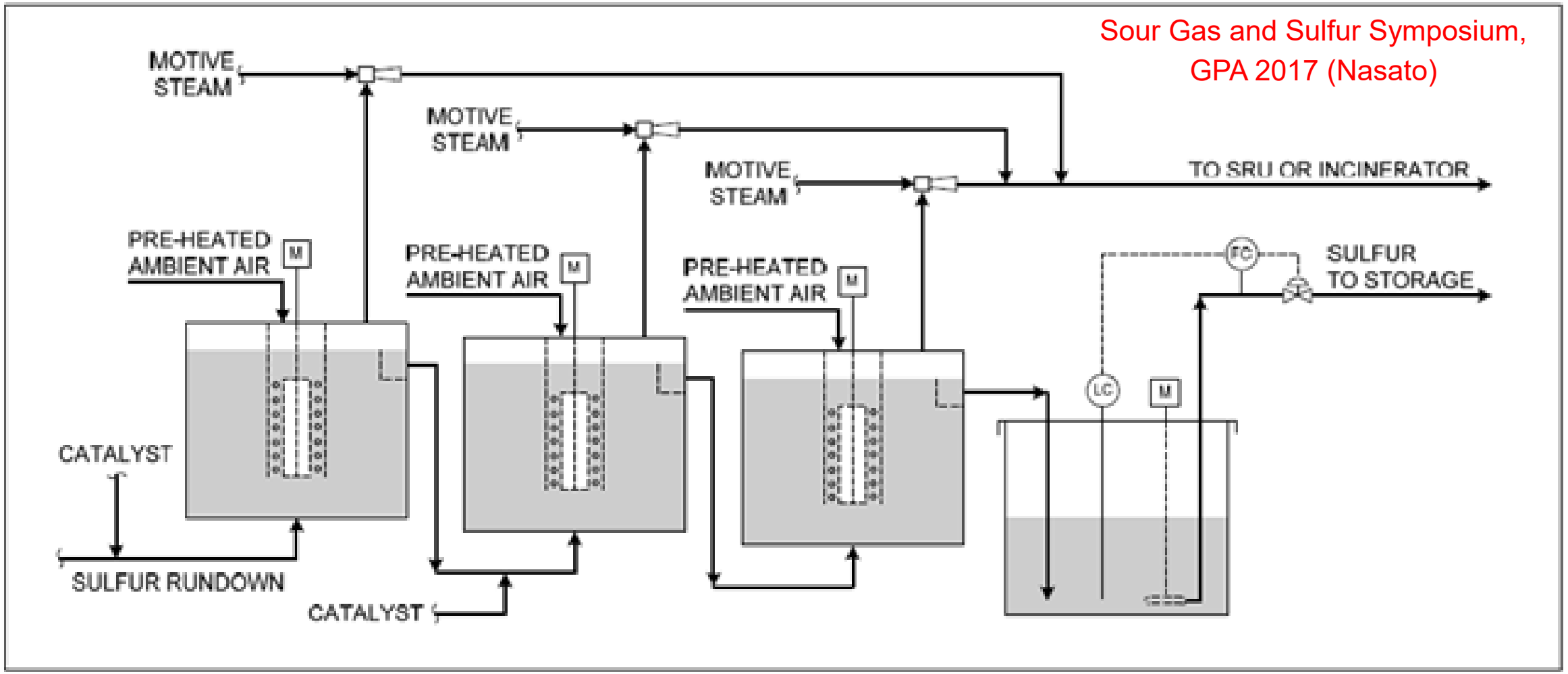
Degassing Technologies: External, Elevated P

Fluor D'GAASS



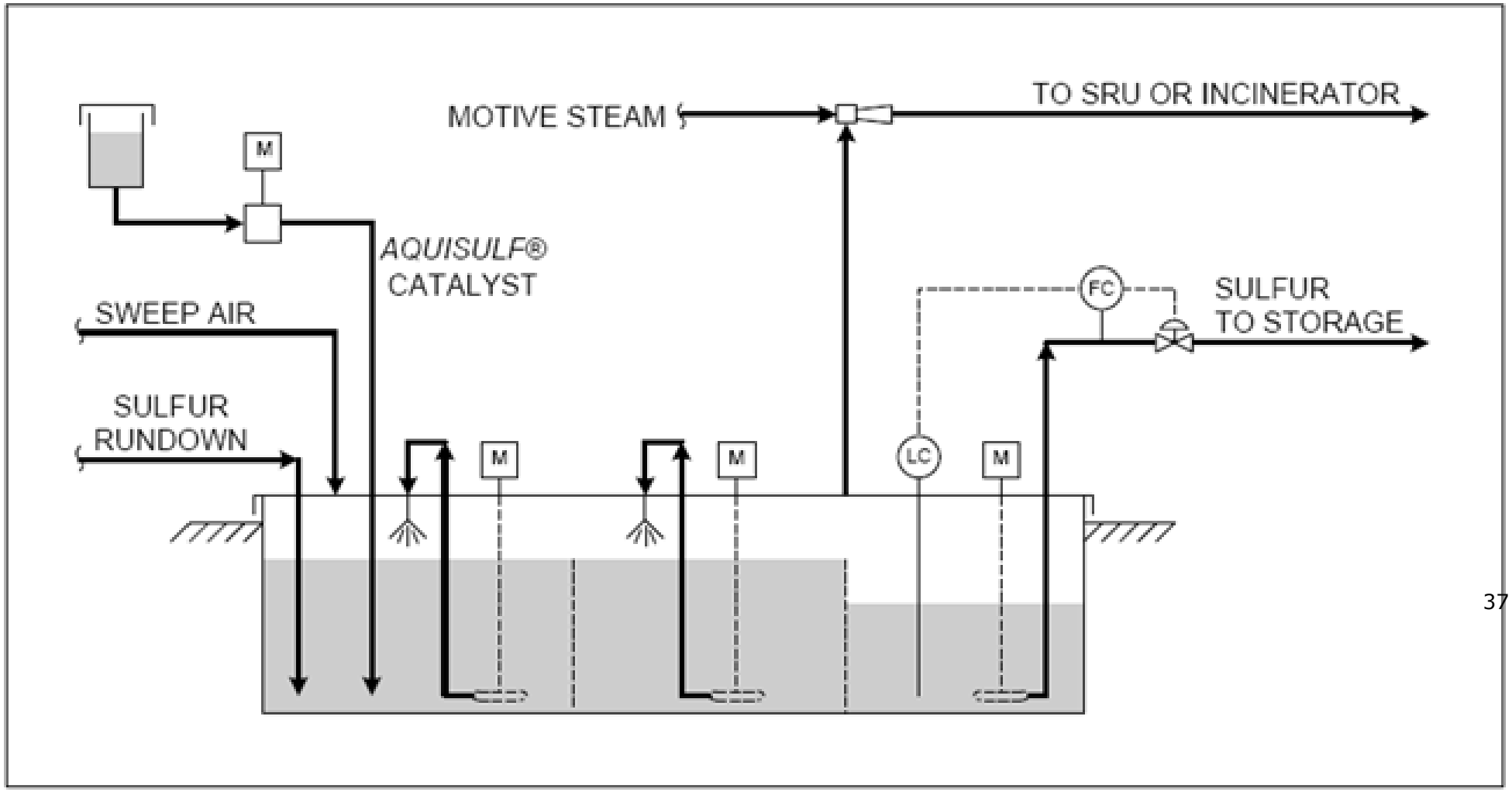
Degassing Technologies: Mechanical Agitation

Hyspec



Degassing Technologies: Proprietary Catalyst, No sparge

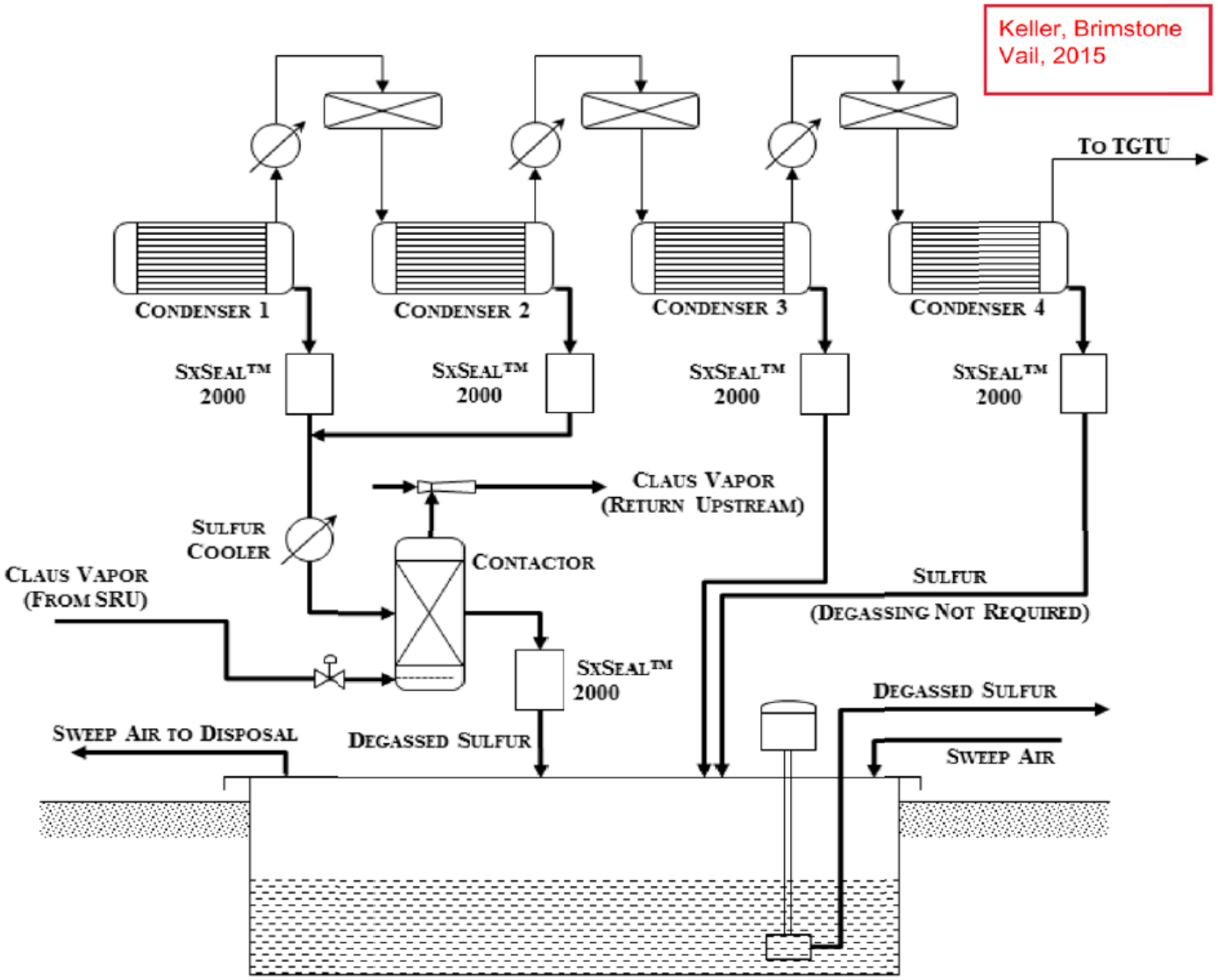
Aquisulf / SNEA / Lurgi



Aquisulf (Lurgi)

Degassing Technologies: Multiple Options

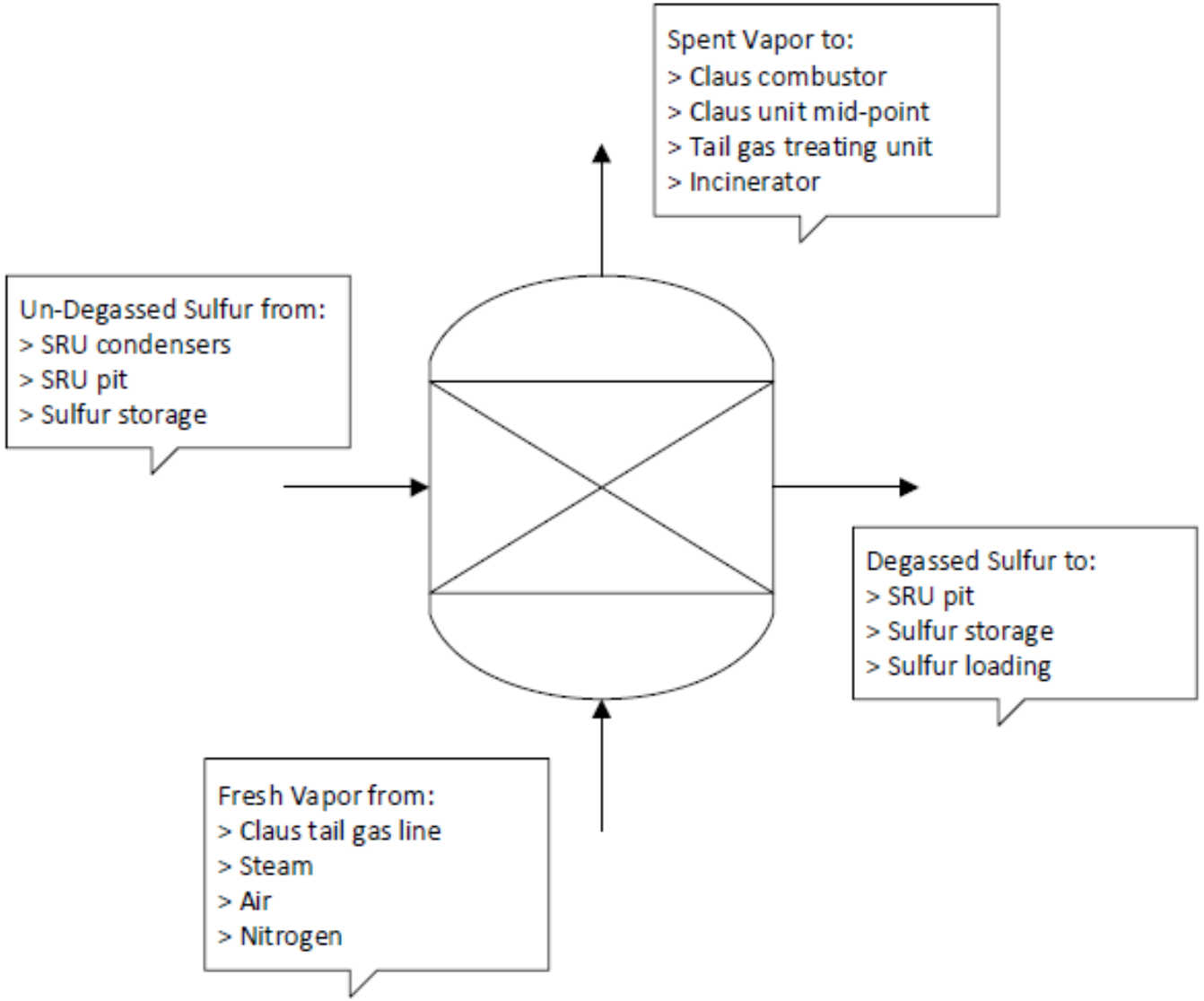
CSI ICOn



Degassing Technologies: Multiple Options

CSI ICOn:

Many Configurations and Process Options

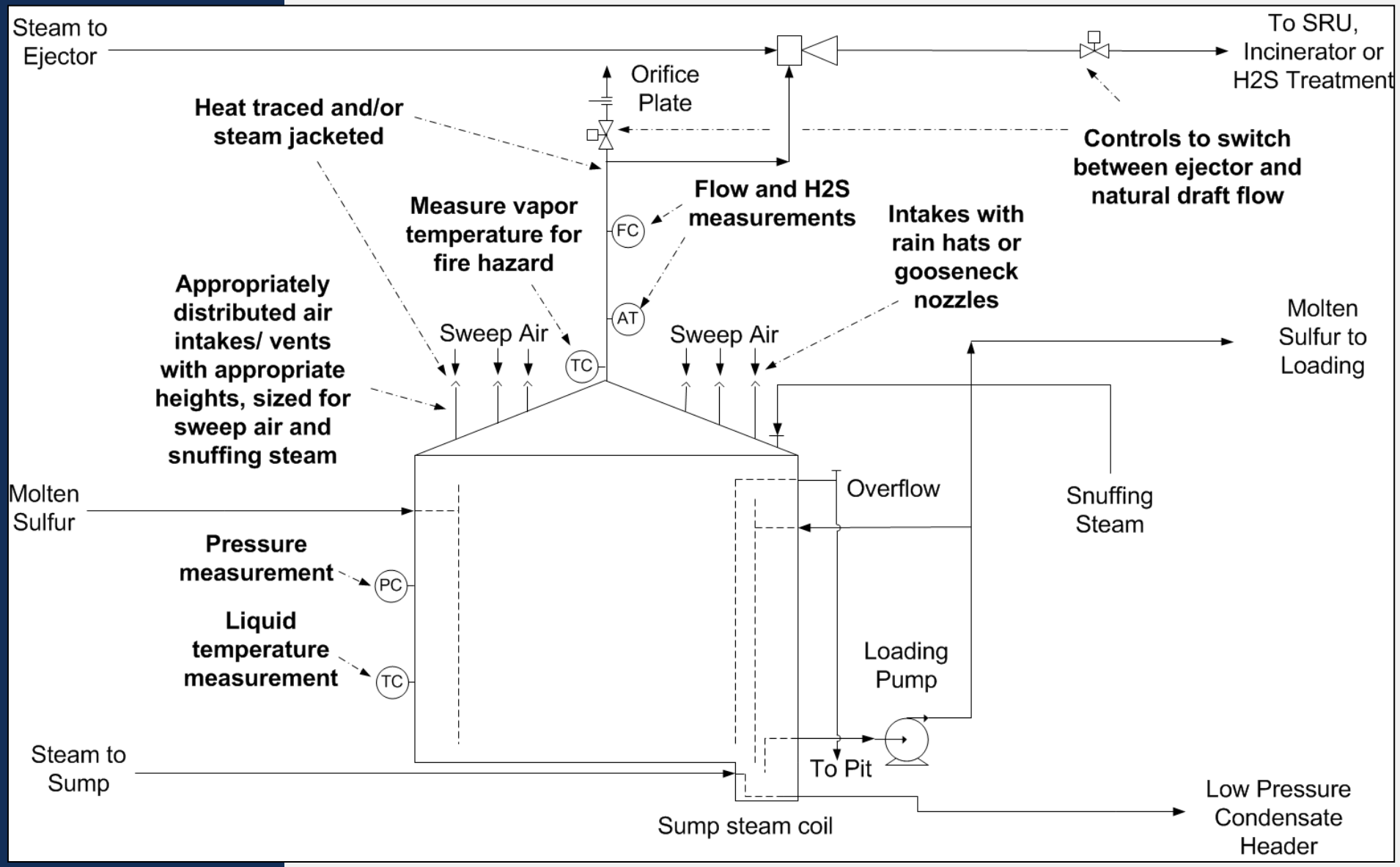


Motive Devices for Air Sweep

	Mechanical Reliability	Consistent Air Flow	Operational Air Flow Flexibility	Other Issues
Natural Draft	Most Reliable: No/few moving parts	Least Consistent: Dependent on ambient conditions	None	
Ejector	Very Reliable: Erosion is biggest risk	Very Consistent	None	If steam is motive, water is introduced to downstream processes
Blower	Least Reliable: Corrosion, plugging, etc.	Very Consistent	Most Flexible	

Natural draft backup used at some sites

Molten Sulfur Tank Design Features



Sweep vs. Purge