

Estimating H₂S Evolution in Molten Sulfur Storage and Handling Equipment

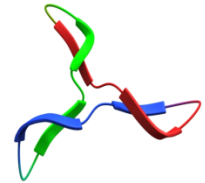
Trimeric Corporation

Darshan Sachde, Ph.D. (presenter)

Ken McIntush, P.E. (presenter)

Steven Fulk, Ph.D.

Carrie Beitler



2021 Brimstone Sulfur Symposium– Virtual

Trimeric Background & Question Policy

- ❑ 20 regular staff ChEs & 5 Senior Assoc. ChEs
- ❑ Specialized = Process Chemical Engineers
- ❑ Generalized = Experience Across Industries and Processes
- ❑ Depth of Experience in Sulfur Applications
 - See Trimeric publications at www.trimeric.com for examples
- ❑ Written technical paper available on request
- ❑ Question Policy



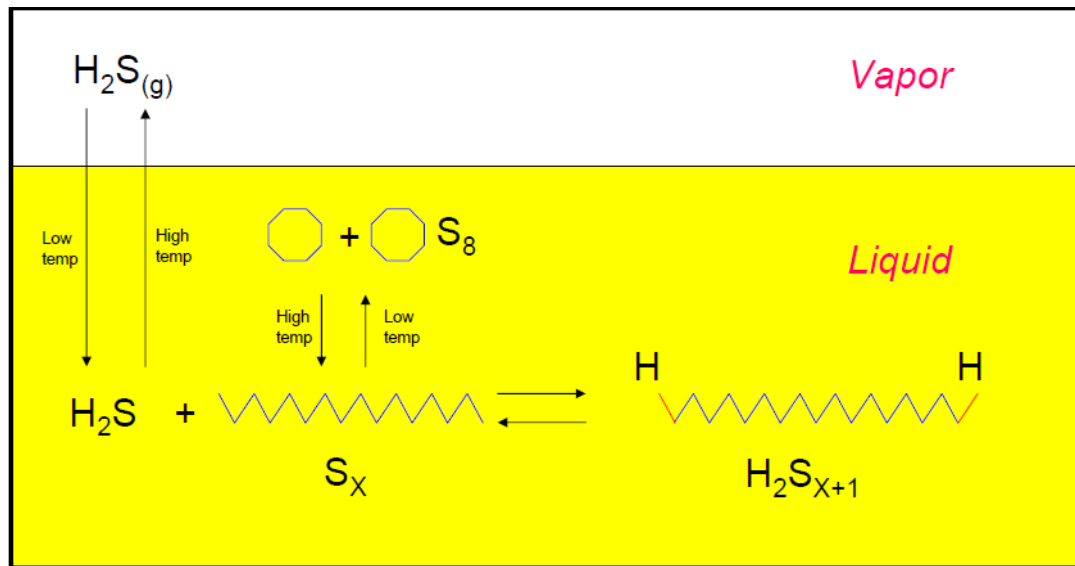
Topics

- Background – Why Does H₂S Evolution Matter?
- What Are We Trying to Model?
- Heuristics for Estimating H₂S Evolution
- “Modeling” H₂S Evolution
- Mitigating Risk in the Field
- Conclusions



Background: Chemistry

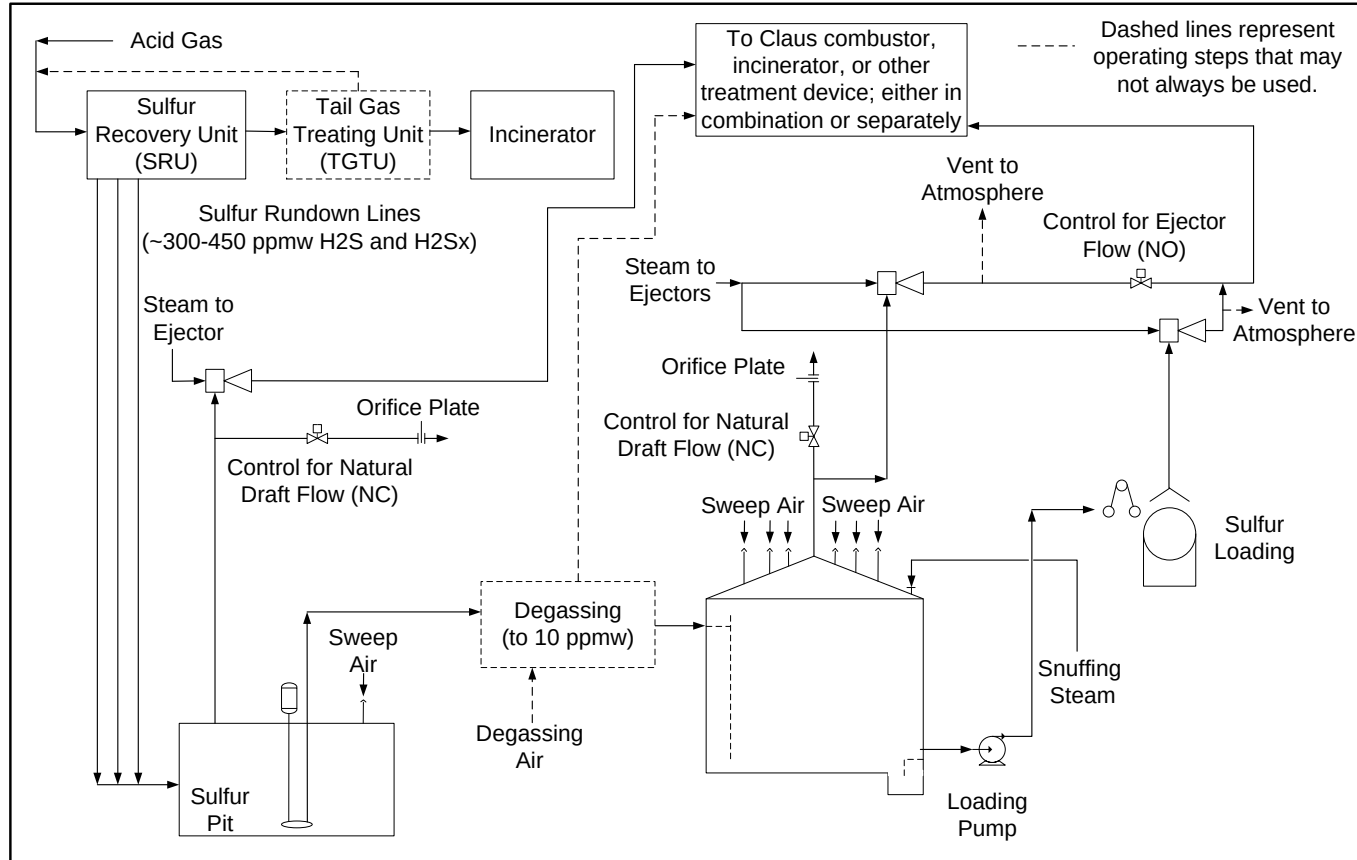
■ Claus SRU “Sulfur”



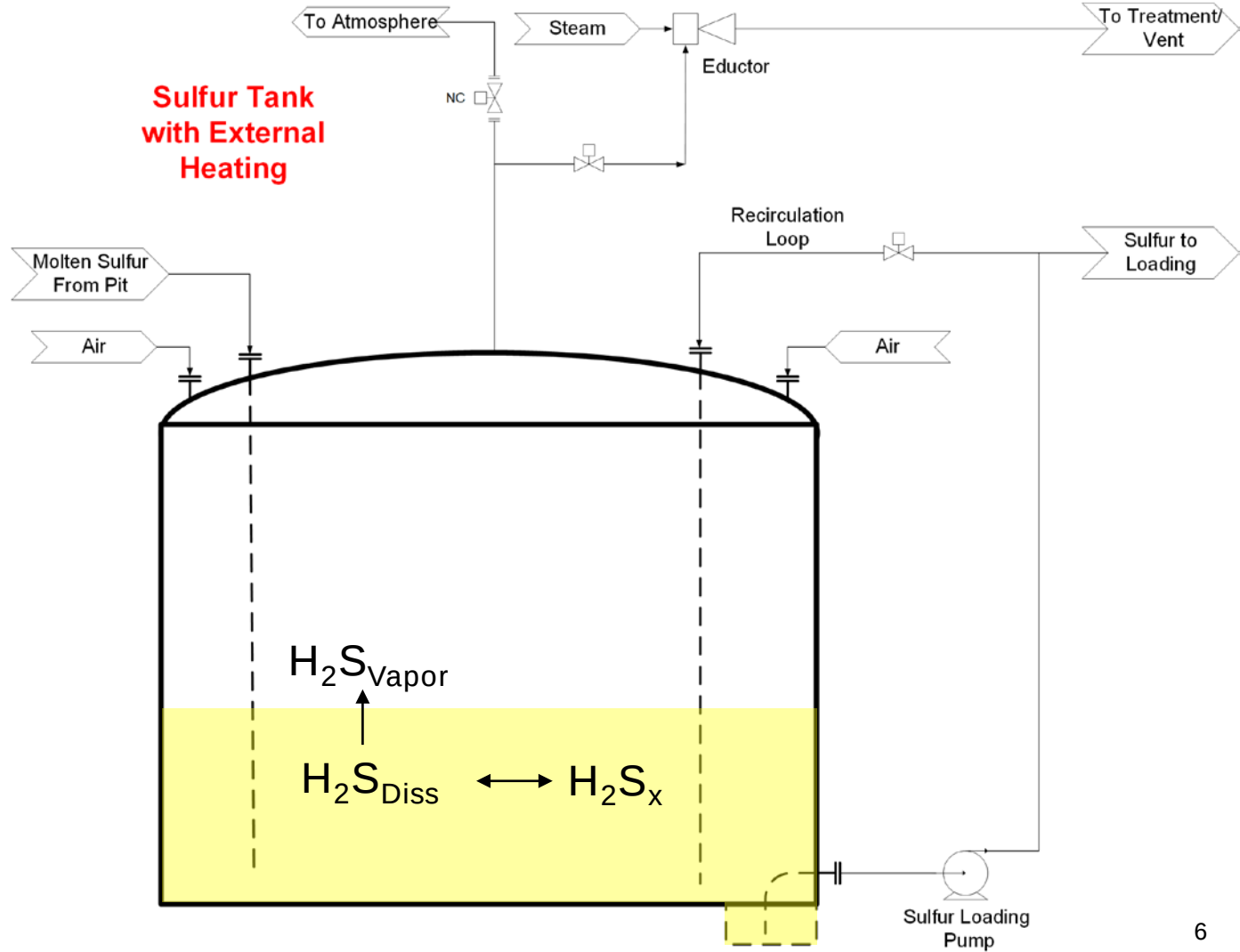
Source: 2007
LRGCC
Fundamentals

■ As sulfur cools, free H_2S is favored and degassing is enhanced.

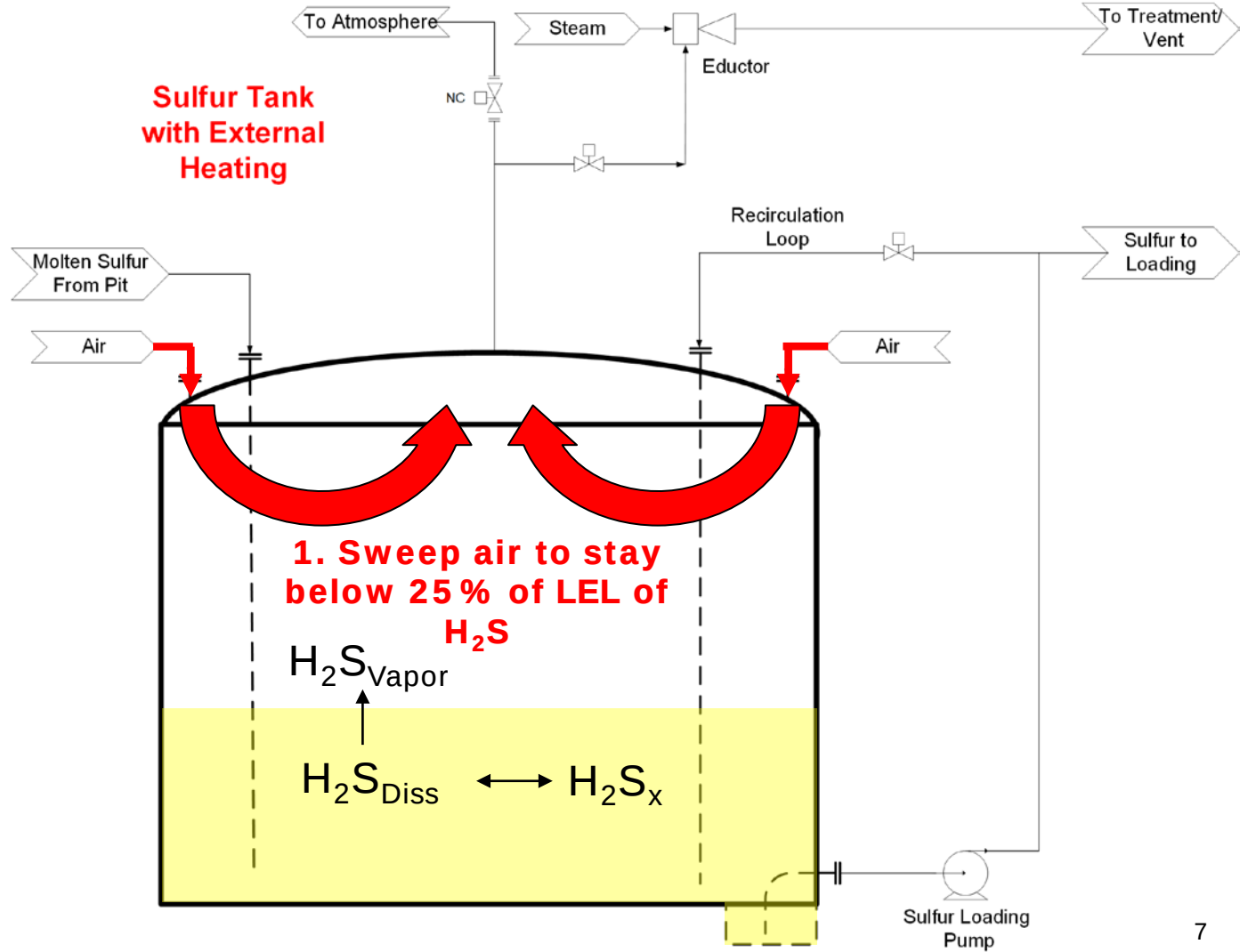
Background: Molten Sulfur Storage and Handling



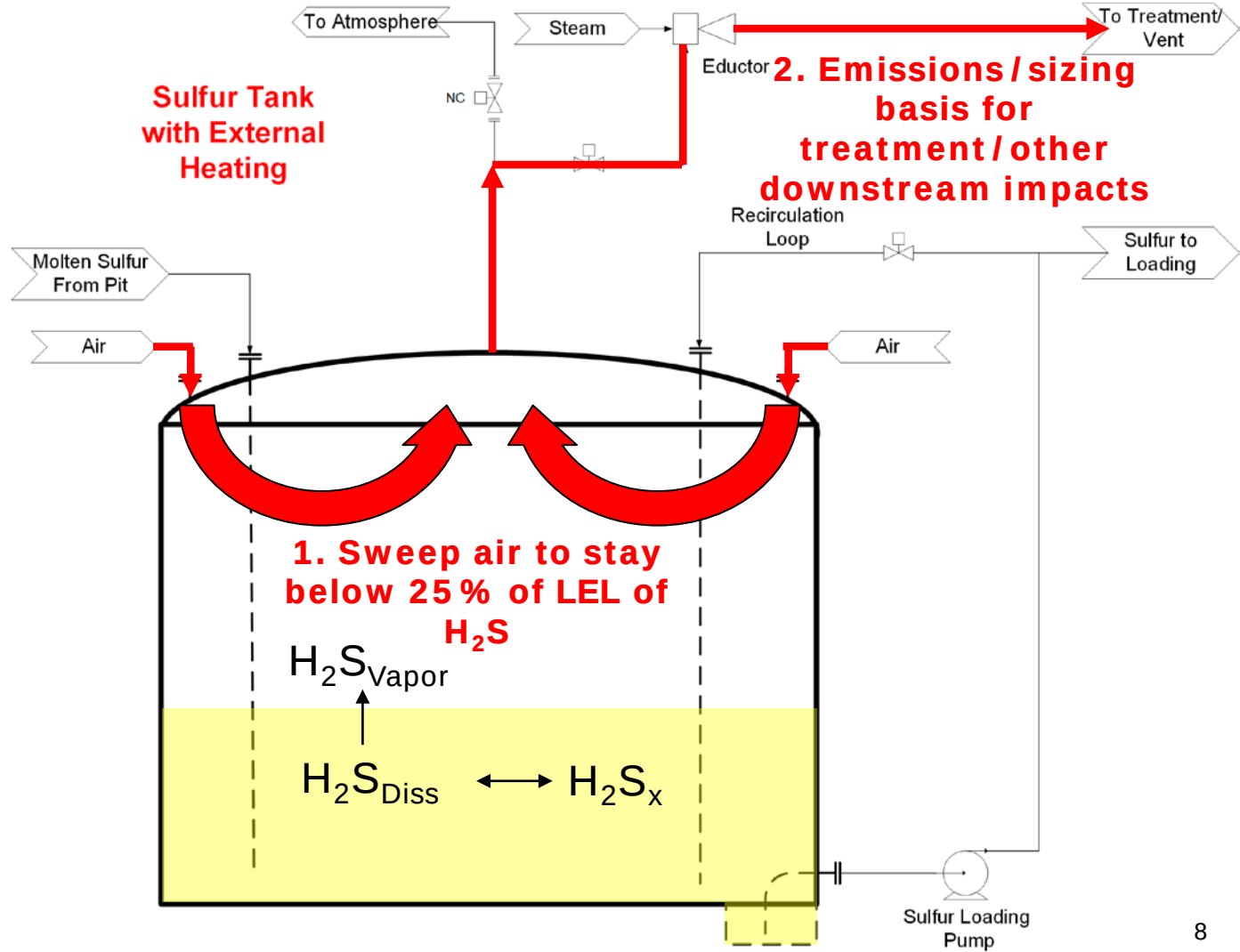
Why do we
need to
estimate H_2S
evolution?



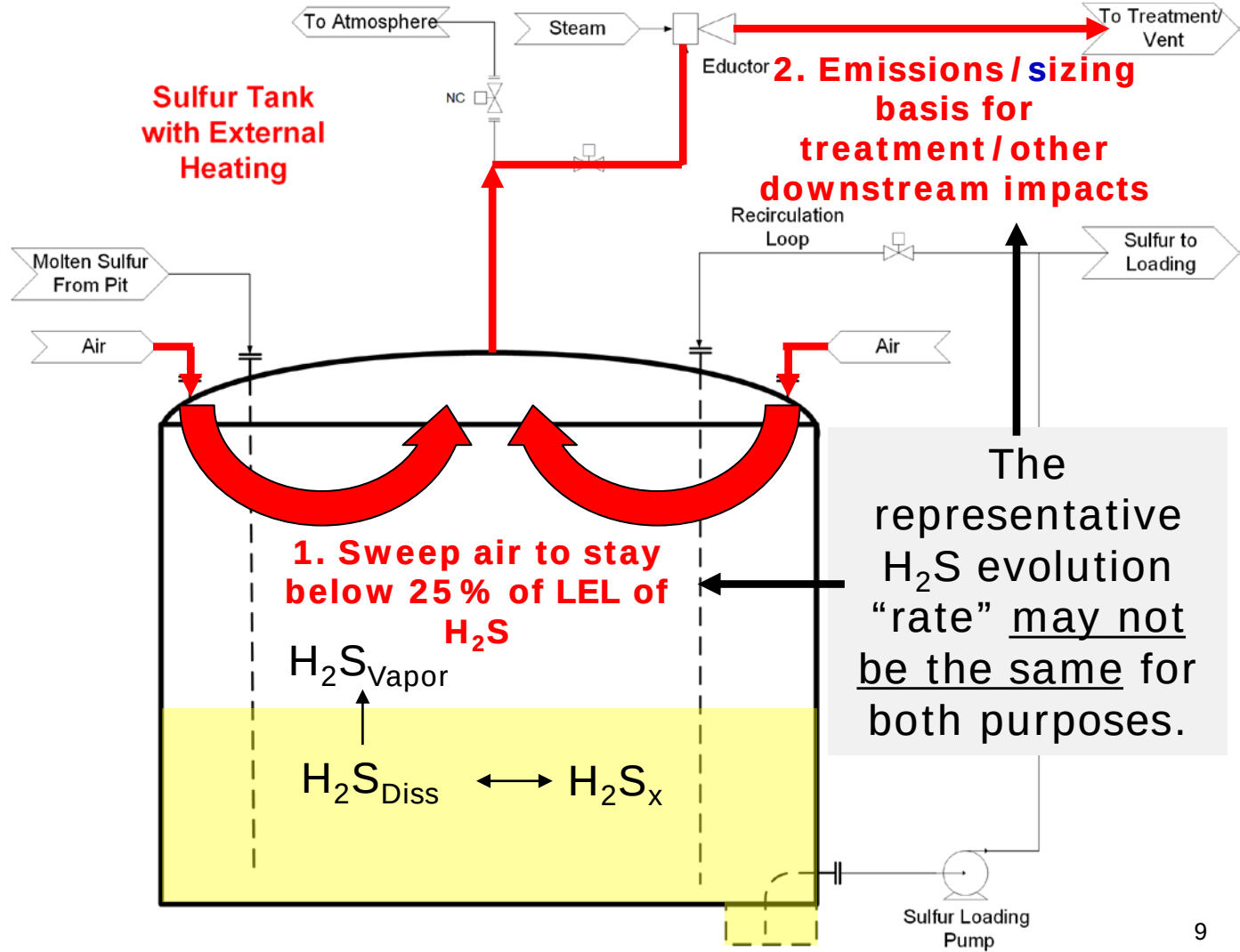
Why do we need to estimate H_2S evolution?



Why do we
need to
estimate H_2S
evolution?



Why do we need to estimate H_2S evolution?



Consequences of Inaccurate Estimation

Overestimation

- ❑ High air rate generates additional emissions (SO_2 , elemental S, more H_2S)
- ❑ Increased heat loss
- ❑ Oversized vent piping, downstream treatment equipment
- ❑ Negative impact on existing downstream processes (e.g., recycle to Claus)

Underestimation

- ❑ Risk of explosive atmosphere in equipment
- ❑ Costly re-design of system if initially under-designed

Decision is not as simple as being “conservative”



Goals for Today's Talk

- ▣ Use a case study approach to illustrate concepts
- ▣ Generate discussion
- ▣ Solicit new ideas or approaches

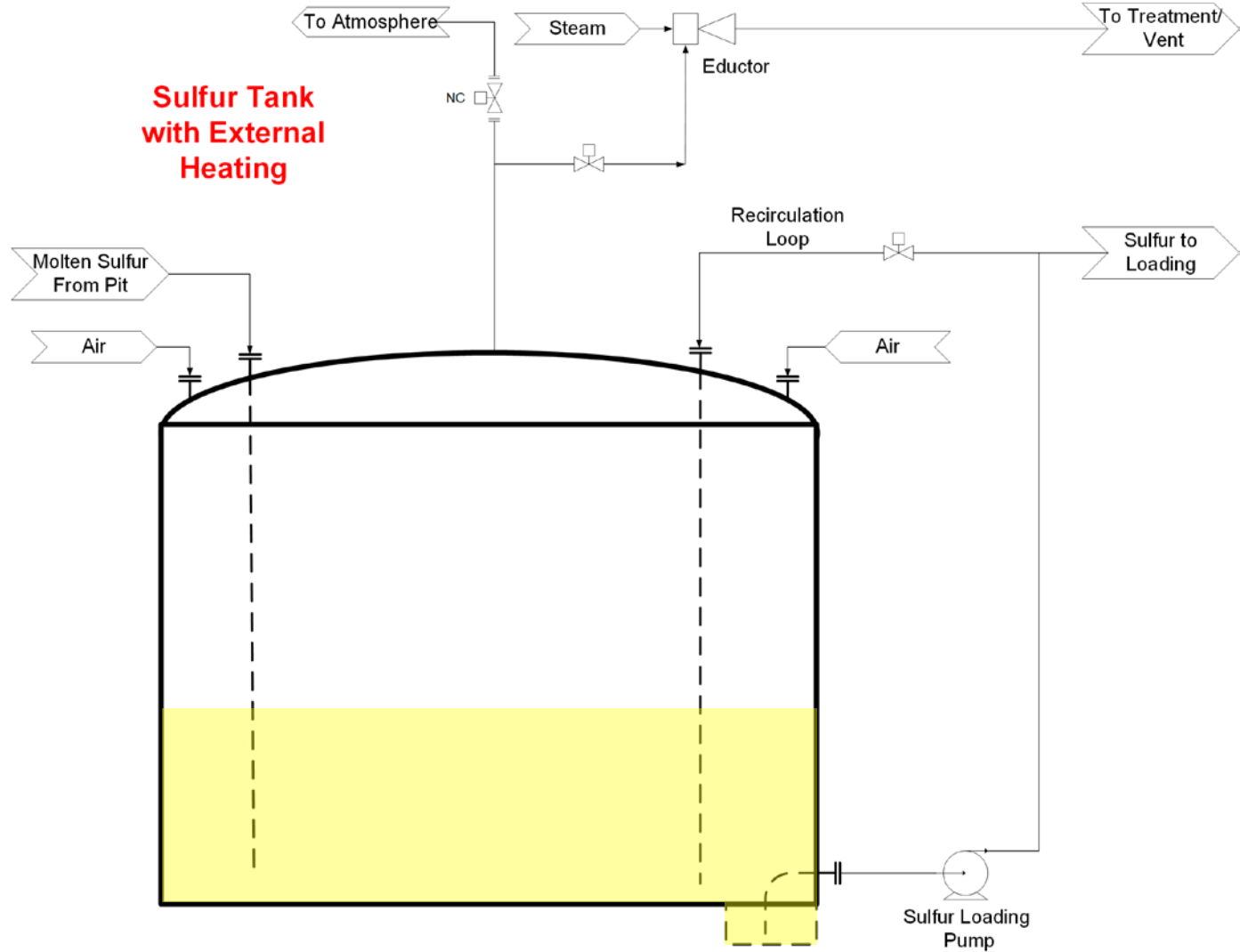


Topics

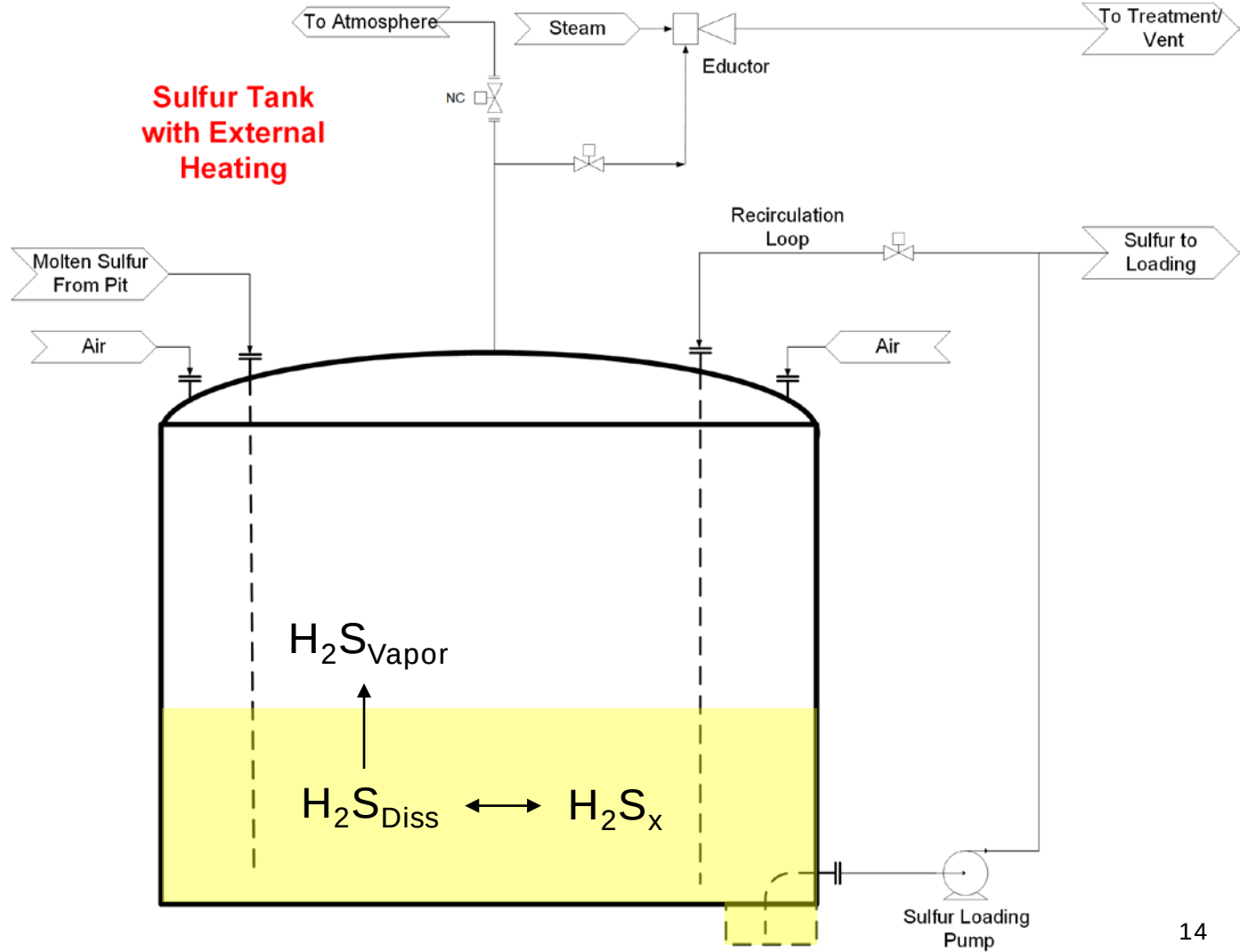
- ▣ Background – Why Does H₂S Evolution Matter?
- ▣ What Are We Trying to Model?
- ▣ Heuristics for Estimating H₂S Evolution
- ▣ “Modeling” H₂S Evolution
- ▣ Mitigating Risk in the Field
- ▣ Conclusions



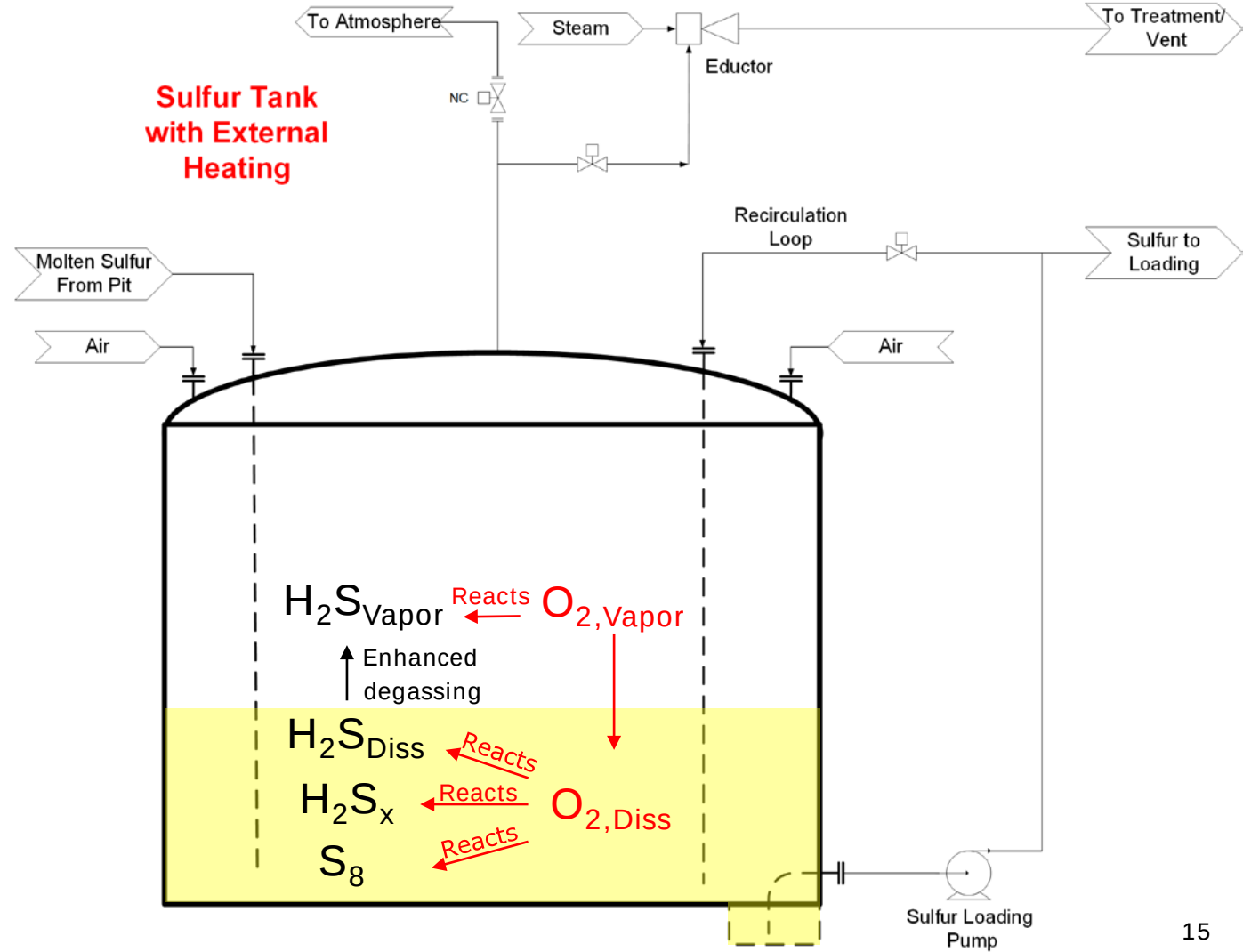
What are we
trying to
model?



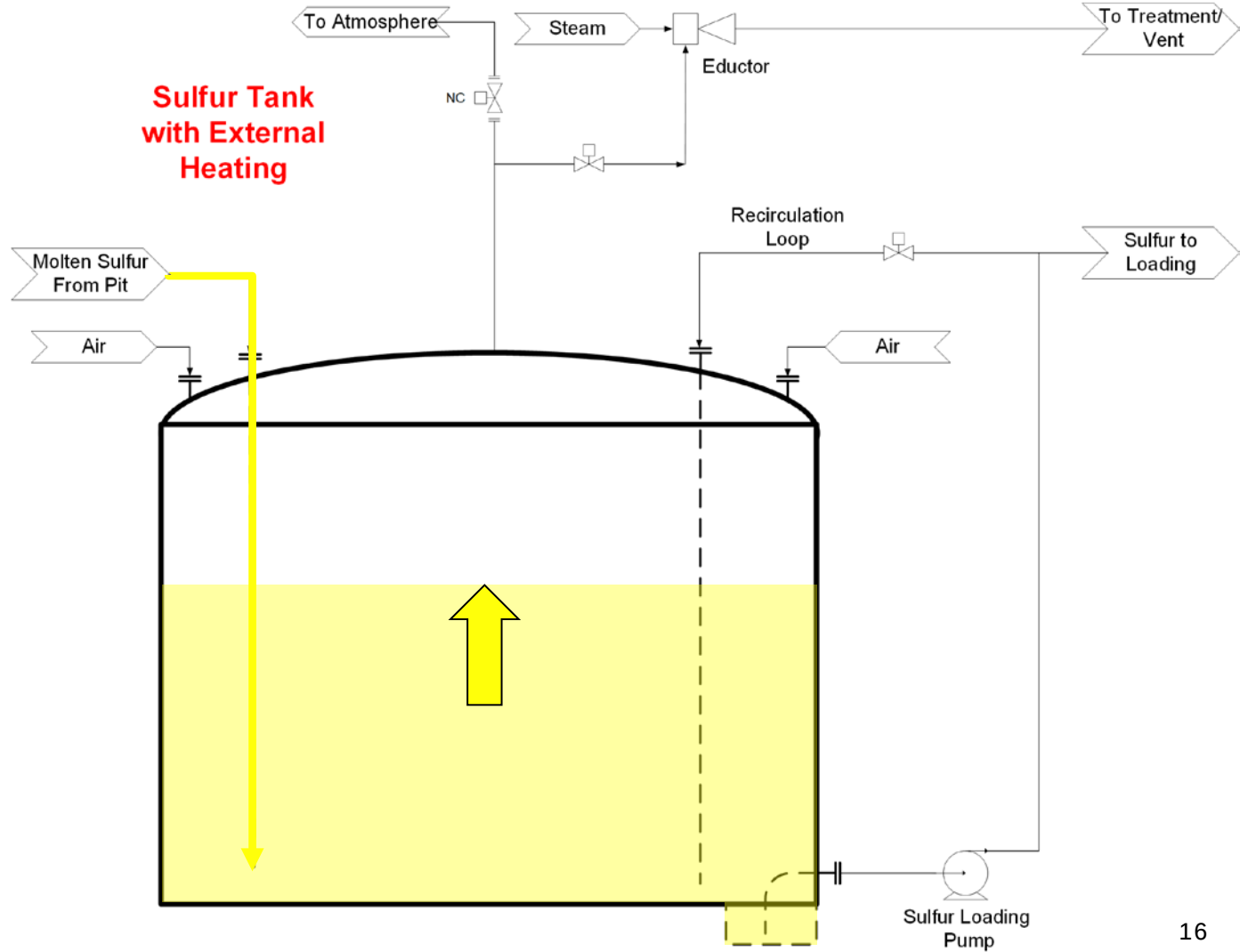
H₂S Evolution



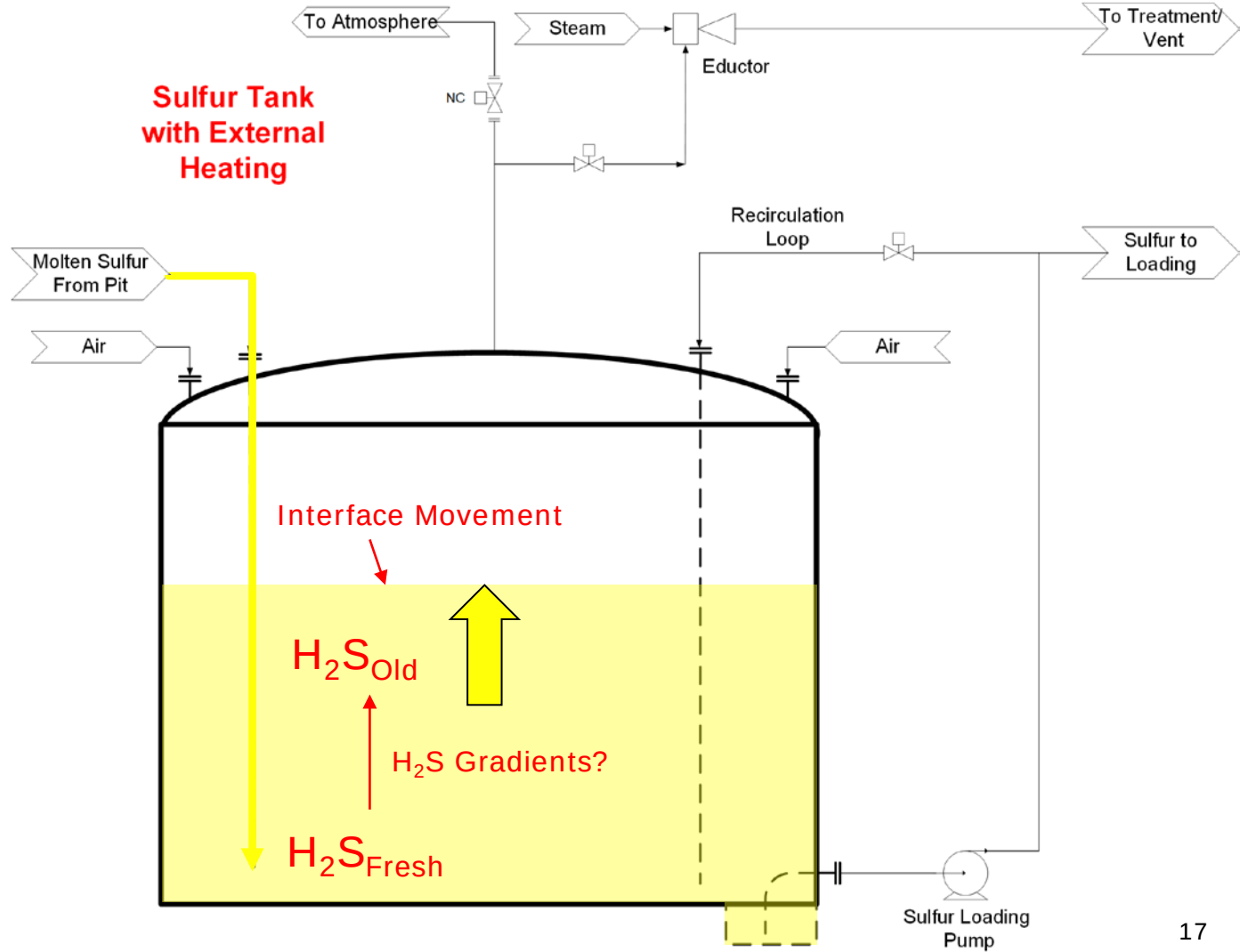
But also: O_2 Mass Transfer



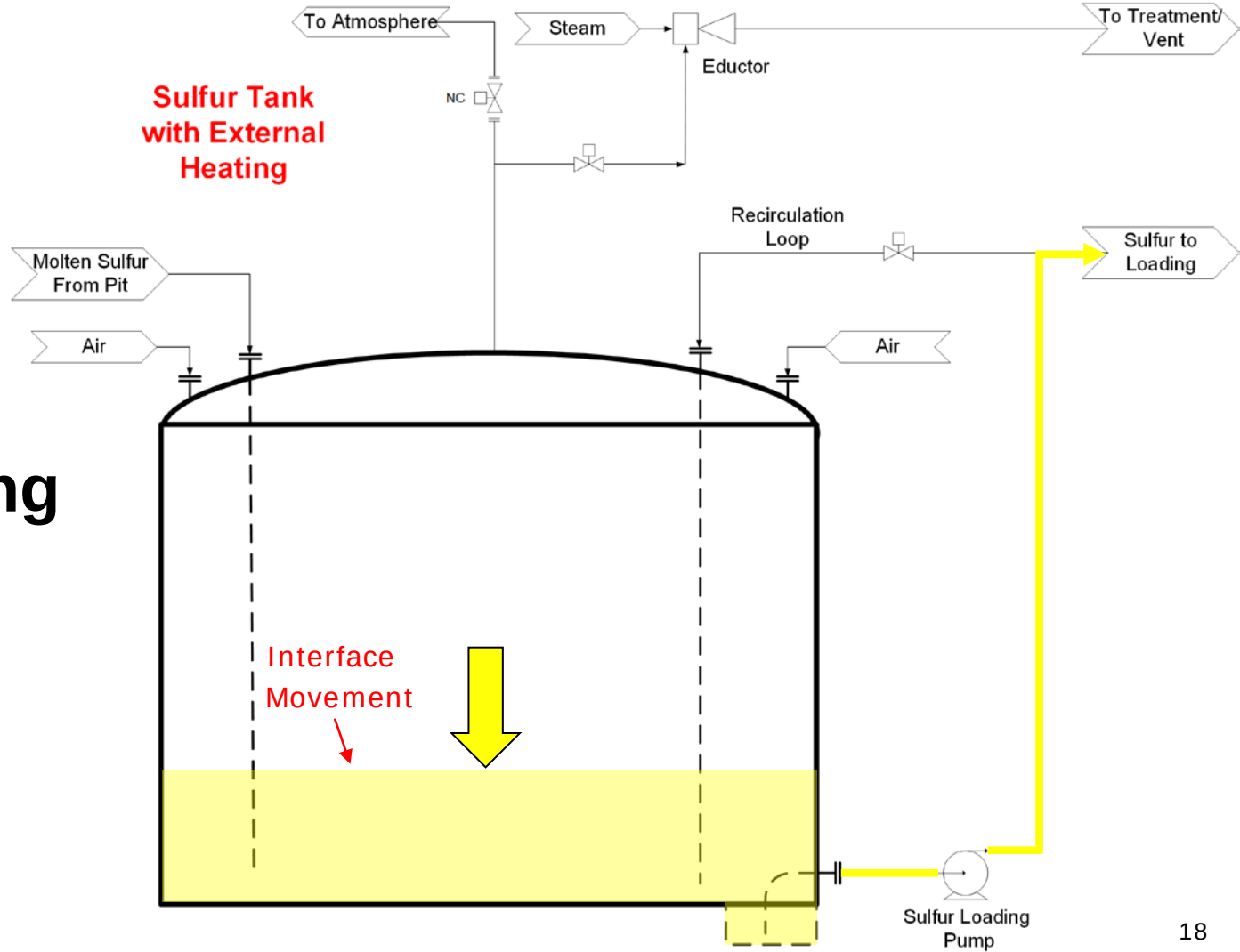
Intermittent Tank Filling



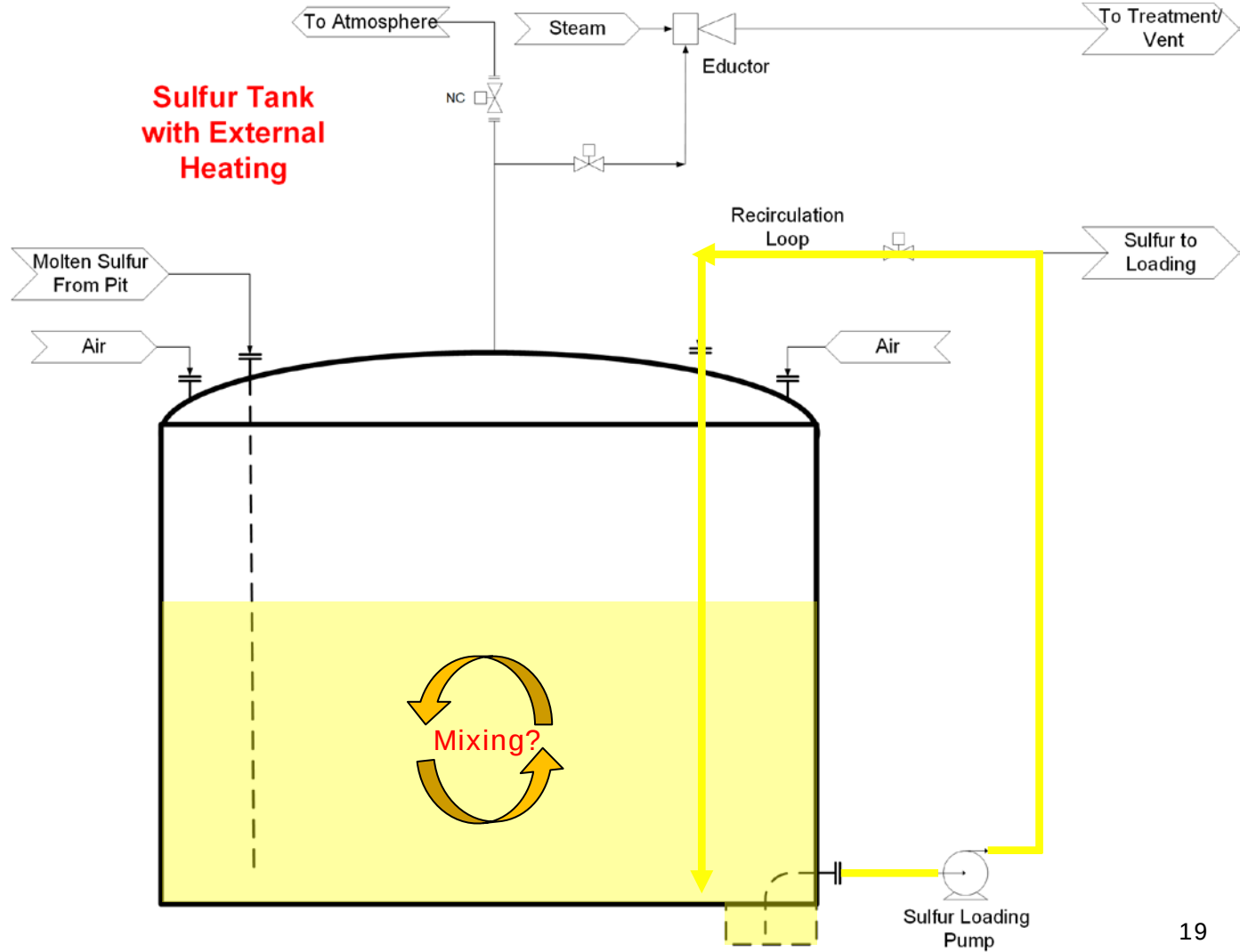
Intermittent Tank Filling



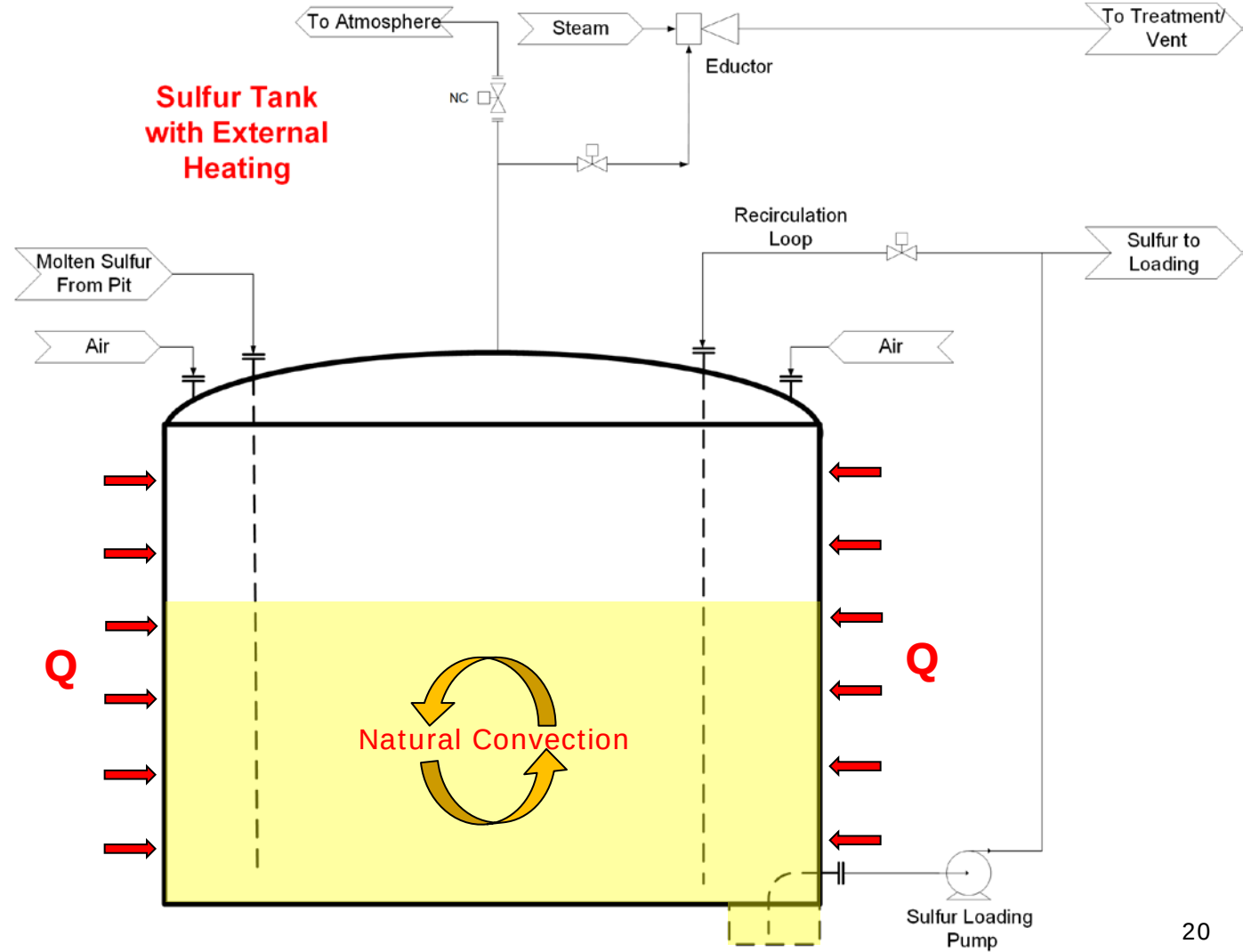
Intermittent Tank Unloading



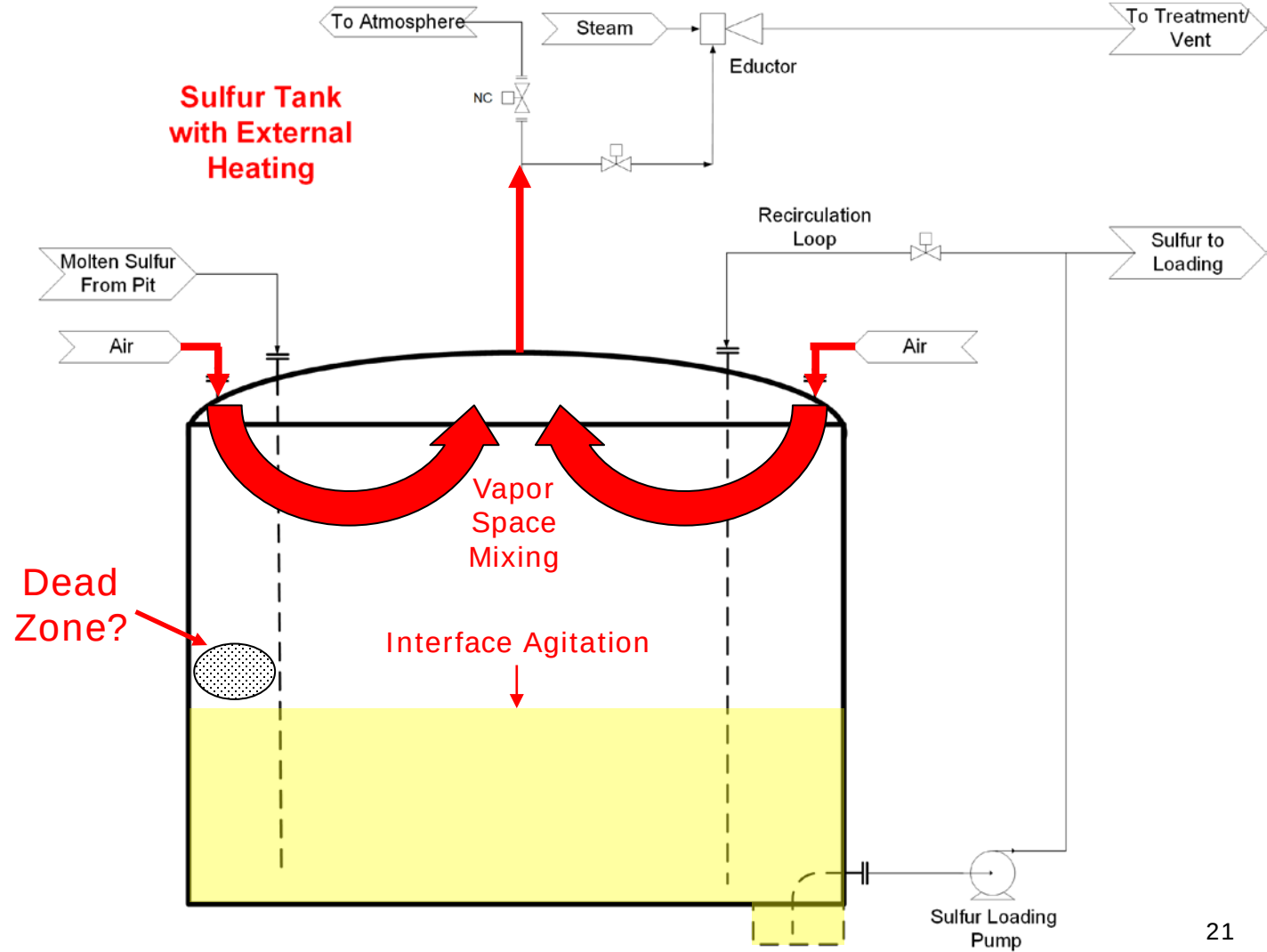
Sulfur Pump Recirculation



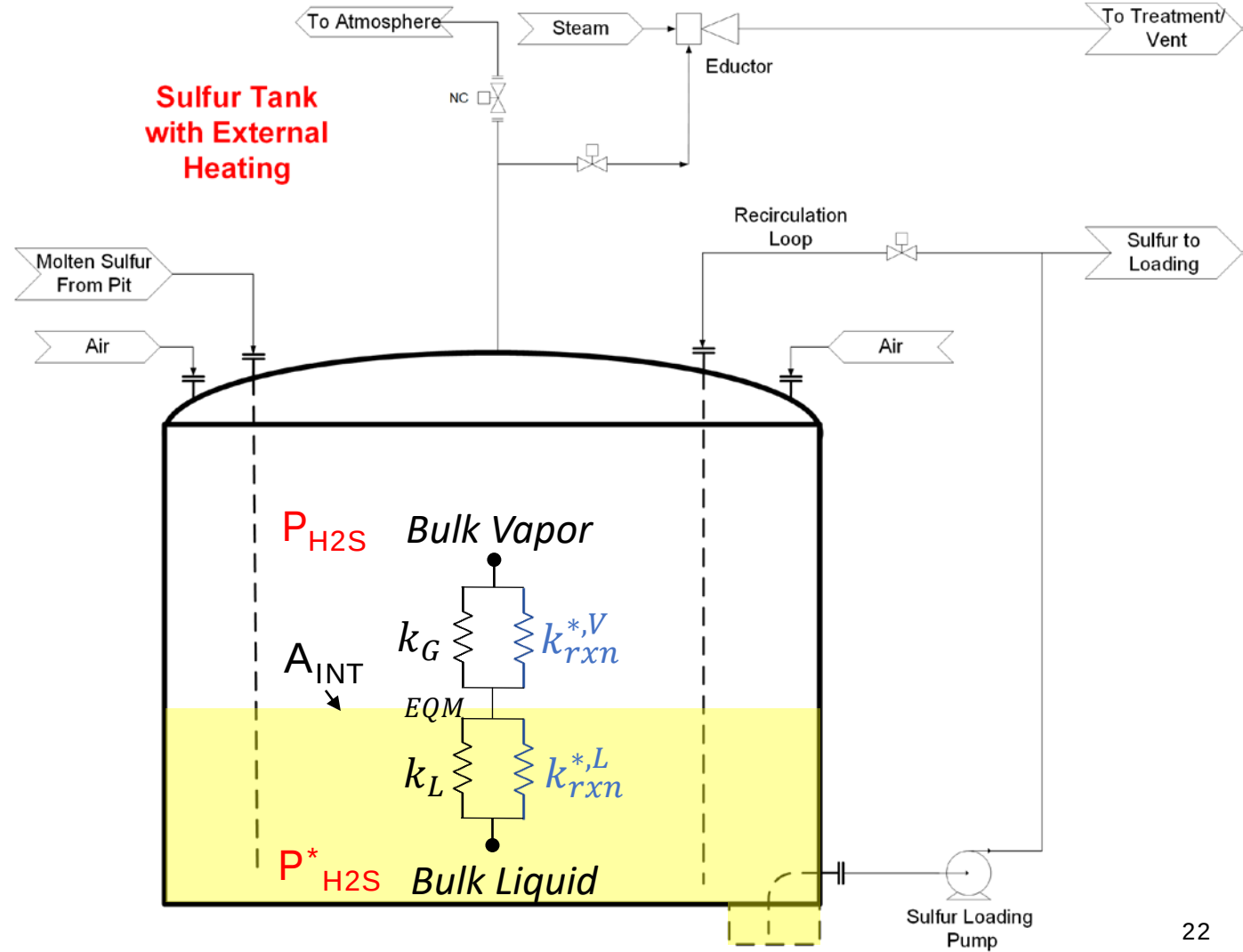
Natural Convection



Air Sweep



“First Principles” Model



All Models Are Wrong, Some Are Useful

- Even more complexity in other areas (e.g., loading)
- Cannot capture all “real world” conditions in a tractable model
- The goal is to define simplifications that are useful without sacrificing all connection to reality
- Heuristics vs. “Simple” Models



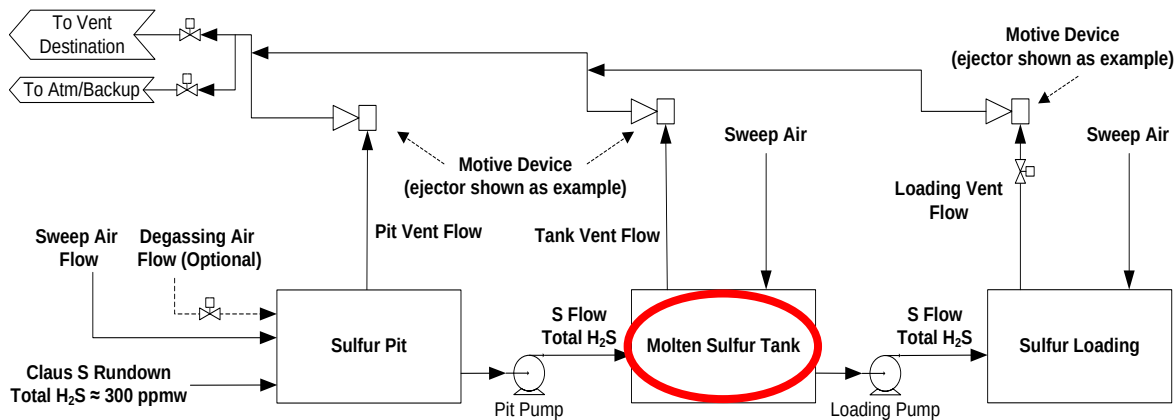
Topics

- ▣ Background – Why Does H₂S Evolution Matter?
- ▣ What Are We Trying to Model?
- ▣ Heuristics for Estimating H₂S Evolution
- ▣ “Modeling” H₂S Evolution
- ▣ Comparing Approaches – What Did We Learn?
- ▣ Mitigating Risk in the Field
- ▣ Conclusions



Case Study Approach

- Make Rate = 500 LTPD
- Pump Rates = 1500 LTPD
- Total H_2S ($H_2S + H_2S_x$) = 300 ppmw
- 25% approach to LEL of H_2S at 330°F
- Focus on Sulfur Tank:
 - $T = 280^\circ F$
 - Free H_2S /Total $H_2S = 75\%^1$



¹ R. Marriott, P. Clark, P. Davis, E. Fitzpatrick and K. Lesage, "A Re-examination of H_2S Solubility in Liquid Sulfur," in Brimstone Sulfur Recovery Symposium, Vail, CO, 2007.



Choosing a Sulfur Feed Rate

Make-Rate

- ❑ Implies a steady-state or “average” rate of H_2S evolution over time
- ❑ Ensures H_2S evolution calculations are consistent with material balance
- ❑ Better approach for estimating emissions, average H_2S to downstream processes, etc.

Pump-Rate

- ❑ H_2S can evolve at the rate it enters equipment
- ❑ More conservative, less physically representative
- ❑ “Instantaneous degassing”: short periods of higher H_2S evolution due to higher H_2S feed rate (e.g., loading operations)
- ❑ System design (e.g., sulfur feed via down pipe, low feed velocities) can limit “instantaneous degassing”



Heuristics – All H₂S at Any Point

- ❑ Commonly cited¹ conservative approach
- ❑ All H₂S (H₂S + H₂S_x) that enters the sulfur handling & storage system can evolve at any point downstream
- ❑ Logic:
 - H₂S content (liquid and vapor) is rarely monitored online
 - Site-to-site & operating variability make generalizations difficult/unreliable
 - Higher sweep air rates may help air distribution/mixing
- ❑ Limitations:
 - Inconsistent w/ material balance – not appropriate for emissions, etc.
 - “Total H₂S” evolving is not consistent with reality (H₂S_x → H₂S)
 - When used w/ pump rate, ignores mass transfer resistance and reaction kinetics



Heuristics – Free H₂S at Any Point

- ▣ Simple modification to “All H₂S” assumption
- ▣ Free H₂S evolves much more quickly than H₂S_x
- ▣ As sulfur cools, more of the total H₂S is present as free H₂S and “free H₂S” modification is less useful
 - At 280°F, Free H₂S/Total H₂S = 75%¹

1: R. Marriott, P. Clark, P. Davis, E. Fitzpatrick and K. Lesage, "A Re-examination of H₂S Solubility in Liquid Sulfur," in Brimstone Sulfur Recovery Symposium, Vail, CO, 2007.



Heuristics – Enforce H₂S Material Balance

- Cumulative H₂S that evolves in the whole system is $\leq$ total H₂S (H₂S + H₂S_x) entering system
- Basis is typically field measurements of H₂S in sulfur (if possible)
- May miss transients since H₂S measurements are not continuous
- For this case study (focused on tank):
 - Sulfur Pit: 50% of incoming evolves (150 ppmw H₂S remaining)
 - Sulfur Tank: 50% of incoming evolves (75 ppmw H₂S remaining)



Heuristics – Case Study Results for Sulfur Tank

Sweep Air Estimates (lb/hr)		H ₂ S Evolution Assumptions		
		All H ₂ S at Any Point	Free H ₂ S at Any Point	H ₂ S Material Balance
S Feed Basis	Sulfur Make-Rate ("Average Degassing Rate")	Case 1a: 1,580	Case 1b: N/A	Case 1c: 395
	Sulfur Pump Rate ("Instantaneous Degassing Rate")	Case 2a: 4,741	Case 2b: 3,555	Case 2c: 1,185

- Estimates span a factor of 12
- “Material Balance” approach highlights potential value of reliable field data
- Pump rate with “double jeopardy” type heuristics (All H₂S, Free H₂S) yield very conservative values



Topics

- ▣ Background – Why Does H₂S Evolution Matter?
- ▣ What Are We Trying to Model?
- ▣ Heuristics for Estimating H₂S Evolution
- ▣ “Modeling” H₂S Evolution
- ▣ Mitigating Risk in the Field
- ▣ Conclusions



Simplified Models: Overview

- Use experimental data on sulfur degassing to derive “rate constants” for H_2S evolution
- Use simple model forms (batch, CSTR) to incorporate experimental “rate constants” (lumped parameter)
- Interpret results in the context of the actual system



Experimental Data: Overview

- Focus on two older ASRL degassing studies^{1,2} for this example – see ASRL for latest, greatest data

Experiment	Liquid Conditions	Half-Life	1st Order Rate Constant
		min	1/min
ASRL 1a	Stagnant T = 140°C (284°F)	1440 ^{Note 1}	4.81E-04
ASRL 1b	Stirred T = 140°C (284°F)	50 ^{Note 1}	1.39E-02
ASRL 2a	Stagnant T = 135°C (275°F)	328 ^{Note 2,3}	2.11E-03 ^{Note 3}
ASRL 2b	Stirred T = 135°C (275°F)	36 ^{Note 2,3}	1.95E-02 ^{Note 3}
Notes: 1. Only H ₂ S _x loss in the liquid phase was measured in these experiments. 2. Total H ₂ S (H ₂ S + H ₂ S _x) loss in the liquid phase was measured in these experiments. 3. Values were estimated by Trimeric from the data in the report strictly for illustration.			

- P. D. Clark, K. L. Lesage, T. McDonald, A. Mason and A. K. Neufeld, "Investigations into the Chemical Mechanisms of Liquid Sulfur Degassing and Their Relevance to Industrial Degassing Systems," ASRL Quarterly Bulletin, vol. XXXI, no. 1, pp. 23-64, April - June 1994.
- J. B. Hyne and B. Wassink, "Degassing Liquid Sulfur," ASRL Quarterly Bulletin, vol. XXVII, no. 4, pp. 14-42, January - March 1991.



Experimental Data: Overview

- Experimental intent:
 - High-level screening to determine relative importance of parameters for degassing (stirred vs. stagnant, catalyst vs. no catalyst)
 - **Not** intended for scale-up or design
- Potential limitations for estimating H₂S evolution:
 - Mass transfer “lumped” into rate constants – mass transfer is scale dependent
 - Measuring free H₂S degassing was not the focus of either study
 - Actual mixing of sulfur in tanks between experimental agitation and stagnant cases
 - Vapor space does not include air sweep
- Used in this case study for illustration only



Experimental Data: H_2S_x vs. Total H_2S

- Difference in stagnant sulfur cases – 1a measured H_2S_x loss, 2a measured total H_2S loss

Experiment	Liquid Conditions	Half-Life	1st Order Rate Constant
		min	1/min
ASRL 1a	Stagnant T = 140°C (284°F)	1440 ^{Note 1}	4.81E-04
ASRL 1b	Stirred T = 140°C (284°F)	50 ^{Note 1}	1.39E-02
ASRL 2a	Stagnant T = 135°C (275°F)	328 ^{Note 2,3}	2.11E-03 ^{Note 3}
ASRL 2b	Stirred T = 135°C (275°F)	36 ^{Note 2,3}	1.95E-02 ^{Note 3}
Notes: 1. Only H_2S_x loss in the liquid phase was measured in these experiments. 2. Total H_2S ($\text{H}_2\text{S} + \text{H}_2\text{S}_x$) loss in the liquid phase was measured in these experiments. 3. Values were estimated by Trimeric from the data in the report strictly for illustration.			

Experimental Data: Stagnant vs. Stirred

- Stirring – major impact on H_2S degassing rate
- Liquid-film mass transfer limited in stagnant system
- Not clear if it is O_2 , H_2S , or both

Experiment	Liquid Conditions	Half-Life	1st Order Rate Constant
		min	1/min
ASRL 1a	Stagnant T = 140°C (284°F)	1440 ^{Note 1}	4.81E-04
ASRL 1b	Stirred T = 140°C (284°F)	50 ^{Note 1}	1.39E-02
ASRL 2a	Stagnant T = 135°C (275°F)	328 ^{Note 2,3}	2.11E-03 ^{Note 3}
ASRL 2b	Stirred T = 135°C (275°F)	36 ^{Note 2,3}	1.95E-02 ^{Note 3}
Notes: 1. Only H_2S_x loss in the liquid phase was measured in these experiments. 2. Total H_2S ($\text{H}_2\text{S} + \text{H}_2\text{S}_x$) loss in the liquid phase was measured in these experiments. 3. Values were estimated by Trimeric from the data in the report strictly for illustration.			

Modeling Approaches: CSTR vs. Batch

	CSTR	Batch
Operating Mode	Steady-State: Continuous feed and withdrawal of sulfur. May miss periods of high and low H ₂ S evolution	Unsteady-State: Batch of sulfur of a given volume sitting idle for a fixed time between sulfur transfers. Difficult to define transfer and batch times.
Vapor Phase Mass Transfer Resistance	Ignored: May be reasonable if vapor space is well-swept/well-mixed.	
Liquid Phase Mass Transfer Resistance	Ignored (Well-Mixed) : Concentration everywhere is the same as the outlet H ₂ S concentration.	Ignored (Well-Mixed) : Concentration everywhere is the same at any given point in time.

- ❑ Liquid-phase mass transfer is biggest assumption – mass transfer is only accounted for in experimental parameter
- ❑ Only batch model covered today – see paper for CSTR details

Modeling Approaches: Batch Model

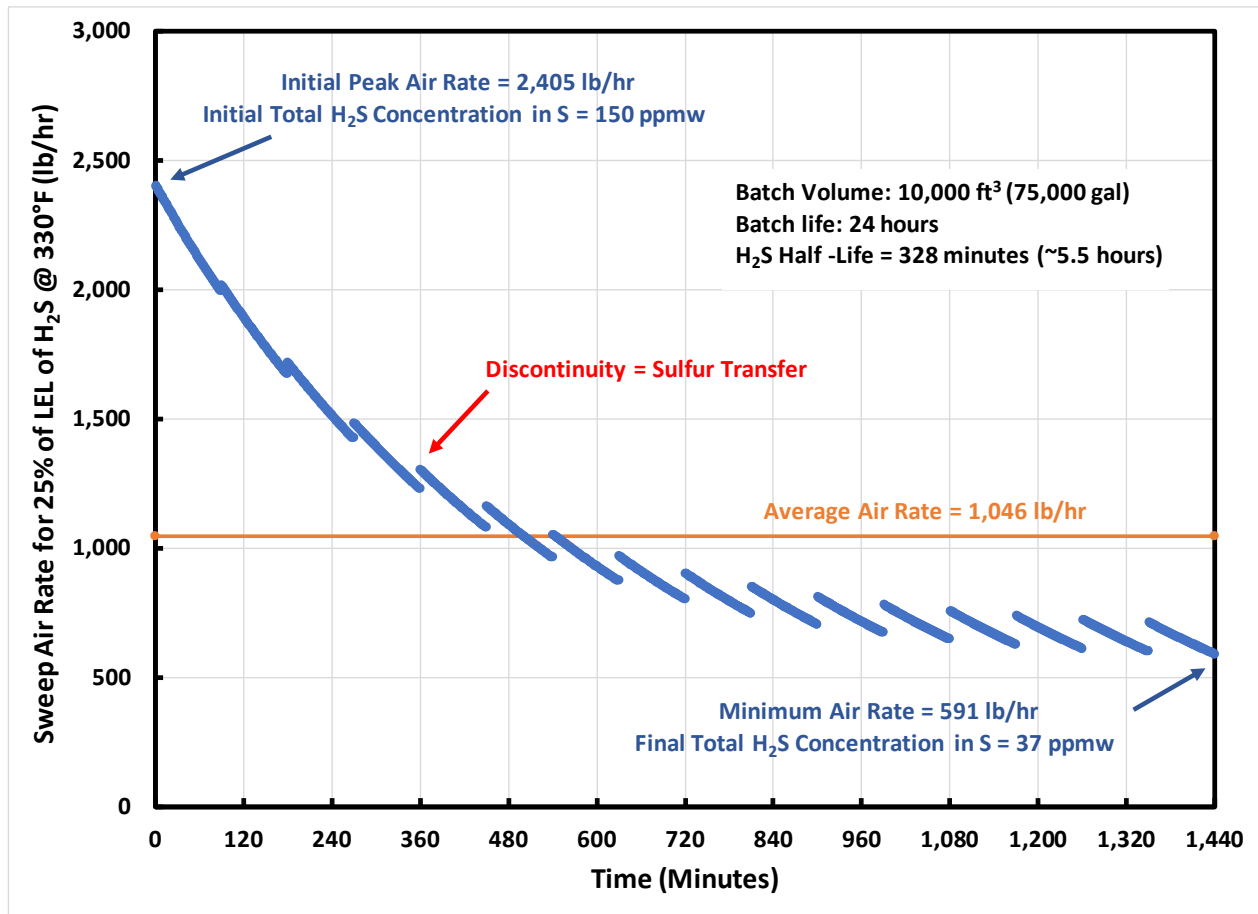
- ❑ “Batch” Volume = 10,000 ft³ (~75k gallons)
- ❑ “Batch” Lifetime = 24 hours (time to turnover tank volume)
- ❑ 16 sulfur transfers in 24 hours (assume fill/withdrawal @ same time)
- ❑ “Batch” starts with sulfur at 150 ppmw total H₂S (50% of H₂S evolved in pit, no consideration for evolution during tank initial fill)

$$\frac{VdC_{H_2S}}{dt} = QC_{H_2S}^{In} - QC_{H_2S}^{Out} + VR_{H_2S}$$

- ↓
1. No flow in or out during “batch”
 2. Fixed “batch” volume
 3. Use experimental rate constant in “reaction” term

$$C_{H_2S}^{Final} = C_{H_2S}^{Initial} e^{-k_{exp}t_{Batch}}$$

Batch Calculation: What does it mean?



Modeling Approaches: Summary of Results

- Simplified model results still include large range and require judgement
- More information on system dynamics than heuristics, but less transparency about assumptions
- Modeling cases may provide some bounds – stagnant vs. stirred, minimum vs. average or max

Experiment ID	Experimental Half-Life	Sweep Air Requirement Estimates		
		Final/Minimum	Average	Initial/Max
	minutes	lb/hr	lb/hr	lb/hr
ASRL 2a (Stagnant)	328	595	1,047	2,405
ASRL 2b (Stirred)	36	763	1,507	22,210

Comparing Approaches: Heuristics vs. Models

- Extreme cases for both approaches appear to deviate from physical reality
- Modeling may support a decision on a heuristic approach
- Important – Case study approach is too narrow to make broad conclusions

	Heuristic Cases	Simplified Models
Least Conservative	Case 1c: H ₂ S Mat. Balance + Make-Rate = 395 lb/hr	ASRL 2a Stagnant + Batch Minimum = 595 lb/hr
Intermediate	Case 2c: H ₂ S Mat. Balance + Pump Rate = 1,185 lb/hr	ASRL 2a Stagnant + Batch Average = 1,047 lb/hr
	Case 1a: All H ₂ S + Make Rate = 1,580 lb/hr	ASRL 2b Stirred + Batch Average = 1,507 lb/hr
Most Conservative	Case 2a: All H ₂ S + Pump Rate = 4,741 lb/hr	ASRL 2b Stagnant + Batch Max = 2,405 lb/hr

Topics

- ▣ Background – Why Does H₂S Evolution Matter?
- ▣ What Are We Trying to Model?
- ▣ Heuristics for Estimating H₂S Evolution
- ▣ “Modeling” H₂S Evolution
- ▣ Mitigating Risk in the Field
- ▣ Conclusions



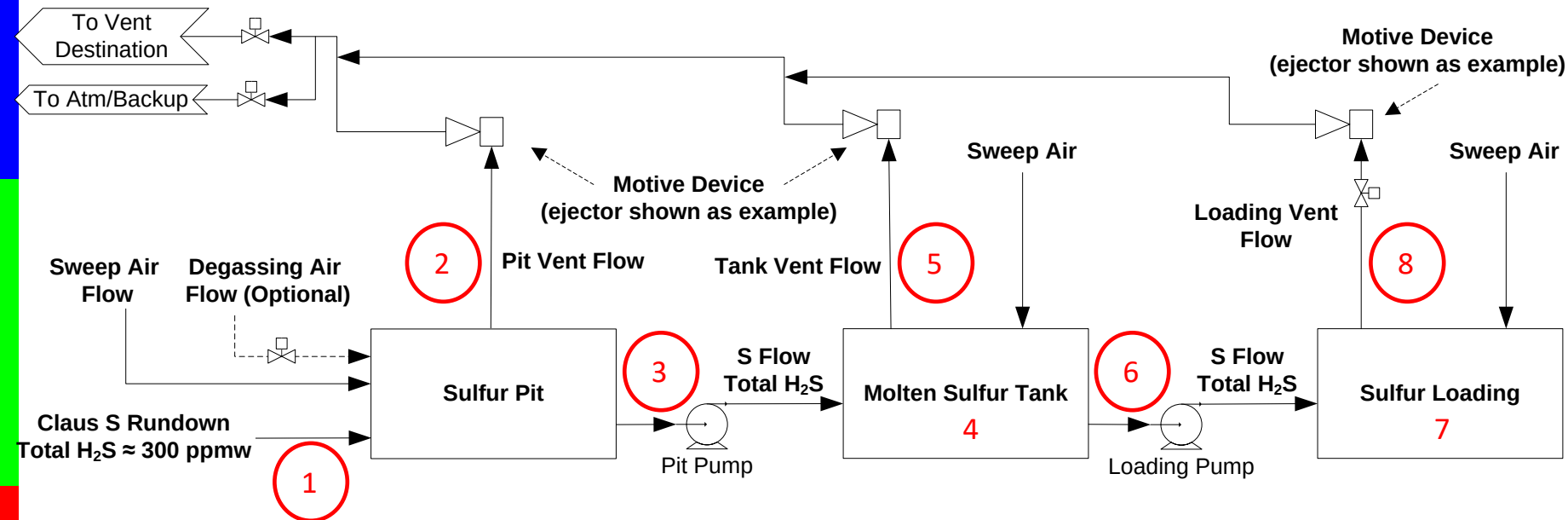
Approaches to Offset Risk of High H₂S Evolution

▣ Real-time measurements

- Continuous H₂S/LEL monitors in vapor headspace
- Used in pits and tanks
- Do not prevent hazardous conditions, just detects them
- Cannot measure the entire headspace
- Long-term data may help identify high-risk periods (e.g., sulfur transfer)



Field Measurements



- ❑ Timing and frequency are key
- ❑ Example: Repeated measurements of vapor space during and after sulfur transfer
- ❑ Each point above may represent multiple points (e.g., headspace)

Topics

- ▣ Background – Why Does H₂S Evolution Matter?
- ▣ What Are We Trying to Model?
- ▣ Heuristics for Estimating H₂S Evolution
- ▣ “Modeling” H₂S Evolution
- ▣ Mitigating Risk in the Field
- ▣ Conclusions



Summary

- ❑ Estimating H₂S evolution - more than the “most conservative” approach
 - Sweep air basis vs. emissions/treatment basis
 - Unintended consequences (increased emissions, SO₂, oversized equipment)
- ❑ Wide range of results from heuristic approaches, some departing from physical reality
- ❑ Simplified models w/ experimental data provide insight into mechanisms, but risk oversimplification and need data collected for the purpose
- ❑ A combination of heuristic approaches, simple modeling, and field data collection can guide selection of a reasonable basis
- ❑ Absent data for modeling and/or field data, heuristic approaches have a known track record and protect against the “worst case”



Trimeric Corporation

❑ Other Related Technical Topics

- Caustic Scrubbers in Molten Sulfur Service
- Molten Sulfur Vapor Ejection Systems
- Sour Water Stripper Internals
- Natural Draft Ventilation of Sulfur Storage Tanks/Pits
- Preventing/extinguishing molten sulfur tank and pit fires
- Disposition of molten sulfur tank and pit vents
- Strategies for short term H₂S removal
- Others – See Trimeric Publications
 - ❑ <http://www.trimeric.com/publications.html>

Contact Us:
ken.mcintush@trimeric.com
darshan.sachde@trimeric.com



Experimental Data: Overview

- Focus on two older ASRL degassing studies^{1,2} for this example
– see ASRL for latest, greatest data

	Reference 1	Reference 2
Key Conditions	- Isothermal @140°C (284°F) - With & w/out sulfur agitation With & w/out air sparging	- Isothermal @135°C (275°F) - With & w/out sulfur agitation With & w/out air sparging
H ₂ S Measurement	Measured H₂S_x loss	Measured Total H₂S loss
Derived Rate Parameters	H ₂ S half-life ^{Note 1}	Raw data: H ₂ S loss vs. time ^{Note 2}
Notes: 1) Half-life data derived from pseudo-first order regression of rates with measured H ₂ S _x loss. See reference 1. 2) Trimeric estimated half-life and rate constants from the data for illustration only.		

- P. D. Clark, K. L. Lesage, T. McDonald, A. Mason and A. K. Neufeld, "Investigations into the Chemical Mechanisms of Liquid Sulfur Degassing and Their Relevance to Industrial Degassing Systems," ASRL Quarterly Bulletin, vol. XXXI, no. 1, pp. 23-64, April - June 1994.
- J. B. Hyne and B. Wassink, "Degassing Liquid Sulfur," ASRL Quarterly Bulletin, vol. XXVII, no. 4, pp. 14-42, January - March 1991.