

Estimating H₂S Evolution from Molten Sulfur Storage and Handling Systems

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Abstract

Molten sulfur produced in Claus sulfur recovery units (SRUs) contains H₂S as dissolved molecular H₂S and hydrogen polysulfides (H₂S_x). H₂S can evolve from the molten sulfur and enter the vapor space as part of the normal operation of sulfur handling, storage, and transport processes downstream of the Claus SRU. The environmental, safety, and health hazards associated with H₂S necessitate safe handling of the vent vapors from this downstream molten sulfur equipment. Therefore, the presence of H₂S in the vapor space of molten sulfur processes directly impacts the design and operation of the molten sulfur storage and handling equipment. In addition, the amount of H₂S that evolves and the rate at which it evolves serves as the basis for designing and implementing measures to manage H₂S risk and disposition of vapors leaving these systems. Developing an appropriate estimate of H₂S evolution at each point in the process where vent vapors are present/managed underpins all of the subsequent engineering design work and operational philosophy.

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1.0 Overview of Sulfur Handling and H₂S Evolution

Hydrogen sulfide (H₂S) is a byproduct of processing natural gas and refining crude oils. Environmental regulations often require that the H₂S be removed before emitting gases to the atmosphere. A modified Claus sulfur recovery unit (Claus SRU) is one common method for converting the removed H₂S to molten elemental sulfur. The molten sulfur produced in a Claus SRU is stored and handled in a number of steps as depicted in the example in Figure 1.

The molten sulfur produced in the Claus SRU contains soluble H₂S and hydrogen polysulfides (H₂S_x). During the storage of the sulfur, the H₂S_x compounds decompose to form elemental sulfur plus H₂S as the sulfur cools and is agitated. This results in dissolved H₂S in the liquid sulfur that desorbs into the gas phase. The potential release of H₂S creates several safety, environmental, and health risks. H₂S represents a flammability / explosion hazard at conditions (e.g., H₂S vapor concentrations) that may easily occur in storage and handling processes. In addition, the OSHA permissible exposure limits for H₂S in the atmosphere are: 10 ppmv, 8-hr TWA, for construction and maritime industries; and 20 ppmv ceiling limit for general industry [1]. Finally, the refinery may be limited in its ability to vent H₂S due to environmental regulations. Therefore, there are several points in the sulfur storage and handling process where vent gas streams that contain H₂S (and other sulfur species) may need to be managed.

The sulfur from the Claus unit often flows to a sulfur pit as the first step in the storage and handling process. The molten sulfur flowing into the pit (or first receiving vessel) from a Claus SRU is often assumed to contain roughly 300 ppmw H₂S and H₂S_x ([2], [3], [4]) although oxygen enrichment and sub-dewpoint operation can produce higher levels, e.g. 450 ppmw [5]. Trimeric's experience with field measurements of the H₂S and H₂S_x indicate that the 300 ppmw is a reasonable value for many plants, although measurement is recommended to account for specific operating conditions of each unit.

The sulfur may be degassed, either in the pit or in separate degassing equipment, to reduce H₂S down to approximately 10 ppmw. Even if there is no degassing equipment, some H₂S will evolve in the pit, but the amount of H₂S evolution depends on several factors including the pit temperature, residence time, degree of agitation, whether sweep gas is used, etc. Therefore, when degassing systems are present or air sweep is used in the sulfur pit, an H₂S-laden vapor stream will be produced that must be managed safely in some fashion. This is the first point in the process where estimating H₂S evolution can impact the system design and operation.

The molten sulfur then often flows to a storage tank where it is stored until it can be loaded into railcars, trucks, or other means of transportation to customers. The storage tank provides buffer capacity for sulfur storage to allow for intermittent off-loading of sulfur without disrupting the sulfur plant and refinery operations. Because of the higher H₂S content in undegassed molten sulfur, the H₂S concentrations in the headspace of a tank storing undegassed sulfur could reach the tens of volume percent levels [3], which could lead to an explosion and/or pose a significant exposure hazard to personnel. Even with degassed sulfur (e.g., H₂S ≤ 10 ppmw), it is theoretically possible that additional H₂S could evolve during the residence time in the storage tank leading to dangerous concentrations of H₂S in the tank vapor space (hundreds of ppmv to low volume percent levels) [3].

The lower explosive limit (LEL) of H₂S in newer literature data is ~3 vol% at 330°F [11], a value that can be readily exceeded when undegassed sulfur is stored in equipment with a stagnant headspace¹. Therefore, many molten sulfur storage tanks are designed to prevent explosive gas mixtures

¹ Note that even tanks that normally receive degassed sulfur are often designed to accommodate the scenario where the degassing unit is out of service and the tank must receive undegassed sulfur to allow the SRU to operate uninterrupted.

from forming in the tank headspace. This may be accomplished by: 1) minimizing the combustible component (H_2S) concentration by applying a diluting sweep gas, or 2) minimizing the oxidant concentration by using an inert gas blanket for the tank headspace. Details on sweeping and blanketing of sulfur storage tanks can be found elsewhere [6]. Air-based tank sweep systems are often favored over inert-blanketed tanks from a safety standpoint due to the risk of pyrophoric iron sulfide formation in the reducing environment of blanketed tanks. Specifying the sweep air rate to maintain a specific margin below the LEL of H_2S requires an estimate of the H_2S that is expected to evolve in the tank headspace. Therefore, the molten sulfur tank represents the second place that estimating the H_2S evolution rate from molten sulfur impacts the design and operation of sulfur handling equipment.

Finally, the sulfur from the storage tank is usually loaded into a truck, train, or barge for transport away from the site. In the process of pumping sulfur and loading the transport vessel, the sulfur is once again agitated, and the transport vessel may be open to atmosphere. This creates the possibility of H_2S evolution at the loading station. Even though H_2S may evolve at the preceding handling steps (i.e., pit, tank) and the sulfur may be degassed, it should not be assumed that low H_2S will be present during loading. H_2S concentrations in the molten sulfur may not be uniform and the degree of “degassing” in the preceding handling steps may vary extensively from site to site and based on the specific operating conditions at the time. In addition, for sulfur loading processes, there are frequently personnel in the immediate vicinity of the loading operation (e.g., truck driver). For these reasons, the sulfur loading area represents the third location in the process where the H_2S evolution rate may need to be estimated.

This paper focuses on approaches used to estimate H_2S evolution from the molten sulfur at different points in the sulfur handling and storage processes. The amount of H_2S that is expected to be present in the vapor phase directly serves as the basis for designing and implementing measures to manage H_2S risk and disposition of vapors leaving these systems. The paper will review theoretical aspects of H_2S evolution, common industry practices and assumptions used to estimate H_2S evolution, and experimental data on H_2S evolution. The paper will highlight unintended consequences of defaulting to the “most conservative” approach of estimating H_2S evolution, but will also highlight challenges and limitations in obtaining accurate or realistic estimates of H_2S evolution. Recommendations to improve estimation of H_2S evolution, measurements to verify the H_2S concentration present in molten sulfur handling and storage vapor space, and accompanying safety and mitigation measures to reduce the risk of inaccurate H_2S evolution estimation will also be presented.

This paragraph is meant as a guide to the reader. The following Section 2.0 reviews theory of H_2S evolution and explores the possibility of a first-principles model. Section 3.0 then discusses estimating H_2S evolution in practice. Section 4.0 discusses alternate approaches for estimating H_2S evolution. Then, Section 5.0 compares H_2S evolution approaches and gives recommendations. Section 6.0 discusses how to validate H_2S evolution estimates and mitigate the risks of inaccurate estimates.

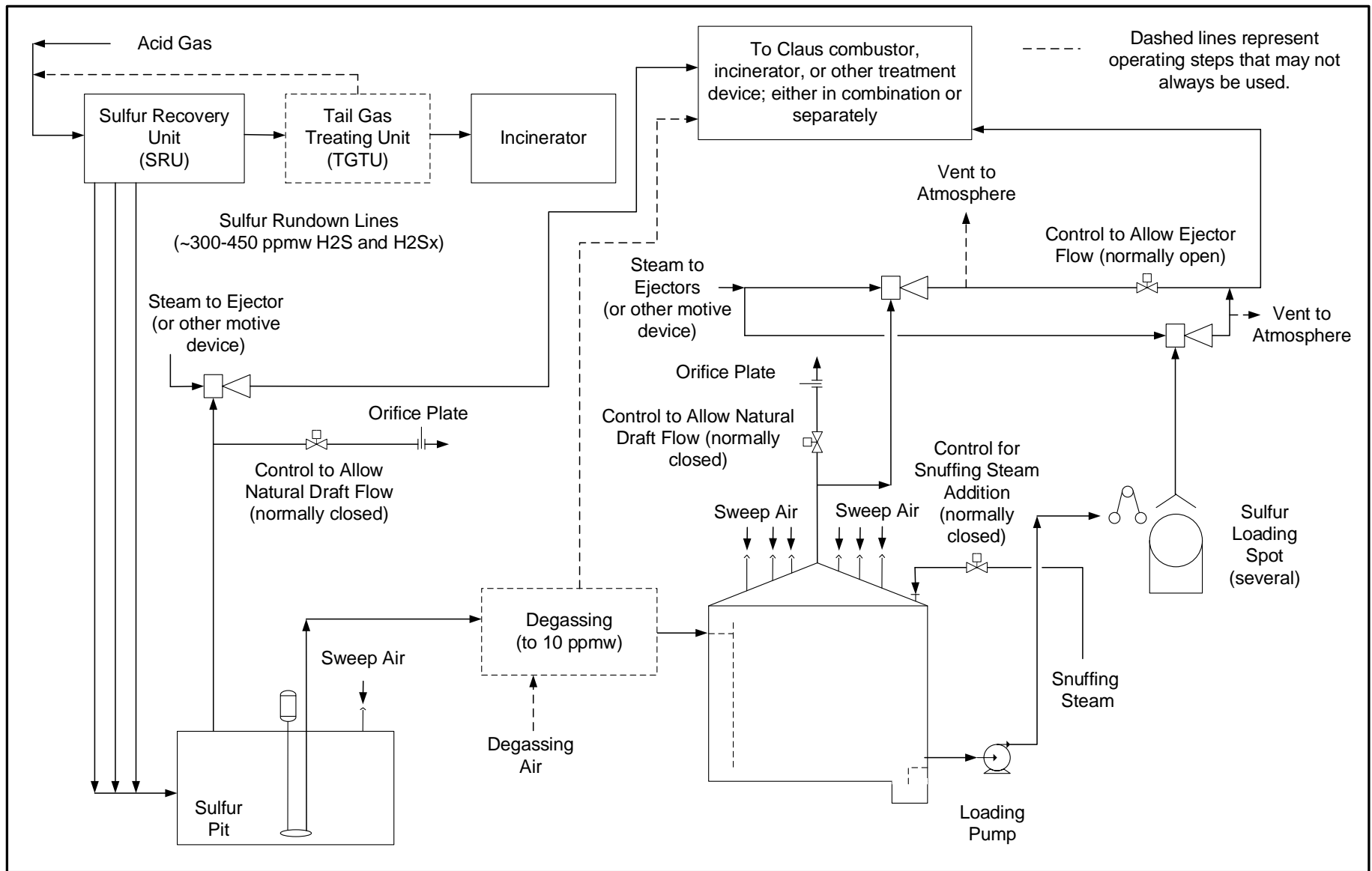


Figure 1: Molten Sulfur Storage and Handling System

2.0 Theoretical Background on H₂S Evolution – Exploring the Possibility of a First-Principles Model

This section will focus on providing a brief theoretical background of H₂S evolution to provide insight into the mechanisms that influence H₂S evolution. The following is not intended to be an exhaustive discussion of mass transfer processes but is intended to provide enough background to connect underlying mechanisms that influence mass transfer to the properties and operating conditions of the molten sulfur handling system.

The rate of H₂S evolution is a complicated, multistep transport process involving mass transfer with chemical reactions in both the liquid and vapor phases. Generally, the rate processes considered depend on many physical and transport properties of the fluids as well as the equipment design and operation. Physical and transport properties are dependent on the temperature, pressure², and composition of the fluids. The vapor-liquid interface as well as the mixing characteristics for each phase are heavily influenced by equipment design and operation. Therefore, the H₂S evolution rate may vary as a function of conditions and design/operation choices throughout the sulfur handling process.

During H₂S evolution, free, dissolved H₂S transfers through the molten sulfur to the vapor-liquid interface and desorbs. Once desorbed, H₂S transfers from the vapor-liquid interface into the bulk vapor. As H₂S transfers out of molten sulfur, the H₂S_X present in the molten sulfur depolymerizes to create additional free H₂S in the molten sulfur which can subsequently degas. Under circumstances where oxygen or SO₂ are present, additional reactions may take place in both the vapor and liquid phases leading to accelerated loss of H₂S from the molten sulfur. Figure 2 presents these various mechanisms in terms of mass transfer or transport resistance (mass transfer analogy for an electrical circuit diagram).

H₂S will evolve from the molten sulfur until phase and chemical equilibrium are achieved at the new conditions. Achieving equilibrium is not instantaneous but rather occurs at a finite rate - each of the previously listed steps occurs at a finite rate. The overall rate of H₂S mass transfer can be defined by the concentration difference (driving force) of H₂S in the liquid and vapor phases and an overall mass transfer coefficient that represents the underlying mass transfer properties and processes of the system in terms of a mass transfer “velocity”. As illustrated in Figure 2, the overall mass transfer coefficient is actually representing a network of rates occurring in parallel and in series. Parallel rates are additive whereas rates in series are limited by the slowest step.

Resistance terms in Figure 2 include vapor and liquid mass transfer (k_L, k_G) and chemical reaction kinetics. Without oxygen, only H₂S_X depolymerizes in the molten sulfur ($k_{H_2S_X}$). When oxygen is present, several reactions can occur in the vapor and liquid ($k_{rxn}^{*,G}, k_{rxn}^{*,L}$), greatly increasing the rate of H₂S evolution. The Claus reaction for both phases is indicated in short-hand notation by the combination of H₂S and/or H₂S_X reacting to form elemental sulfur “S”.

² Note that pressure is not a practically important parameter in most molten sulfur handling systems, where equipment is typically operating at or near atmospheric pressure.

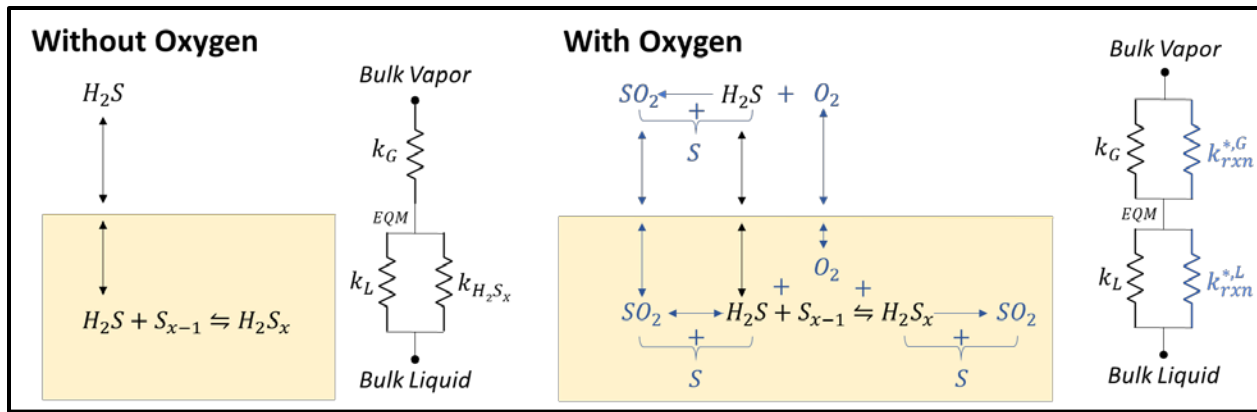


Figure 2: The transport resistance network for H₂S evolution with and without oxygen.

The following sections discuss the individual components of the mass transfer network represented in Figure 2 and discuss the dependence of each component on physical and transport properties of the fluid and ultimately the equipment design and operation.

2.1 Mass Transfer

2.1.1 Mass Transfer Coefficients

Mass transfer coefficients represent both diffusive and convective mass transfer mechanisms. Both mechanisms are relevant for H₂S transfer in molten sulfur handling equipment and are discussed in this section.

Mass transfer in unmixed, quiescent/stagnant fluids occurs solely by diffusion. The rate of transfer is proportional to the concentration gradient; mass transfer is faster with larger concentration difference, but slower over longer transfer path lengths. The diffusion coefficient is the proportionality constant between the mass transfer rate and concentration gradient, and it is dependent on the properties of the molecule being transferred and the media in which it is being transferred (e.g., physical properties of the media).

In the context of molten sulfur handling equipment, diffusion will be important to overall H₂S transfer rates when the sulfur and/or vapor phase are stagnant. If an air sweep is applied, the vapor space should not be stagnant in most cases. However, molten sulfur may well be stagnant or moving slowly enough to be approximated as stagnant when sulfur is not actively being transferred in or out (e.g., the sulfur in a tank or pit without mechanical agitation or pump recirculation will move only based on free convection due to temperature gradients, which is a slow process). Diffusivity in liquids is a strong function of viscosity and mass transfer rates can be very slow for viscous fluids over long distances (e.g., from the bulk of the sulfur in a tank or pit to the surface of the sulfur). Because the geometry of the tank and pit system is well-defined and the properties of molten sulfur are well-known, the assumption of a stagnant liquid in a sulfur tank or pit allows for a tractable analytical solution for mass transfer in the liquid phase. However, although tanks and pits may be represented as stagnant liquids and/or vapors under some conditions, loading operations cannot be represented by a stagnant liquid or vapor phase.

The mass transfer rate can be greatly increased by bulk transport (convective mass transfer) caused by turbulence or by agitation – mass transfer coefficients are used to quantify the impact of bulk transport. Mass transfer coefficients correlate the overall transport rate to physical and transport

properties (including diffusion coefficients) of the fluid and the flow conditions within the process equipment or piping.

During transport and storage of molten sulfur, forced convection may occur resulting from pumping, splashing, and sparging in equipment and piping. The introduction of sweep air through the headspace of equipment will also serve to mix or agitate the vapor phase (and potentially the vapor-liquid interface). Therefore, the design and operation of each piece of equipment will have a large influence on the internal mixing occurring within each phase and would need to be captured within the mass transfer coefficients for any model of the H₂S transfer. Mass transfer coefficient correlations exist for a wide variety of process equipment, including tanks and vessels and some could potentially be used in the context of the molten sulfur pit, tank, or loading. However, the validity of the mass transfer correlations for the specific situation in molten sulfur handling systems would not be proven until data specific to the molten sulfur handling equipment was collected to support their use.

2.1.2 Interfacial Area

Contact area between phases must be present for mass transfer to occur. The greater the surface area, the more likely it is for a molecule to transfer across the boundary. Surface area can be created by agitation and turbulence of the fluids as well as the use of physical objects such as mass transfer packings or other contact internals. Fluid break-up and spreading increases the interfacial area for mass transfer to take place.

The contact area for mass transfer and the degree of internal mixing is heavily influenced by equipment design and operation. For example, in a sulfur tank or pit, the interfacial area may be readily calculated when the sulfur is stagnant; however, if sulfur transfer creates rapid movement of the sulfur in the tank or pit, the vapor-liquid interface may experience splashing, oscillation, shearing, etc. which may enhance the area available for mass transfer. This represents a challenge of “modeling” H₂S evolution – while the average rate of H₂S transfer may be reasonably represented by a “quiet” interface and the associated area for mass transfer, there may be periods of enhanced H₂S degassing corresponding to turbulence at the interface. Making measurements of H₂S in the vapor space of equipment during these transitional periods may be one approach to assessing the importance of these disturbances on actual mass transfer rates. For sulfur loading, the interface is difficult to define and may change through the loading process and constant agitation of the sulfur should be expected. Modeling of the interfacial area for sulfur loading is not likely practical in most cases and limits the potential usefulness of modeling mass transfer for loading processes.

2.2 Reaction Rates

H₂S and H₂S_x form an equilibrium amongst themselves and may undergo several additional reactions including direct oxidation to form SO₂ and elemental sulfur as well as the Claus reaction. Reaction mechanisms for H₂S degassing are presented in the literature and summarized for convenience in the Appendix of this paper [7]. Since H₂S_x is non-volatile, it reacts in the liquid phase only, whereas H₂S can react in both phases. Each of these reactions occurs at a rate proportional to concentration and the phase temperature. Under stagnant conditions, H₂S_x depolymerization is very slow, requiring up to 12-24 hours to reach equilibrium [8]. To increase the rate of polymer decomposition, degassing equipment often uses sparging gases, spray systems, and catalysts. In the absence of a designed degassing unit, sweep air in storage systems may indirectly serve the same function to enhance degassing of molten sulfur by introducing oxygen and creating turbulence.

Note also that chemical reactions are closely coupled to mass transfer in systems such as the molten sulfur handling equipment. Reactants and products undergo convection and diffusion to-and-from reaction sites, and reactions produce and consume species which effect mass transfer by altering concentration gradients. For example, for oxidation and Claus reactions, the transport of the reactants across the vapor-liquid interface or within phase concentration gradients may be slower than the reaction kinetics themselves. This coupling of reaction and mass transfer (sometimes referred to as the reaction-diffusion problem) often requires numerical solutions (i.e., computer simulation) for the mass transfer rates and represents an obstacle to a simple modeling framework for H₂S evolution in molten sulfur handling system. Even aside from the modeling complexity, accurate modeling of the chemical reactions requires reaction kinetics constants for all relevant reactions in the system - while simplifying assumptions (e.g., pseudo-first order reactions) can reduce the number of kinetic parameters required, they do not eliminate the need for good data on reaction kinetic parameters at the conditions of the operating system. This represents another challenge and source of uncertainty when attempting to model the H₂S transfer in sulfur handling equipment.

2.3 *Obstacles to a First-Principles Mass Transfer Model*

The preceding sections provided a high-level overview of the mechanisms associated with mass transfer of H₂S in molten sulfur handling systems. One goal of reviewing the theoretical aspects of H₂S evolution is to explore the possibility of building a first-principles mass transfer model to represent H₂S evolution and mitigate some of the shortcomings of the commonly used assumptions that will be reviewed in subsequent sections (e.g., Section 3.2). However, the theoretical discussion also included the challenges or limitations of representing some of the underlying mechanisms and parameters representing mass transfer for the case of the molten sulfur handling system. For example, the sulfur loading process is significantly complicated by the constantly changing gas-liquid interfacial area available for mass transfer, making it an essentially intractable mass transfer problem for modeling without collecting system and equipment-specific data (e.g., a lumped mass transfer coefficient and area parameter for the loading system).

The Appendix to this report formulates a generic first-principles model, including the representative differential equations. However, the first-principles model cannot be solved in its full form without simplifying assumptions or without a numerical solution for the system of equations that results. In addition, some of the parameters in the first principles model may include significant uncertainty (e.g., enhancement factor to represent chemical reactions) or require collection of additional data specific to the system being evaluated (e.g., mass transfer coefficient data). Therefore, the practical utility and value of the first-principles model is very limited in industry applications and is not of further interest in this paper. Instead, the following sections will review commonly applied industry assumptions to estimate H₂S evolution and investigate the potential to use experimental data that has already been collected to estimate H₂S evolution.

3.0 Estimating H₂S Evolution in Practice

3.1 *Overview of H₂S Evolution Estimation*

Figure 3 is a conceptual diagram of an example molten sulfur handling system from the SRU through sulfur loading that will be used to illustrate the potential impacts of H₂S evolution assumptions on the design of the system. Note that there are alternative configurations, equipment (e.g., different

motive devices), and a variety of vent gas disposition approaches that are covered in more detail elsewhere in the literature (e.g., [9]).

One important consideration for the subsequent discussion and estimates of H₂S evolution rates is the end-use or goal of estimating H₂S evolution rates. Two common reasons to estimate H₂S evolution rates are the following:

- 1) Calculate the sweep air required to keep the equipment headspace and vent system safely below the LEL of H₂S (e.g., 25% of LEL).
- 2) Estimate the composition and/or emissions rate of H₂S in the vent vapors from the sulfur handling equipment.

It is important to note that these two purposes are not necessarily complementary – for example, a more conservative estimate of H₂S evolution may be desired for sweep air estimates while an estimate of composition or emissions rates (e.g., for design of downstream treating equipment) may necessitate a more representative H₂S evolution rate for the process. In this paper, the focus will be on sweep air rate estimates, but comments and discussion regarding the estimate of H₂S evolution for vent gas composition predictions will be added when particularly important or relevant.

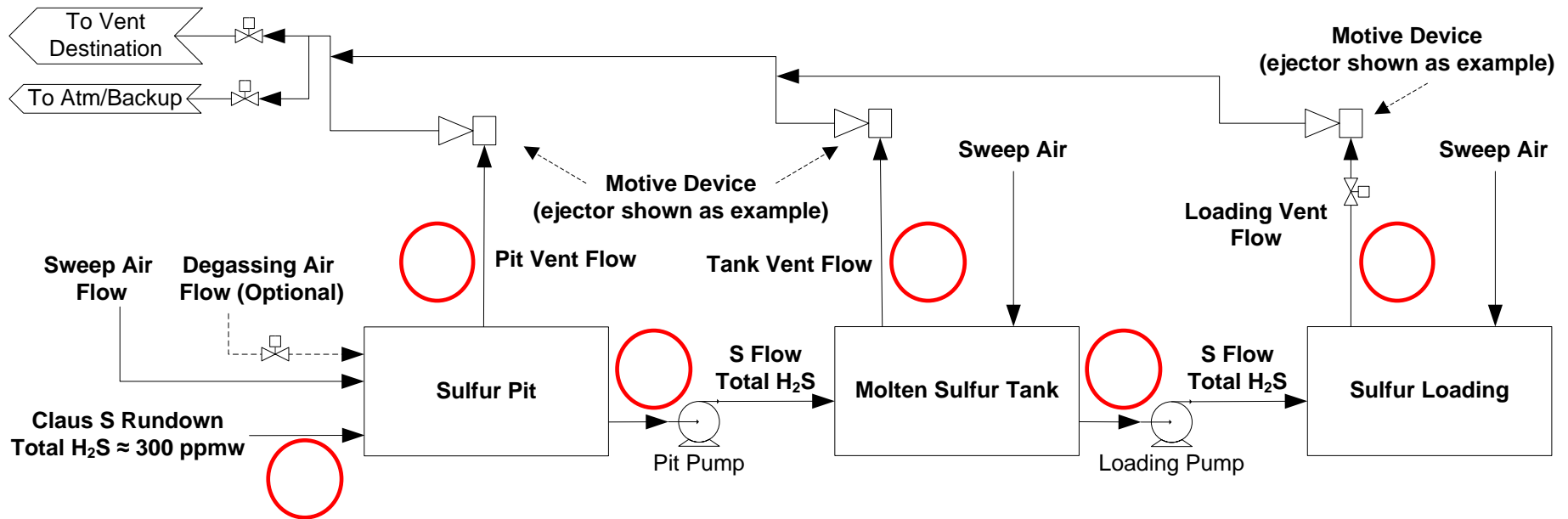


Figure 3: Example Molten Sulfur Handling System - H₂S Material Balance and Sweep Air Requirements. Individual air sweep and motive device per source. Originally published in [9]. Points in red denote H₂S measurement points. These are discussed in Section 6.1.

3.2 *Heuristics to Estimate H₂S Evolution Rates*

This section will focus on heuristics that can be used to estimate H₂S evolution rates, including discussion on the logic behind the assumptions. The section will conclude with estimates of sweep air rates for an example case outlined using the assumptions reviewed. The consequences of selecting a specific set of assumptions on the operation and design of the molten sulfur handling system will also be summarized.

3.2.1 *Continuous vs. Batch Operation*

One high-level assumption that dictates the method for H₂S evolution calculations is the operating mode (batch vs. continuous) of each unit operation in the sulfur handling system. This assumption is not usually made explicitly in calculations of H₂S evolution – rather, choices like using molten sulfur flow rate instead of the volume of sulfur and residence time in the equipment as the basis for estimation of the H₂S evolution imply a specific operating mode (i.e., continuous). However, it is important to compare the assumption implied in the H₂S evolution calculations to the actual operating mode of the equipment to understand the impact on the accuracy of the calculations. In addition, experimental data may be available that is consistent with a specific operating mode (usually batch), so using that data properly requires understanding the basis for the H₂S evolution calculations. In practice, the way sulfur handling equipment is operated may vary site-to-site. Table 1 describes common operating modes for the individual storage and handling steps, allowing for the fact that the details may vary in practice.

Table 1: Operating Mode of Sulfur Handling Equipment

	Sulfur Pit	Sulfur Tank	Sulfur Loading
Actual Operating Mode	Semi-Batch <u>Sulfur Feed</u> : Continuous <u>Sulfur Withdrawal</u> : Intermittent <u>Sweep Air</u> : Continuous	Semi-Batch <u>Sulfur Feed</u> : Intermittent <u>Sulfur Withdrawal</u> : Intermittent <u>Sweep Air</u> : Continuous	Semi-Batch <u>Sulfur Feed</u> : Continuous during batch loading. <u>Sulfur Withdrawal</u> : NONE <u>Sweep Air</u> : Continuous ^{Note 2}
Approximation for Continuous Operation	Assume sulfur enters and leaves continuously at the sulfur make-rate of the SRU.	Assume sulfur enters and leaves continuously at either the sulfur make-rate or the upstream feed pump rate to the tank.	Assume sulfur enters continuously at either the sulfur make-rate or the upstream feed pump rate to loading.
Approximation for Batch Operation	Estimate the residence time of sulfur in the pit based on the working capacity of the pit and the sulfur make-rate. Evaluate the liquid phase as a batch system operating from time = 0 to time = residence time.	Estimate the residence time of sulfur in the tank based on the <u>average</u> ^{Note 1} working capacity of the tank and the sulfur make-rate. Evaluate the liquid phase as a batch system operating from time = 0 to time = residence time.	NONE ^{Note 3} - Batch volume changes continuously throughout loading.
<p>Notes:</p> <ol style="list-style-type: none"> 1. The working capacity is an average value in the case of the tank since filling and discharge may vary over time, creating varying tank levels with time. 2. For loading operations, the air does not actively sweep the head space, but is typically pulled in at the connection of the loading arm assembly to the vessel where the air is mixed with recovered vapors. 3. A semi-batch calculation with continuous feed and varying batch volume would be required. 			

The initial focus of this paper is on the assumption of continuous operation for each of the unit operations since this is the simplest and most common assumption for the H₂S evolution analysis. Batch calculations are re-visited in Section 4.1.

3.2.2 Sulfur Make-Rate vs. Sulfur Pump Rate

With the underlying assumption of continuous operation of the sulfur handling system, one of the first choices that must be made in calculating the H₂S evolution rate is the molten sulfur flow rate basis (which in turn sets the H₂S flow rate entering unit operations with the sulfur). As noted, two options for the molten sulfur flow basis will be considered in this paper:

- 1) Sulfur Make-Rate: Using the sulfur make-rate in the continuous calculation effectively represents an “average” rate of H₂S evolution for the actual dynamic operation of the system (i.e., it should be identical to assuming the H₂S evolved at a steady rate over a “batch” lifetime in one of the sulfur handling processes).

- 2) Sulfur Pump Rates (Pit-to-Tank & Tank-to-Loading): Using the sulfur pump rate as part of a continuous H₂S evolution calculation represents a peak or “instantaneous degassing” rate by assuming that all of the H₂S that enters the system at the pump rate is capable of evolving immediately (vs. averaging this H₂S content over time, as the sulfur make-rate implies).

The molten sulfur pump rate represents a more conservative calculation scenario and while it is used in a calculation that represents steady-state continuous operation of the system, it is intended to represent a dynamic scenario where H₂S evolves at a higher rate during the period when sulfur is pumped into equipment (a proxy for “instantaneous degassing” of H₂S entering the equipment). Therefore, a sweep air flow rate calculated based on this “peak rate” of H₂S evolution associated with the pump rate of sulfur represents a worst-case scenario for sweep air requirements. Additional considerations regarding the use of sulfur pump rates in the H₂S evolution calculations include the following:

- When sulfur is pumped into a storage vessel, such as a tank, specific design practices and features can limit agitation of the sulfur and prevent the “instantaneous” degassing implied by using the pump rates. Examples of these design features include:
 - Down pipe that feeds sulfur well-below the existing sulfur liquid-level in the tank (often within a few inches of the bottom of the tank). This prevents splashing of sulfur and minimizes agitation. Furthermore, the “fresh” H₂S that enters the tank must migrate from the bottom of the tank to the gas-liquid interface before it is transferred to the vapor phase.
 - Limiting sulfur velocity in the feed piping (via the size of sulfur feed piping) also limits agitation and/or splashing of sulfur.
- For loading operations, the sulfur pump rate may be a more representative basis for calculations since there is a higher likelihood of physical agitation of the sulfur during transfer that can create periods of higher-than-average H₂S off-gassing. Feeding the sulfur below the liquid level is often not practiced in loading operations.
- When the goal of the H₂S evolution calculations is to estimate the steady-state composition of the vent stream or average H₂S emissions from the equipment as opposed to estimating sweep air rates, the sulfur pump rate is likely not an appropriate basis (will overestimate H₂S content of the vent streams).

Both options (sulfur make-rate and sulfur pump rates) will be evaluated in this paper to illustrate the impact of the assumptions.

3.2.3 H₂S Evolution Heuristics

The preceding assumptions define the amount of H₂S entering the system, which in turn serves as the basis for H₂S evolution calculations. Absent rigorous mass transfer calculations for the molten sulfur handling equipment, additional assumptions are needed to determine how much of the incoming H₂S evolves in each process step. The following sections outline heuristics to estimate the rate of H₂S evolution.

All H₂S at Any Point Assumption

The first commonly used assumption for H₂S evolution in molten sulfur handling systems is to assume that all of the H₂S (both as H₂S and H₂S_x) entering the system may evolve at any point downstream. This assumption is specifically cited [3] in the context of estimating sweep air requirements (not for material balance or vent gas composition estimates).

The logic behind the assumption is clear – i) H₂S content is rarely, if ever, monitored continuously in the liquid or vapor phase in sulfur handling systems, ii) individual molten sulfur systems may have varying designs and operating conditions making general statements or calculations for the rate of H₂S evolution difficult/impossible, and iii) conditions in the system may vary (e.g., as a result of short-term transients or long-term operational changes). These issues make specific assumptions about H₂S evolution difficult to validate and can potentially create a safety or environmental hazard in the system if the H₂S evolution rate is estimated improperly. Furthermore, specifying a bulk sweep air flow rate to dilute the expected H₂S evolving in a vessel does not guarantee that the air is well-distributed or that the vapor space is well-mixed, which may lead to pockets of the vapor space where the H₂S concentration is higher than the design intent of the sweep air flow. The higher sweep air flow that is dictated by assuming all of the H₂S can evolve at each point may yield better headspace mixing and air distribution [3]. Therefore, the most conservative approach to estimating H₂S evolution rates in sulfur handling systems is to assume all of the H₂S can evolve at any point in the system to represent a potential worst-case scenario everywhere in the system.

Potential shortcomings or over-simplifications associated with the “All H₂S at Any Point” assumption include the following:

- The assumption is not consistent with the material balance for total H₂S in the system, i.e., more H₂S can be estimated to evolve than enters the system. As noted, this may be acceptable if the only use of the assumption is to estimate a required sweep air rate at each point in the system (intended use of the assumption). However, if the assumption is also used to estimate the H₂S content of the vent gas stream at each point in the system, it can lead to significant overestimation of the average H₂S content entering downstream systems for managing the vent vapors (e.g., treatment system). Therefore, a second set of assumptions/calculations may be required if H₂S evolution rates are needed for both sweep air estimates and vent gas composition estimates.
- The “All H₂S at Any Point” assumption may represent a simplification of multiple mechanisms in the mass transfer process when coupled with the sulfur pump rate to represent “instantaneous evolution” of H₂S:
 - Instantaneous degassing of H₂S from the sulfur neglects mass transfer resistance.
 - Instantaneous degassing of all of the H₂S implies that both the free H₂S and H₂S chemically bound as hydrogen polysulfides (H₂S_x) can evolve instantaneously. This requires neglecting mass transfer resistance (free H₂S transfer to vapor phase) and treating the chemical conversion of H₂S_x to H₂S as instantaneous, which is inconsistent with experimental data on the subject [7].

The use of the “All H₂S at Any Point” assumption may be prudent in the absence of any additional information on H₂S evolution in the system and when the goal is to apply the most conservative estimate of sweep air. However, it may have unintended consequences that need to be carefully considered alongside the level of conservatism provided by other design choices (e.g., design margins) and the end-use of the assumption (i.e., not intended to estimate H₂S composition of vapor spaces/vents).

Free H₂S at Any Point Assumption

A modification of the “All H₂S at Any Point” assumption is to relax the constraint that the total H₂S (as both H₂S and H₂S_x) can evolve at each point and only allow for the free H₂S in the incoming sulfur to evolve at each point. This assumption is primarily useful in the case where the goal is to represent “instantaneous degassing” via application of the sulfur pump rate as the H₂S feed basis but the evolution of all H₂S (as both H₂S and H₂S_x) is deemed overly conservative or inconsistent with the physical reality of the system. Therefore, in this paper, the “Free H₂S at Any Point” assumption will only be applied when used alongside the sulfur pump rate basis.

In order to apply the “Free H₂S at Any Point” assumption, the speciation of H₂S in the molten sulfur at the operating conditions of the equipment must be known (i.e., the split between free H₂S and H₂S_x). This information may be obtained via field measurement (H₂S measurements in molten sulfur frequently include speciation) or via literature correlations [10].

H₂S Material Balance Assumption

An alternative to the “All H₂S at Any Point” assumption enforces the H₂S material balance for the sulfur handling system. This approach necessitates that the cumulative H₂S that evolves throughout the system must be equal to or less than³ the total H₂S (as H₂S and H₂S_x) that enters the system. In Trimeric’s experience, the basis for developing H₂S evolution rates consistent with an overall H₂S material balance occurs via measurement of the total H₂S in the molten sulfur at several points through the sulfur handling system (e.g., sulfur rundown, leaving the sulfur pit, leaving the sulfur tank, and at the loading rack). By taking measurements of total H₂S at these individual points, an estimate of the fraction of H₂S that evolves at discrete points in the system can be developed (e.g., 50% of the H₂S evolves at the pit, 25% evolves at the tank, and the remainder evolves at loading).

Note that H₂S is measured by field sampling molten sulfur at discrete points in time (i.e., not continuous measurements). Therefore, the fractional H₂S evolution estimated from these measurements represents the system operation at that point in time and may not be representative of average or maximum H₂S evolution rates. For example, this approach may miss peak H₂S evolution rates that occur in practice in the system (e.g., time period when sulfur is transferred into a tank or truck) and may underestimate sweep flow requirements as a result. However, the fractional evolution measurement can be coupled with other conservative assumptions, such as

³The “H₂S Material Balance” assumption does not require that all of the incoming H₂S evolves in the system (i.e., only some fraction of the total H₂S that enters the sulfur handling system from the Claus rundown may evolve from the liquid phase across the entire handling system). This represents a degree of freedom in the calculation and ideally is informed by field measurements.

using the molten sulfur pump rates instead of the sulfur make-rate, when additional margin is desired in sweep air calculations.

While this approach appears to address the potential overestimation of H₂S evolution from the “All H₂S at Any Point” assumption, it carries its own potential shortcomings and risks:

- The biggest shortcoming of this approach is that field measurements may not be available to support the H₂S evolution estimate at each step. This is particularly true when a new system is being designed and there is no existing reference system with a similar design.
- As noted, field measurements of molten sulfur H₂S content may miss dynamics of periods of higher H₂S evolution (e.g., during sulfur transfer periods) or may not be representative of typical operation for the system.
- When the fractional evolution estimates for H₂S are used with a pump rate (instead of the sulfur make-rate), the H₂S material balance is not maintained, despite the intent of this approach. Therefore, it may still be necessary to have separate estimates of H₂S evolution to calculate sweep air flow (e.g., calculations with the pump rate) and to calculate the composition of the vent gas (e.g., calculations with the sulfur make-rate).

Sulfur Pit H₂S Evolution Rule-of-Thumb

Another H₂S evolution assumption is sometimes referenced in documentation for sweep air requirements for sulfur pits and in discussion with operators who have designed molten sulfur handling systems for sweep air. The assumption is focused on the sulfur pit and not downstream handling equipment and indicates that half of the total H₂S entering the sulfur pit will degas in the residence time of the sulfur in the pit. To Trimeric’s knowledge, this assumption is not explicitly documented alongside a technical basis in writing in any literature we have encountered and appears to be more of an informal industry heuristic, though similar assumptions have been referenced elsewhere [3]. As such, it is important to use this assumption with care. It should also be noted that there is some experimental data that indicates the half-life of H₂S (H₂S and H₂S_x) evolution from the liquid-phase in a completely stagnant vessel (no sulfur agitation or vapor space air flow) is 24 hours (i.e., half of the H₂S will evolve in 24 hours) [7]. A 24-hour residence time is not uncommon for sulfur pits (sometimes referred to as “day pits”), so this sort of experimental data could be the basis for this rule-of-thumb.

For the purposes of this paper, this rule-of-thumb is really a specific case or subset of the “H₂S Material Balance” assumption described in the preceding section and will not be included in subsequent analyses or discussed further in this paper.

3.3 Sweep Air Estimate and Associated Consequences - Example Case Sulfur Tank

The various H₂S evolution assumptions outlined in preceding sections can be evaluated via an example case. The example calculations will focus on the sulfur tank to demonstrate the impact of the H₂S evolution assumptions – the impact of the assumptions on the sweep air rates

on the pit and loading areas will be directionally similar to the tank. The conceptual system in Figure 3 and the following specifications serve as the basis for the example case⁴:

- The sulfur make rate for the Claus SRU is 500 LTPD.
- Sulfur pump rates (Pit-to-Tank & Tank-to-Loading) are three times the sulfur make-rate = 1,500 LTPD (140,000 lb/hr).
- 300 ppmw H₂S + H₂S_X enters the sulfur pit in the rundown line.
- No degassing unit (in pit or out of pit) for the sulfur – i.e., undegassed sulfur only.
 - Note that this assumption can also represent the worst case for a system with degassing, e.g., if the degassing unit is out of service.
- A 25% approach to LEL of H₂S at 330°F (i.e., target 0.75 vol% H₂S in vent gas [11]) will be used to estimate sweep air requirements.
- For the “Free H₂S at Any Step” assumption, the ratio of free H₂S to total H₂S at 280°F (sulfur tank operating temperature) is 75% based on data from literature [10].
- For the “H₂S Material Balance” assumption, the following fractional H₂S evolution occurs at each step:
 - Sulfur Pit: 50% of total incoming H₂S evolves (150 ppmw H₂S remaining).
 - Sulfur Tank: 50% of remaining H₂S evolves (25% of total H₂S entering the system, 75 ppmw H₂S remaining).
 - Sulfur loading H₂S evolution is not required for this sulfur tank example.

The sweep air rate estimates for the sulfur tank based on the preceding assumptions (grouped as a matrix of cases in the analysis) are summarized in Table 2.

Table 2: Sweep Air Estimates as a Function of H₂S Evolution Calculation Basis and Assumptions

Sweep Air Estimates for Sulfur Tank (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
H ₂ 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

The table illustrates the wide range of sweep air rate estimates for the sulfur tank in this example. While the sweep air rate range presented (spans a factor of 12) reflects the specific details of this example (e.g., pump rates), the example case was defined to be a reasonable representation of an actual system. Therefore, the range of sweep air rates in this example should be representative of a situation that could be encountered in practice for an actual molten sulfur handling system.

⁴ Note: The specifications were defined strictly for the purpose of evaluating the example case in this paper (i.e., the conditions are not universally representative)

Other observations can also be developed by reviewing the cases in the table:

- Value of the “Free H₂S at Any Point Assumption”: When comparing Case 2a and 2b in the table, assuming only the free H₂S evolves (vs. the total H₂S) when using the pump rate reduces the required air rate by 25% (as expected, since 75% of the H₂S is free at the conditions of the sulfur tank). However, this is still the second most conservative estimate in the table and highlights that as the sulfur cools as it moves from the pit to the tank and eventually loading, more of the total H₂S that came from the sulfur rundown lines will enter the downstream operations as free H₂S. Therefore, the distinction between total H₂S and free H₂S becomes less significant as the sulfur cools after the pit.
- Enforcing the H₂S material balance (Cases 1c and 2c) yields the lowest sweep air rate requirements in the matrix, regardless of whether the sulfur make-rate or pump rate is used in this example. These cases reflect the potential value of having reliable H₂S measurements in the molten sulfur around the system as it may help justify using lower H₂S evolution rates in basis calculations.

As part of assessing the viability of the various H₂S evolution approaches, it is important to consider the context of the consequences of the specific method selected for the design. There are safety, cost, and operational consequences for both under- and over-estimating the H₂S evolution rate and corresponding sweep air rate. The following lists attempts to document some of the expected consequences.

Consequences of Overestimation of H₂S Evolution Rate and Sweep Air Rate:

- Generates additional species beyond the H₂S that was expected to evolve:
 - SO₂ may form via reaction of O₂ with H₂S, H₂S_x, or elemental sulfur (similar mechanisms govern sulfur degassing with air, where SO₂ is also known to form). Because the formation of SO₂ occurs most readily in the liquid phase, high sweep air rates serve to maintain a high partial pressure of oxygen in the vapor phase and agitate the air-sulfur interface to enhance the transfer of oxygen into the molten sulfur. This is an issue with degassed or undegassed sulfur. SO₂ is toxic (OSHA PEL = 5 ppm, 8-hour time-weighted average [1]) and represents an environmental hazard.
 - Excessive air rates may also lead to additional entrainment of elemental sulfur as droplets/fog, increasing the risk of plugging downstream piping or equipment.
 - If the vapor from the sulfur handling equipment is vented to atmosphere, the higher flow of air through the headspace may mean a higher total level of emissions from the equipment. In some cases, this may violate total emissions limits (e.g., SO₂) for a site.
- Increased heat loss from the system:
 - This is specifically relevant to molten sulfur tanks which are heated either via internal steam coils or external heat-trace panels (e.g., ControTrace). The sweep air represents heat loss for the tank and increases the cost of the heating system.
 - In addition, because sweep air is most commonly ambient air pulled in from the surrounding environment, the tank heating system must be designed for the worst-case scenario (e.g., cold winter day). A high sweep air rate with low ambient temperatures can lead to costly tank heating systems and/or lead to other

design/operating changes to maintain the target sulfur temperature (e.g., maintain a higher sulfur liquid level, reducing working capacity).

- Increased size of downstream piping, treating equipment, or other negative impacts:
 - Large vent gas flow rates will directly increase the size of all downstream vent vapor handling systems (piping, motive devices, treatment systems) and may significantly increase the cost of the vent vapor handling.
 - In some cases, the vent vapors may be traveling over long distances in the facility – the large piping, which will be heat-traced or jacketed, may represent a significant part of the overall system costs.
 - If the vent gas is recycled to the front-end of the Claus Unit (e.g., to the thermal reactor), the sweep air displaces combustion air fed to the system. The turndown of the existing system must be verified. In addition, if the vapor includes any water (e.g., via steam from an ejector), it can impact the performance of the Claus unit (impacts conversion via chemical equilibrium) [9].
 - If the H₂S evolution calculations are used to estimate the vent gas composition, over-estimation of the H₂S content can also lead to over-sized treating equipment and/or overestimation of operating costs (e.g., chemical consumption) that may impact investment decisions for the treatment process.

Consequences of Underestimation of H₂S Evolution Rate and Sweep Air Rate:

- Risk of generating explosive atmosphere in the vapor headspaces
 - The estimate of H₂S evolution could be inaccurate in general or there may simply be short periods where H₂S evolution is higher than expected by the design basis. In either case, an explosive atmosphere could form in equipment, representing a significant risk and undermining the purpose of the air sweep.
- Costly re-design of system components
 - While overestimation may lead to larger systems and higher initial costs (vent gas handling and treatment systems), if the system is built and more vent vapor capacity is needed to handle higher than expected H₂S evolution, the cost of expanding or modifying the system may be more significant than the initial costs of oversizing. This applies for both underestimated sweep air rate and underestimated H₂S content of the vent gas stream.

As the preceding discussion shows, while a major trade-off of the level of conservatism in H₂S evolution estimates is the cost of the system vs. safe operation, the consequences are more nuanced in practice (e.g., higher SO₂ emissions with higher sweep air rate). Therefore, there is a potential value to understanding the H₂S evolution process at a more fundamental level to either develop alternate approaches to estimate H₂S evolution rates or to help justify the use of a specific set of the assumptions discussed in this section.

The remainder of the paper will focus on alternate approaches to estimating H₂S evolution and other recommendations to offset the risk/uncertainty in H₂S evolution estimates.

4.0 Alternative Approaches to Estimating H₂S Evolution

This section will outline methods that use experimental data and simplifications of the first-principles approach to estimate H₂S evolution rates and corresponding sweep air rates. The results of the alternate approaches will be compared and contrasted with the results of the estimates presented in Section 3.0 and conclusions will be derived regarding the utility of the various calculation approaches presented in this paper.

4.1 Simplified Models and Experimental Data

4.1.1 Experimental Data – H₂S Half-Life

Sulfur degassing rates have been measured experimentally under a range of conditions by ASRL [7], [8]. Select experiments were chosen for the purposes of illustrating the use of experimental degassing data to estimate H₂S evolution – the studies selected are not intended to be representative of all available data. Key features of the selected experiments are summarized in Table 3.

Table 3: Summary of Literature Experiments

	ASRL Reference: [7]	ASRL Reference: [8]
Key Conditions	<ul style="list-style-type: none"> • Isothermal @140°C (284°F) • With & w/out sulfur agitation • With & w/out air sparging 	<ul style="list-style-type: none"> • Isothermal @135°C (275°F) • With & w/out sulfur agitation • With & w/out air sparging
H₂S Measurement	Measured H ₂ S _x loss	Measured Total H ₂ S loss
Derived Rate Parameters	H ₂ S half-life ^{See Note 1}	Raw data on H ₂ S loss vs. time ^{See Note 2}
Notes: <ol style="list-style-type: none"> 1) Half-life data derived from pseudo-first order regression of rates with measured H₂S_x loss. See reference for details. 2) Trimeric estimated half-life and rate constants from the data for illustration only. 		

For the purposes of this paper, only a select subset of the experiments summarized in Table 3 were considered:

- Air sparging is not relevant to sulfur storage (absent degassing equipment) and these experiments were not considered further.
- Experiments with and without agitation of liquid sulfur (i.e., well-mixed vs. stagnant) were included to bracket applicable conditions in sulfur storage conditions.

Note that for both datasets in Table 3, the intention of the researchers was to develop relative comparisons between the experiments in each paper to identify parameters that influence degassing (e.g., degassing effectiveness with and without catalyst, with and without agitation). The experiments were not developed with the intent of estimating H₂S degassing or evolution in commercial scale equipment and did not consider H₂S evolution in any context outside of sulfur degassing. As such, the experiments may have limitations when used alternate purposes, e.g., for representing a sulfur storage or handling process, including:

- Influence of both reaction and mass transfer limitations were apparent when representing the data as half-life values (and corresponding rate constants).
 - When deriving empirical parameters to represent physical mass transfer, the effects of experimental scale should not be present in the parameters (e.g., parameters should be derived from dimensionless form of underlying mass transfer equations). The effects of scale in the experiments are lumped into the half-life values and associated rate constants and this introduces significant uncertainty when applied to full-scale equipment.
 - Reaction kinetics for the complex system described in the Appendix are reduced to a single pseudo-first order constant, which ASRL carefully defined in the context of the degassing experiments and for conditions expected in commercial degassing equipment. However, it is unknown a-priori if the conditions for the pseudo-first order approximation are valid in the sulfur handling and storage systems operating system (e.g., oxygen may limit reaction rates).
 - The gas-liquid interface area and liquid volume should influence overall mass transfer rates in a reaction-diffusion system. Measuring these experimental parameters and deriving empirical mass transfer rate parameters independent of these scale-dependent parameters would allow application of the parameters to systems of different scales. In this paper, the half-life values reflect the specific experiments and have not been corrected for these scale effects.
- Agitation or mixing in actual sulfur equipment likely falls between the stagnant and vigorous agitation used in the experiments (e.g., mixing due to thermal gradients in operating equipment).
- Vapor space is not representative of actual storage and handling processes (i.e., sweep air is used in tanks and pits without degassing).
- Since initial free H₂S evolution occurs early in the experiments and is not captured in the half-life estimation in [7], these experiments may underestimate peak rates of H₂S evolution unless some accommodation is made for the free H₂S transfer in calculations.

Based on these limitations, we would not recommend using the experimental degassing data for H₂S evolution calculations in sulfur handling equipment as the sole means of defining the sweep air rate in the system. The experiments were not designed for that purpose, which is reflected in the aforementioned discussion. Nevertheless, this paper will use the literature data for H₂S evolution and sweep air estimates to illustrate the approach and compare the results to the heuristic methods discussed previously.

For the original raw experimental data and associated experimental details, the referenced ASRL documents should be consulted. Trimeric generalized the results in terms of half-life and associated rate constants for a subset of experiments. The results of this analysis are summarized in Table 4.

Table 4: Summary of H₂S Degassing Half-Life Estimates

Experiment	Liquid Conditions	Vapor Conditions	Half-Life	1st Order Rate Constant	Reference
			min	1/min	
ASRL 1a	Stagnant T = 140°C (284°F)	No Air Flow	1440 ^{Note 1}	4.81E-04	[7]
ASRL 1b	Stirred T = 140°C (284°F)	No Air Sparge	50 ^{Note 1}	1.39E-02	[7]
ASRL 2a	Stagnant T = 135°C (275°F)	No Air Flow	328 ^{Note 2,3}	2.11E-03 ^{Note 3}	[8]
ASRL 2b	Stirred T = 135°C (275°F)	No Air Sparge	36 ^{Note 2,3}	1.95E-02 ^{Note 3}	[8]

Notes:

1. Only H₂S_x loss in the liquid phase was measured in these experiments.
2. Total H₂S (H₂S + H₂S_x) loss in the liquid phase was measured in these experiments.
3. Reference [8] did not report half-lives or rate constants. These values were estimated by Trimeric from the data in the report strictly for illustration in this paper.

Key points from the half-life data include the following:

- For stagnant systems (1a vs. 2a), the half-life estimates from the two references differ greatly. This likely reflects the fact the reference [7] is only measuring the H₂S_x loss and was not intended to capture the initial free H₂S off-gassing, while reference [8] measured changes in free H₂S and the half-life reflects the associated higher rate of H₂S evolution.
- For stirred systems (1b, 2b), the half-life is much shorter for both experiments than their stagnant counterparts and the results are similar for both experiments (half-life < 1 hour). This implies that the stagnant system is mass transfer limited and therefore the rate constants in those cases include mass transfer resistance. With vigorous mixing, the system becomes more reaction limited and half-lives are representing the conversion of H₂S_x to H₂S more directly (though not necessarily representative of a true kinetic rate constant). **Given the similarity of the results for 1b and 2b, only 2b will be considered further in this paper.**

The H₂S half-life data provides a means to estimate a rate constant for H₂S transfer, but it does not directly predict mass transfer rates in the system of interest (e.g., sulfur tank). This requires a mass transfer model framework where the experimentally derived rate constant can be applied. As noted in Section 2.3, building a first-principles model is not practical in most cases. Therefore, two simplified modeling frameworks in the context of a sulfur tank will be outlined in the following section: CSTR and batch reactor.

4.1.2 CSTR and Batch Reactor Models

This paper will consider batch and continuously stirred tanks reactor (CSTR) modeling frameworks for application of the experimental rate constants. Both modeling approaches include several simplifications and assumptions (summarized in Table 5) to allow for a tractable analytical solution for a sulfur tank to be derived for use with the experimental rate constant data.

Table 5: Modeling Simplifications and Assumptions for CSTR and Batch Models

	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 period of 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) ^{Note 1:} Concentration everywhere is the same as the outlet H ₂ S concentration.	Ignored (Well-Mixed) ^{Note 1:} Concentration everywhere is the same at any given point in time.
Temperature	Isothermal @ 280°F (138°C)	
H₂S entering Tank	Total H₂S (H₂S + H₂S_x) = 150 ppmw ^{Note 2} Ratio of free H₂S to total H₂S at 280°F = 75% [11]	
Equipment Parameters for Modeling	<ul style="list-style-type: none"> • Sulfur Feed Rate = 500 LTPD • Tank Working Volume: 10,000 ft³ (~75,000 gal) • Residence Time^{Note 4} = 24 hours 	<ul style="list-style-type: none"> • Batch Volume^{Note 3:} 10,000 ft³ (~75,000 gal) • Batch Time: 24 hours • Number Sulfur Transfers During Batch: 16 (See text following table)
Notes: <ol style="list-style-type: none"> 1. In practice, a well-mixed liquid phase is not a good simplification for a sulfur tank since the sulfur is not actively agitated or mixed. The ASRL half-life rate constants reflect combined mass transfer and chemical reaction in a single lumped parameter. However, the lumped parameter represents a simplification vs. estimating equipment-specific mass transfer coefficients and may not be an accurate representation of mass transfer in storage systems. 2. Assumes half of total H₂S (300 ppmw) entering the sulfur pit evolves before reaching the tank. 3. Corresponds to 24-hours of sulfur capacity at make-rate. 4. Calculated as tank volume divided by volumetric feed flow rate (based on sulfur make-rate). 		

A few additional comments regarding the modeling approaches:

- As discussed, the sulfur tank is actually a semi-batch operation, often with inconsistent loading and unloading periods, which is not amenable to a simplified model.
- **For this paper, a regular pattern of 16 batch transfers (unloading and reloading of sulfur) will be assumed to occur over the 24-hour batch life (i.e., the 16 transfers will turn the tank volume over 1 time in 24 hours).** This approach will capture the effect of intermittent transfer of fresh sulfur to the tank during a 24-hour sulfur “batch lifetime”.
- **For the batch modeling case, the concentration of H₂S in the tank for the initial fill (time=0) of sulfur will be 150 ppmw total H₂S everywhere in the tank. This is not a realistic representation of any initial condition in an actual sulfur tank as the tank will always be loaded over some period of time and H₂S will evolve as the tank is loaded.** However, this initial condition is unknown and represents a short-lived operating scenario (i.e., when the tank is first filled with sulfur).
- The batch modeling is also based on the calculation that the entire volume of sulfur in the tank loses H₂S at the same rate because the H₂S concentration in the tank is the same everywhere at all times. This is a condition of the batch calculation approach. The potential pitfall with this approach is that the rate constant for the batch calculation was derived from a small-scale experiment, with any mass transfer limitations lumped into the rate constant. Mass transfer is length-scale dependent, so when the same rate constant is applied to a full-scale sulfur tank, the estimated H₂S evolution may be too high (mass transfer resistance in the large batch is underestimated).
- The treatment of liquid phase mass transfer in these models represents the biggest simplification and source of uncertainty in the results.

Considering the preceding assumptions and limitations, the calculations for both models can start with the following H₂S balance around a control volume:

$$\frac{VdC_{H_2S}}{dt} = QC_{H_2S}^{In} - QC_{H_2S}^{Out} + VR_{H_2S} \quad 1$$

Where:

- V = Volume of tank or other handling equipment
- C_{H_2S} = Concentration of H₂S (into or out of system)
- Q = Volumetric flow rate into, or out of, the system volume
- R_{H_2S} = Net production or consumption of H₂S by chemical reactions

For the CSTR, Equation 1 can be simplified for steady state operation, the fact that the outlet concentration of H₂S is equal to the H₂S concentration everywhere in the system, and by substituting the pseudo-first order rate expression for H₂S consumption from the ASRL experiments. The simplifications yield the following re-arranged expression to solve for the H₂S concentration in the system/at the outlet:

$$C_{H_2S}^{Out} = \frac{C_{H_2S}^{In}}{k_{exp}\tau + 1} \quad 2$$

Where:

- τ = Residence time of the system (calculated as V/Q)
- k_{exp} = Pseudo-first order rate constant derived from half-life data from ASRL experiments.

For the batch reactor, Equation 1 can be simplified for no flow in or out of the reactor and by substituting the pseudo-first order rate expression for H₂S consumption from the ASRL experiments. After integration over the batch lifetime, the simplifications yield the following expression to solve for the H₂S concentration at the end of the batch period:

$$C_{H_2S}^{Final} = C_{H_2S}^{Initial} e^{-k_{exp}t_{Batch}} \quad 3$$

Where:

- t_{Batch} = Sulfur batch lifetime.
- k_{exp} = Pseudo-first order rate constant derived from half-life data from ASRL experiments.
- C_{H_2S} = Concentration of H₂S (initial or final concentration in batch)

These expressions can be used with the experimental rate constants to estimate the H₂S evolution from the sulfur tank at the given conditions in this paper. The following sections will summarize the results, focused on sweep air rate predictions.

4.1.1 CSTR Model Results Interpretation

The CSTR modeling approach yields a single H₂S evolution rate as it is a steady-state, continuous model. Because the CSTR model is a steady-state model, it strictly enforces that the H₂S evolution rate is always consistent with the H₂S entering and leaving the system at any point in time, and does not allow for periods where higher or lower H₂S evolution rates might occur and still comply with the material balance over a broader window of time. As discussed in the next section, the batch analysis with sulfur transfer will eventually approach the same steady-state result as the CSTR, but provides additional data points for the changes in H₂S evolution rates over time that the CSTR model cannot provide.

4.1.2 Batch Reactor Model Results Interpretation

Three distinct results can be derived from a batch reactor since the H₂S concentration in the batch and corresponding H₂S evolution vary with time:

- 1) Initial/Maximum Rate: Initial rate of H₂S evolution from the sulfur batch.
- 2) Average H₂S Evolution Rate: Average H₂S evolution over the entire batch lifetime.

3) Final/Minimum Rate: Final steady-state⁵ rate of H₂S evolution

Figure 4 below depicts the batch modeling results using the half-life data from experiment 2a in Table 4. The sweep air rate represents the air flow required to keep the vapor space at or below 25% of LEL of H₂S at 330°F. The graph identifies the initial (max) sweep air rate (2,405 lb/hr), the average sweep air rate over the batch life (1,046 lb/hr), and the final (minimum) sweep rate (591 lb/hr). The large range in the required air rates is explained by considering the underlying batch modeling approach and the experiments that serve as the basis for the rate constant in the batch calculations. Equation 3 indicates that the H₂S concentration will decay exponentially with time as function of the H₂S concentration at that moment in time. This solution for the batch model comes directly from the fact that the H₂S evolution rate is modeled as a first-order “reaction” – that is the rate of H₂S evolution is directly proportional to the H₂S concentration in the sulfur. This is consistent with the experiments which measured the H₂S concentration over time in a batch of sulfur and ultimately derived a first-order rate constant from exponential decay in the data. Therefore, it is expected that the highest H₂S evolution rate will occur at the start of the batch when the H₂S concentration in the system is at its highest and decay rapidly at first. The inclusion of sulfur addition/withdrawal in the model allows a steady-state condition to be approached eventually.

⁵ The batch reactor analysis only reaches steady state because of the periodic addition of sulfur with H₂S. Without this addition, the H₂S content of the sulfur would continue to decay over time.

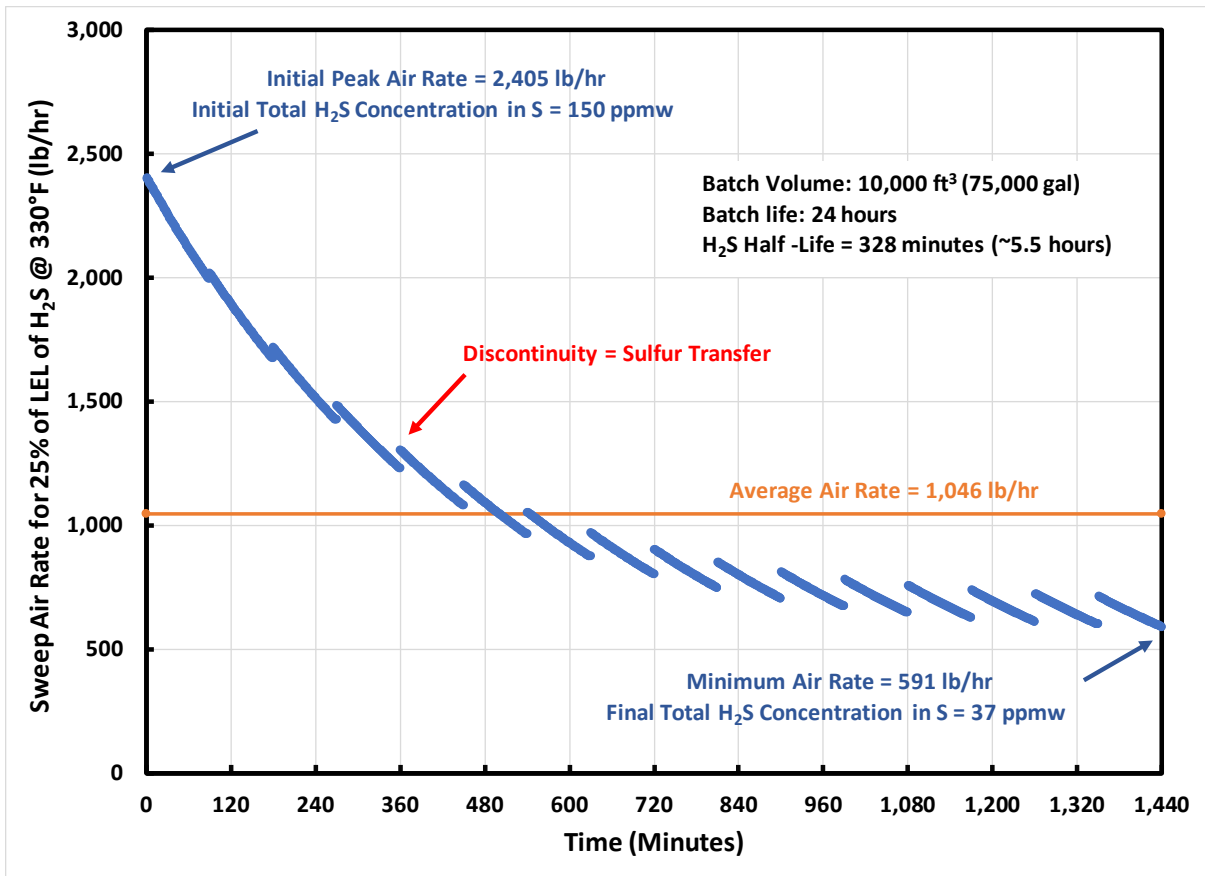


Figure 4: Modeling results from batch model of a sulfur tank using experimental rate constant for H₂S evolution from experiment 2a in Table 4.

Determining which condition is most appropriate for the sweep air estimate is not straightforward (i.e., not as simple as more or less conservative). The three discrete points in Figure 4 each represents a specific limiting case for the batch analysis that have limitations when compared to the actual system operation:

- Initial, maximum sweep air rate and H₂S evolution rate:
 - As noted previously, the batch at time 0 represents a full “fresh” batch of sulfur in the tank (i.e., all sulfur in the tank contains the maximum H₂S from the pit, 150 ppmw in this example).
 - **In practice, this should never occur – intermittent transfers in and out of the tank will likely lead to a range of H₂S concentrations below the maximum value.**
- Average sweep air rate and H₂S evolution rate:
 - The average sweep air rate is equivalent to assuming the H₂S concentration drops linearly from its initial concentration (150 ppmw) to its final concentration (37 ppmw) over the batch life (24 hours).
 - **This approach ignores instantaneous rates which may be much higher or lower than average.**

- Final, minimum sweep air rate and H₂S evolution rate:
 - The final sweep air rate condition rate approaches the CSTR result – that is, given enough time, the batch system with sulfur transfer in and out will approach a steady-state conditions that is identical to a CSTR (Figure 4 is approaching an asymptote for the sweep air rate). The frequency of sulfur transfers determines how long it takes to reach the steady-state condition. If sulfur were continuously transferred in and out, the calculations would be identical to a CSTR at all times.
 - This condition does not allow for the possibility of any transient condition where H₂S concentrations in the tank vary with time.
 - **Due to the fact that this condition is approaching the CSTR case, it is not considered further in this paper and only CSTR results are presented.**

Regardless of the tank operation and design, it would be reasonable to expect that the tank will exhibit periods of higher and lower H₂S concentration in the sulfur with corresponding variation in the H₂S evolution rate. Therefore, the batch modeling method leaves a wide range of uncertainty in sweep air estimates before considering any other limitations of the model or data. This underscores the value of field data to support calculations.

4.1.3 Summary of Results for CSTR and Batch Reactors

The modeling results for the batch and CSTR cases are summarized in terms of sweep air requirements in Table 6.

Table 6: Modeling Results for CSTR and Batch Models

Experiment ID	Experimental Half-Life	Sweep Air Requirement Estimates		
		CSTR	Batch - Average	Batch - Max
	minutes	lb/hr	lb/hr	lb/hr
ASRL 1a (Stagnant)	1440	323	433	548
ASRL 2a (Stagnant)	328	595	1,047*	2,405*
ASRL 2b (Stirred)	36	763	1,507*	22,210

* Value in red may be useful as bounding cases (stagnant vs. stirred, average vs. max batch)

Several conclusions can be developed from reviewing the modeling results together:

- For all conditions, the CSTR predicts the lowest sweep air requirements. This is due to the fact that the CSTR is not capturing peak rates of H₂S evolution. As such, the CSTR case does not have a clear advantage over batch “average” cases.
- The batch average sweep air rates are higher than the CSTR for two primary reasons:
 - The batch average does include the effect of peak H₂S evolution rates on air rate requirements. The CSTR model does not have a means to capture transients.
 - The batch model includes periodic transfers of sulfur into the system. This creates periods of higher H₂S content sulfur entering the system and raises the average H₂S evolution and sweep rate when compared to a batch system without transfer.
- For the two stagnant cases (1a, 2a), the discrepancy in half-life estimates yields a large difference in sweep air estimates. The experiments in 1a only measured H₂S_x loss, and therefore may not be capturing the significant free H₂S transfer that is occurring. This

illustrates the shortcoming of using data that is used in a way that was not originally intended by the researchers (i.e., experiments designed to study a specific degassing mechanism – conversion of H_2S_x to H_2S).

- As the H_2S half-life falls, particularly for case ASRL 2b (stirred experiment), the H_2S evolution rate and sweep air rate both increase as expected for all modeling cases. However, the maximum batch air rate (last column) stands out as an extreme value vs. the others in the table (~10x greater than any other value). This is due to the fact that the higher rate of H_2S evolution for the stirred experiment (reflected in the half-life and rate constant) is amplified at the peak H_2S concentration at the start of the batch. Therefore, this condition is the least representative of the actual system in the table – the stirred system is already inconsistent with a real tank (inflates H_2S evolution rate) and the initial evolution rate is also not representative of the actual tank (see preceding discussion).

As was noted previously, all of the underlying assumptions and uncertainty in using the degassing data in simplified models leads to our recommendation to avoid using this simplified modeling approach as the sole means of estimating a sweep air requirement. This uncertainty is reflected in the very wide range of sweep air estimates derived from the same set of experimental data. However, to the extent that the results are used to guide understanding of H_2S evolution rates, the batch results in the table may provide some bounding cases (stagnant vs. stirred and average vs. max) – bounding cases are denoted in red text in Table 6 .

5.0 Comparison of H_2S Evolution Approaches and Recommendations

With heuristic methods and simplified models utilizing experimental data evaluated in this paper, the approaches can be compared. Rather than compare every case evaluated in this paper, select representative and bounding cases were selected from each category (heuristic vs. simplified models). The cases are organized from least to most conservative in terms of the key underlying assumptions for the calculation approach – see Table 7.

Table 7: Comparison of H_2S Evolution Calculations – Heuristic vs. Simplified Models

	Heuristic Cases	Simplified Models
Least Conservative	Case 1c: H_2S Material Balance + Make-Rate = 395 lb/hr	ASRL 2a Stagnant + Batch Average = 1,047 lb/hr
Intermediate	Case 2c: H_2S Material Balance + Pump Rate = 1,185 lb/hr	ASRL 2b Stirred + Batch Average = 1,507 lb/hr
	Case 1a: All H_2S + Make Rate = 1,580 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
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Some key conclusions from Table 7 include:

- The range of results for the simplified models is similar to the heuristic approaches. While the absolute values in the table reflect the example case in this paper, the results are illustrative of the fact that both approaches leave significant room for judgement from the user.
- The use of the “All H₂S at Any Place” assumption with the pump rate stands out as a particularly conservative case and understanding the physical mechanisms in the system may provide enough justification to rule this approach out as a reasonable approach for estimating sweep air rates.
- The “All H₂S at Any Place” assumption with the sulfur make-rate falls in the middle of the range of cases in the table. This heuristic approach includes a layer conservatism while avoiding assumptions that are wholly inconsistent with the physics of the system (e.g., assuming the total H₂S entering the tank evolves instantaneously). It appears to represent a reasonable approach to estimating sweep air, particularly in the absence of field data to justify less conservative approaches.

While the simplified models using experimental data have appeal due to the apparent connection to actual physical mechanisms associated with H₂S evolution, they also require many assumptions and simplifications that introduce uncertainty in addition to the inherent uncertainty of experimental data. Furthermore, the modeling assumptions are less transparent than the heuristic approaches and the calculations are more complex. Even if a more rigorous modeling approach could be developed (e.g., estimating mass transfer coefficients for the actual system) to reduce some of the uncertainty, it would come at the expense of more complexity in the calculations and less transparency in the assumptions and model inputs. That leaves the question of whether modeling approaches reduce uncertainty in the H₂S evolution estimation and if any such reduction in uncertainty is enough to justify the additional complications of the approach.

In short, modeling approaches may provide a sanity check on heuristic methods by providing bounding cases for some of the physical mechanisms that impact H₂S evolution in the systems. However, they do not represent a stand-alone solution for estimating sweep air rates and the heuristic methods are more readily defensible given the transparent nature of the assumptions and the impact on safety of the assumptions.

6.0 Validating H₂S Evolution Estimates and Mitigating Risks of Inaccurate Estimates

Aside from the H₂S evolution estimation approach, there are other options to help mitigate the uncertainty in the sweep air estimates. These methods fall into two general categories: 1) gathering field data to validate calculation assumptions and 2) real-time monitoring of H₂S in equipment.

6.1 Field Measurements of H₂S in Sulfur Handling Systems

As noted at several points in this paper, if sweep air is being applied to an existing sulfur handling system or if a similar sulfur handling system is already in operation, measuring H₂S in the sulfur and vapor headspace of handling equipment may provide data that directly supports the selection of a specific sweep air rate or estimation approach. However, H₂S measurements must be taken at the proper points in the system and at times that are representative of the various operating conditions that are experienced in the dynamic sulfur handling processes. Figure 3 (in Section 3.0 of this paper) and Table 8 below provide general guidance on locations and timing of H₂S measurements for the generic case evaluated in this paper.

Table 8: H₂S Sampling Points and Strategy

Measurement Point	Phase & Location	Description	Timing ^{Note 1}
1	Molten Sulfur in Rundown Line to Sulfur Pit	Measure total H ₂ S entering sulfur handling system.	<ul style="list-style-type: none"> • During normal steady state operation of Claus unit. • Repeat for any regularly occurring off-design operating conditions for Claus (e.g., reduced capacity).
2	Vapor space or vent line from sulfur pit ^{Note 2}	Measure sulfur pit headspace H ₂ S.	<ul style="list-style-type: none"> • During normal steady state operation. • Repeat for any regularly occurring off-design operating conditions. • Repeat during sulfur transfer out of the pit and for a period after the transfer (e.g., every 5 minutes for half an hour)
3	Molten sulfur leaving pit (e.g., pit pump sample/recirc line)	Measure total H ₂ S to sulfur tank.	
4	Molten sulfur in the sulfur tank ^{Note 3}	Measure total H ₂ S in the sulfur tank as a function of time.	
5	Vapor space or vent line from sulfur tank ^{Note 2}	Measure sulfur tank headspace H ₂ S.	<ul style="list-style-type: none"> • During idle periods between sulfur transfers (collect time series of points). • Repeat during sulfur transfer into and out of the tank and for a period after each transfer (e.g., every 5 minutes for half an hour)
6	Molten sulfur leaving tank (e.g., loading pump sample/recirc line) ^{Note 3}	Measure total H ₂ S to sulfur loading.	
7	Molten sulfur in the sulfur loading vessel (e.g., truck)	Measure total H ₂ S in the sulfur loading vessel as a function of time.	<ul style="list-style-type: none"> • Time series of measurements^{Note 4} throughout loading and for a short period after loading, if possible.

8	Vapor space or vent line from sulfur loading vessel ^{Note 2}	Measure sulfur loading headspace H ₂ S.	
<p>Notes:</p> <ol style="list-style-type: none"> 1. Whenever a time series of data can be collected, this is preferred over a single point in time. 2. If vapor space measurements at multiple locations in the headspace are possible, these should be collected in addition to the single vent line measurement. 3. The molten sulfur leaving the tank (point 6) may be different than the sulfur in the tank (point 4) if the tank is not well-mixed - this measurement will help confirm mixing. 4. The more frequent the measurements, the more representative the measurements are of a rate H₂S evolution. 			

In practice, the measurement approach should be defined on a case-by-case basis for the specific facility under evaluation.

6.2 Real-time monitoring of H₂S in Sulfur Handling Equipment

Once a sweep air basis is finalized, the design of the sulfur handling system can incorporate continuous H₂S vapor headspace measurement in handling equipment to detect potentially dangerous levels of H₂S in the headspace. Several companies provide H₂S analyzers that may be used to measure the H₂S concentration in the head space of sulfur pits and tanks, and these instruments have been used in practice. Some considerations for continuous H₂S measurement include the following.

- In general, the online H₂S analyzer may serve to avoid the worst consequences of underestimated sweep air flow rates and may provide support for removing some margin from the sweep air estimation basis.
 - While H₂S detection may be able to prevent a catastrophic outcome, regular or repeated shutdown of the equipment is not a long-term operating solution, and more extensive design modifications to provide additional sweep air may ultimately be needed. As noted, this may be more costly than using the more conservative approach upfront in the equipment design.
- Potential drawbacks of the H₂S headspace analyzer may include the following:
 - The entire headspace cannot be measured by the analyzer and adding multiple points can be costly and will still not fully cover potential stagnant zones in the headspace. Thus, the measurement is not a guarantee of safe headspace conditions.
 - The analyzers add cost to the system, including the need for a structure or housing for the analyzer itself.
- Over time, the H₂S vapor space data collected may identify specific periods or operating practices that yield higher H₂S concentrations in the vapor spaces of equipment. For example, a spike in the vapor space H₂S concentration of the sulfur tank during sulfur transfer into the tank may indicate that the sulfur pump rate or velocities in sulfur piping are too high. This information can support operational changes to reduce H₂S evolution, with the H₂S analyzer serving as the method to validate the effectiveness of the change.
- Periodic validation of the online analyzer can be performed by field testing of the vapor space. For example, the field testing at the vapor space may be able to measure H₂S concentration at multiple points in the headspace and determine how representative or

skewed the online analyzer is in practice. This can offset some of the aforementioned risk of the analyzer not being representative of the full headspace (i.e., relate the analyzer measurement to the variation in the actual headspace H₂S concentration).

The details of H₂S analyzers are beyond the scope of this paper – an appropriate supplier should be contacted for more detailed guidance.

7.0 Conclusions

TBd

References

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Appendix A : Formulating a First-Principles Mass Transfer Model

The continuity equation can be written for each component in each phase as shown below in Equation A.1. An energy balance may be similarly written.

$$\frac{\partial C_i^\varphi}{\partial t} = -\frac{\partial N_i^\varphi}{\partial z} + \sum_j^{n_{Rxn}} v_{i,j} R_j \quad \text{A.1}$$

Where:

- C_i^φ = Concentration of species i in phase φ
- N_i^φ = Flux of species i in phase φ
- n_{Rxn} = Number of chemical reactions
- $v_{i,j}$ = Stoichiometric coefficient of species i for reaction j
- R_j = Rate of reaction j per unit volume

Flux is a combination of diffusion and convection which can be described by Fick's Law or more rigorously the generalized Maxwell-Stefan equations. Note that under turbulent conditions, a description of the velocity field is required for the convective transport term. The network of kinetic reactions is typically described using rate-laws, kinetic constants, and stoichiometry. Phase and chemical equilibrium expressions complete the set of equations.

To solve the coupled partial differential equations, an initial condition and two boundary conditions are required:

- **IC:** the initial concentration of species i is equal to the feed concentration
- **BC1:** equilibrium occurs at the vapor-liquid interface for all species
- **BC2:** vapor and liquid flux are equal at the vapor-liquid interface for all species

Simplifications are often used to solve the convection-diffusion system of equations. Flux at phase boundaries can be described using mass transfer coefficients, which are defined as the rate of flux divided by the local concentration difference between the bulk fluid and the interface. Mass transfer coefficients are generally simple functions of dimensionless groups which account for the influence of physical and transport properties and the system geometry. When reactions are present, the physical transfer of material is "enhanced" by changes to the concentration gradient of reactants and products. Component flux is multiplied by an additional factor, called the enhancement factor, to account for accelerated mass transfer caused by chemical reactions. The enhancement factor is defined as the ratio of mass transfer with reactions to that without reactions.

By using mass transfer coefficients, integrating the convection-diffusion equations can be avoided. Instead, macroscopic component mass balances may be written for an arbitrary control volume.

$$\frac{\partial V C_i^\varphi}{\partial t} = F_i^{In} C_i^{In} - F_i^{Out} C_i^{Out} - N_i^\varphi A + \sum_j^{n_{Rxn}} \nu_{i,j} R_j \quad \text{A.2}$$

$$N_i^\varphi = E_i^\varphi k_i^\varphi \Delta C_i^\varphi \quad \text{A.3}$$

Where:

- V = Control volume
- C_i^φ = Concentration of species i in phase φ
- F_i = Volumetric flow rate into, or out of, the system volume
- A = Interfacial area of the control volume
- E_i^φ = Enhancement factor for species i in phase φ
- k_i^φ = Mass transfer coefficient for species i in phase φ
- ΔC_i^φ = Concentration difference between the bulk fluid and interface for species i in fluid φ

Concentration driving forces are usually defined in terms of volumetric concentrations, mole fractions, and partial pressures. Consistency must be ensured between concentration driving force and mass transfer coefficient units.

When interphase flux is absent, Equation A.1 describes a continuous stirred tank reactor (CSTR); when a differential volume is used, Equation A.2 describes a plug flow reactor (PFR).

Appendix B: Potential Reactions in Molten Sulfur Systems

Table 9: Summary of Reactions Occurring in Molten Sulfur and the Vapor Headspace

H₂S/H₂S_x Polymerization Equilibrium
$H_2S + S_{x-1} \rightleftharpoons H_2S_x$
Direct Oxidation to Elemental Sulfur
$H_2S + \frac{1}{2}O_2 \rightarrow H_2O + \frac{1}{8}S_8$
$H_2S_x + \frac{1}{2}O_2 \rightarrow H_2O + S_x$
Direct Oxidation to SO₂
$H_2S + \frac{3}{2}O_2 \rightarrow H_2O + SO_2$ $H_2S_x + \frac{3}{2}O_2 \rightarrow H_2O + SO_2 + S_{x-1}$
Claus Reaction
$2H_2S + SO_2 \rightarrow 2H_2O + \frac{3}{8}S_8$ $2H_2S_x + SO_2 \rightarrow 2H_2O + \frac{(2x+1)}{8}S_8$