

## **Molten Sulfur Vent Stream Disposition –Vent Stream Routing, Managing Emissions, and Impact of Process Conditions/Equipment**

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### **Abstract**

This paper will review the process of recovering vapors from molten sulfur pits, tanks, and loading areas, including a review of some of the impact of operating conditions in the SRU and storage and handling systems on the vent stream characteristics.

In addition, the paper will outline the typical options for disposition of the vent streams including sending the vent streams to the front end of the SRU, sending the vent streams to an incinerator, sending the vent streams to a tail gas treating unit, and/or treating the vent streams to remove particulate, H<sub>2</sub>S, and/or SO<sub>2</sub>. The technical merits and challenges of each option will be reviewed generically, but also in the context of site-specific considerations based on actual field experience with these systems.

The paper will also review routing options for vent streams from molten sulfur pits, tanks, and loading operations. For example, some refineries route each vent stream (generally sweep air streams) separately to its final destination, be that the Claus thermal reactor, the incinerator, the tail gas unit, or a different emission control unit. Other refineries route such vent streams sequentially, e.g., from the loading operations, through a sulfur storage tank, through the pit headspace, then to the final destination. Each choice has advantages and disadvantages. For example, routing all vent vapors through the molten sulfur pit, in route to another destination in the SRU, has several potential benefits including: A single path to the destination of the vent stream (e.g., Claus furnace) limits the paths for reverse flow from the Claus unit and the associated necessary safeguards. This benefit has to be balanced against the impact on the operation of the pit, control of vent stream flows at each location, etc. The vent system design choices will be presented to highlight the trade-offs and provide guidance for choosing and designing a system based on site-specific constraints.

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## 1.0 Introduction

Plants that operate Claus Sulfur Recovery Units (SRUs) have to contend with the vapors that come from the equipment handling molten sulfur. The Claus process converts  $\text{H}_2\text{S}$  gas into molten sulfur at natural gas plants and refineries. The  $\text{H}_2\text{S}$  reacts over a catalyst with air ( $\text{O}_2$ ) to form elemental sulfur and water. The sulfur is condensed into a liquid (molten sulfur) that must be stored until it can be pumped to truck or railcar loading, or to an end user off site.

The molten sulfur contains soluble  $\text{H}_2\text{S}$  and hydrogen polysulfides ( $\text{H}_2\text{S}_x$ ). The  $\text{H}_2\text{S}_x$  compounds can dissociate to  $\text{H}_2\text{S}$  and sulfur during agitation and cooling. Dissolved  $\text{H}_2\text{S}$  in the liquid sulfur will desorb in the gas phase.  $\text{SO}_2$  is also found in the headspace of sulfur storage equipment containing both degassed and un-degassed sulfur. The  $\text{SO}_2$  originates from the molten sulfur from the Claus unit, and also from the reaction of sulfur with oxygen in the storage tank and loading area. Thus, both  $\text{H}_2\text{S}$  and  $\text{SO}_2$  can accumulate in the vapor space above the liquid sulfur.  $\text{H}_2\text{S}$  is flammable, and  $\text{H}_2\text{S}$  and  $\text{SO}_2$  are both toxic at relatively low levels. Other sulfur species ( $\text{S}_6$  and  $\text{S}_8$ ) as well as sulfur mist or fog can be in the vapor space and can solidify on equipment at cooler temperatures.

The molten sulfur conditions must be managed to i) minimize and limit emissions and exposure to  $\text{H}_2\text{S}$  and  $\text{SO}_2$ , ii) prevent fire/explosive conditions in vapor, and iii) allow reliable transport and loading of sulfur (prevent plugging, freezing, etc.). Sweep gas is often used to keep the  $\text{H}_2\text{S}$  below a maximum of 25% of the lower explosive limit (LEL) for  $\text{H}_2\text{S}$  in air that is above the surface of the molten sulfur in the pits, storage tank, and loading equipment [1]. Refiners often utilize vapor recovery devices (“motive devices”) – e.g., ejectors with steam, air, or  $\text{N}_2$  as the motive fluid or blowers – to capture and transport the sulfur-laden vent gas to its final destination for safe disposal. There are many options to handle or treat the typically  $\text{H}_2\text{S}$ -rich vent gas. Likewise, there are also many factors (environmental, safety, and operational) that need to be considered to identify the optimal destination for the molten sulfur storage and transfer vents.

This paper first presents an overview of the molten sulfur handling and vapor recovery systems used at refineries with Claus SRUs. It discusses the molten sulfur characteristics, typical vent gas composition, and types of motive devices (i.e., compression or pumping equipment) commonly used. Then, the advantages and disadvantages of common vent vapor destinations will be reviewed, including: i) vent to atmosphere, ii) destroy stream via thermal or catalytic means, iii) recycle to the front of the SRU, to the tail gas treating unit (TGTU) or to the sulfuric acid plant (SAP), iv) condense the stream [requires steam sweep], and v) remove  $\text{H}_2\text{S}$  and other objectionable components through caustic scrubbing, liquid redox, or scavenging technologies. Finally, the benefits and impacts of different routing options for the molten sulfur vent gas sources – separate streams from pits, storage tank, and loading versus sequential, combined stream flow – to the final destination will also be reviewed. Applicable field experiences with the vent vapor options will be discussed as well.

## 2.0 Background on Molten Sulfur Handling and Vapor Recovery System

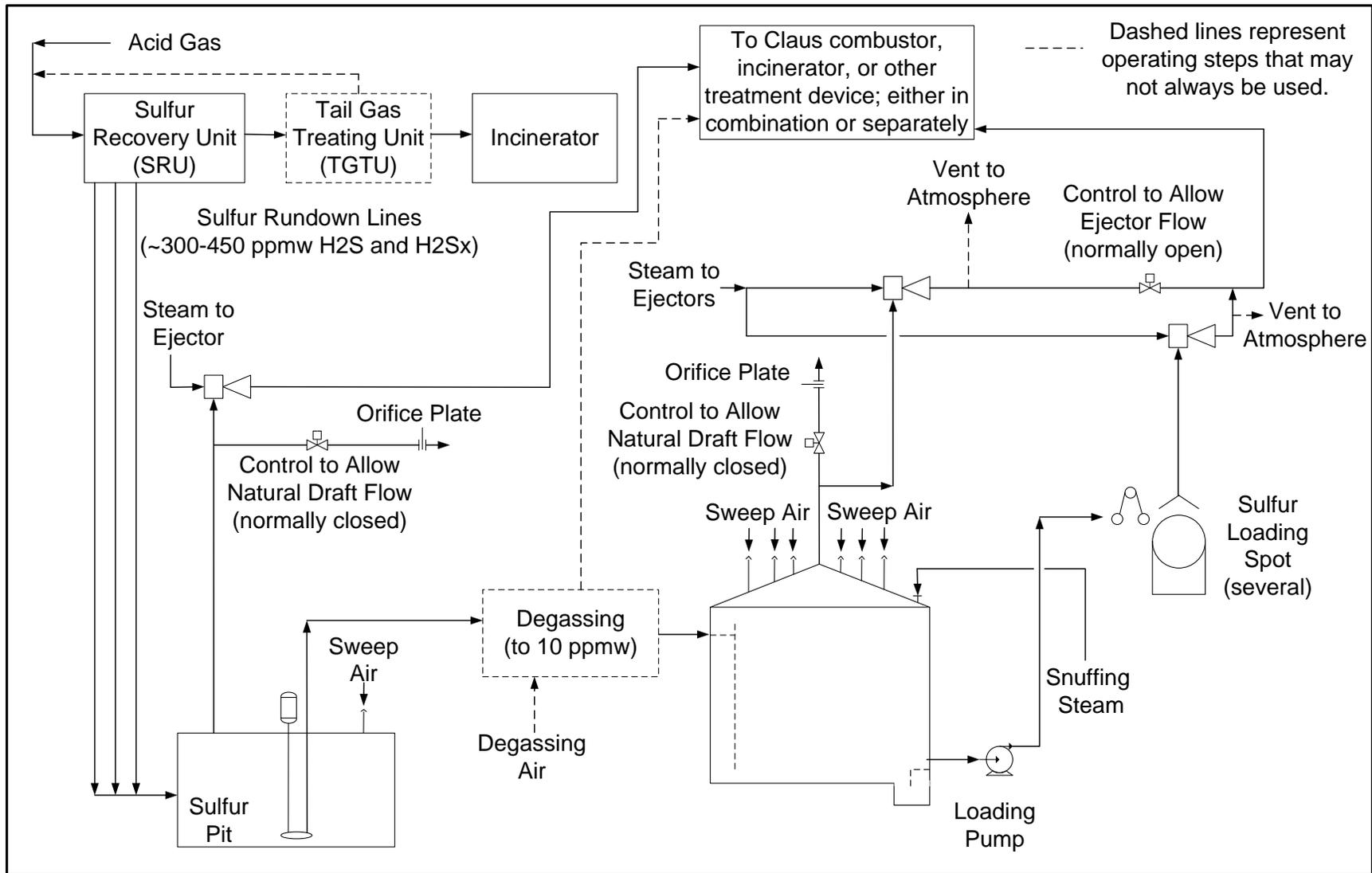
### 2.1 Overview of the System

Hydrogen sulfide ( $H_2S$ ) is a byproduct of processing natural gas and refining crude oils. Environmental regulations often require that the  $H_2S$  be treated before emitting gases to the atmosphere. A modified Claus sulfur recovery unit (Claus SRU) is one common treatment method and involves converting the  $H_2S$  to 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 2-1. The molten sulfur produced in the Claus SRU contains soluble  $H_2S$  and hydrogen polysulfides ( $H_2S_x$ ). During the storage of the sulfur, the  $H_2S_x$  compounds decompose to elemental sulfur and  $H_2S$  as the sulfur cools and is agitated. This results in the formation of dissolved  $H_2S$  in the liquid sulfur that desorbs into the gas phase. The potential release of  $H_2S$  creates several safety, environmental, and health risks.  $H_2S$  represents a flammability / explosion hazard at conditions (e.g.,  $H_2S$  vapor concentrations) that may readily be realized in storage and handling processes. In addition, the OSHA permissible exposure limits for  $H_2S$  in the atmosphere are: 10 ppmv, 8-hr TWA, for construction and maritime industries; and 20 ppmv ceiling limit for general industry [2]. Finally, the refinery may be limited in its ability to vent  $H_2S$  due to environmental regulations. Therefore, there are several points in the sulfur storage and handling process where vent gas streams which contain  $H_2S$  (and other sulfur species) may need to be managed. The following overview will highlight these points in the process.

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  $H_2S$  and  $H_2S_x$  ([1], [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  $H_2S$  and  $H_2S_x$  indicate that the 300 ppmw is a reasonable value for many plants, although measurement is recommended at each site to account for the specific operating conditions of the unit.

The sulfur may be degassed, either in the pit or in separate degassing equipment, to remove  $H_2S$ , e.g., down to approximately 10 ppmw. Even if there is no degassing equipment, some  $H_2S$  will evolve in the pit, but the degree of  $H_2S$  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  $H_2S$ -laden vapor stream will be produced that must be managed safely in some fashion. This is the first point in the process where a vapor recovery system may be needed/utilized to remove vapors containing  $H_2S$  for safety and/or environmental reasons.

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  $H_2S$  content in undegassed molten sulfur, the  $H_2S$  concentrations in the tank headspace could reach the tens of volume percent levels [3], which could lead to an explosion and/or pose a significant exposure



**Figure 2-1. Example Molten Sulfur Storage and Handling System**

hazard to personnel. As shown later in this paper, even with degassed sulfur (e.g., to 10 ppmw H<sub>2</sub>S), it is theoretically possible that additional H<sub>2</sub>S could evolve during the residence time in the storage tank leading to dangerous concentrations of H<sub>2</sub>S in the tank vapor space (hundreds of ppmv to low volume percent levels) [3]. While some literature sources (e.g., [4]) suggest low H<sub>2</sub>S in the tank vapor space of degassed sulfur, presumably due to the oxidation of the residual H<sub>2</sub>S to SO<sub>2</sub>, gas-phase composition measurements should be performed in the headspace of the tank, if possible, to confirm the concentrations of these species. The composition of the tank head space, and the associated risks, will be dependent on many site and process-specific factors. However, SO<sub>2</sub> also represents a health and environmental risk, and therefore even vapors from a degassed sulfur tank with low H<sub>2</sub>S content may need to be managed.

Because H<sub>2</sub>S is flammable, sweep gas is often used to keep the H<sub>2</sub>S content in the tank vapor space below 25% of the lower explosive limit (LEL), although other percentages have been reported in the literature. Air is often used but other gases such as fuel gas, N<sub>2</sub>, steam, or other inert gas purge are sometimes considered to blanket / sweep sulfur tanks. Blanketing the sulfur with a purge gas such as N<sub>2</sub> has been associated with hazards such as tank fires and explosion when air is later introduced to the tank headspace (e.g., during tank maintenance). If oxygen is absent, then the tank headspace will have a reducing environment, which leads to the formation of pyrophoric iron sulfides. Therefore, air-based tank sweep systems that manage the H<sub>2</sub>S concentration in the headspace (as opposed to excluding air/oxygen) are often favored over inert-blanketed tanks from a safety standpoint. The vent stream from swept tanks will contain H<sub>2</sub>S (and SO<sub>2</sub>). Although venting a sulfur tank to atmosphere is not unusual, it is becoming much more common to treat the vent gas from the storage tank before it is emitted to the atmosphere, as a result of environmental air quality regulations and permit conditions. Therefore, the sulfur storage tank represents the second location in the process where vent vapors may need to be recovered and/or managed.

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<sub>2</sub>S evolution at the loading station. Even though H<sub>2</sub>S 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<sub>2</sub>S will be present at truck loading. H<sub>2</sub>S 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. As noted previously, SO<sub>2</sub> may also be present in the sulfur after exposure to air. 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 vapors may need to be recovered and/or managed.

## ***2.2 Special Considerations for Degassed Sulfur***

If a sulfur degassing process is utilized (in-pit or external degassing), the total H<sub>2</sub>S (H<sub>2</sub>S and H<sub>2</sub>S<sub>x</sub>) in the elemental sulfur leaving the degassing system is typically reduced to a low value, e.g., 10 ppmw or less. There will still be a need to manage the vent stream from the degassing unit and/or pit. However, the significant reduction in H<sub>2</sub>S that can evolve in vapor in

downstream storage and handling steps raises several questions about the need for and design of any vent handling systems downstream. The remainder of this section will review the downstream impacts of degassing.

First, is there a need for sweep gas in the downstream storage and handling systems at all? In order to assess this risk, the vapor-liquid equilibrium of H<sub>2</sub>S in molten sulfur should be reviewed. For a stagnant vapor space (e.g., molten sulfur storage tank headspace), Table 2-1 summarizes vapor space H<sub>2</sub>S concentrations and associated risks for several molten sulfur conditions.

**Table 2-1: H<sub>2</sub>S Concentrations in Stagnant Vapor Space Above Molten Sulfur [6]**

Total H <sub>2</sub> S in Sulfur	Temperature	H <sub>2</sub> S in Vapor Space	Notes
ppmw H <sub>2</sub> S +H <sub>2</sub> S <sub>x</sub>	F	vol%	
300	300	29.7	> LEL for H <sub>2</sub> S
300	280	40.5	> LEL for H <sub>2</sub> S
150	300	14	> LEL for H <sub>2</sub> S
150	280	20.4	> LEL for H <sub>2</sub> S
50	300	4.3	> LEL for H <sub>2</sub> S
50	280	6.9	> LEL for H <sub>2</sub> S
10	300	0.7	Degassed Sulfur. Lethal H <sub>2</sub> S levels.
10	280	1.4	Degassed Sulfur, > 25% of LEL of H <sub>2</sub> S

As the table indicates, even with degassed sulfur, the H<sub>2</sub>S can accumulate to dangerous (or even explosive) levels in the vent vapor. This argues for sweeping a vapor space above degassed sulfur. In addition, degassing units may be out of service, may be permanently removed, or may not function properly, increasing the chance that undegassed sulfur will reach the tank. Therefore, the possibility of undegassed sulfur reaching the downstream processes, should at minimum, be considered as a scenario in the vent system disposition and design and could be addressed by having a backup design to allow sweep of the vent vapors (e.g., natural draft for a tank), when needed.

In addition, literature data and discussion of sulfur degassing indicates that degassed sulfur (and the associated vapor) will have higher levels of SO<sub>2</sub> than would be expected in undegassed sulfur [7] [4]. The SO<sub>2</sub> can form as a result of the reaction of oxygen with the elemental sulfur itself (slower mechanism) or via the reaction of oxygen with H<sub>2</sub>S<sub>x</sub> (faster mechanism) as part of the degassing process – air is used in many commercial degassing processes to enhance degassing rate. SO<sub>2</sub> can, in theory, also be formed in the vapor phase as sulfur vapor reacts with oxygen. However, the amount of SO<sub>2</sub> that remains in the sulfur after it leaves the degasser, the amount of SO<sub>2</sub> that forms downstream (liquid or vapor phase), and the amount of SO<sub>2</sub> evolves downstream into the vapor phase are all sources of uncertainty in

determining the SO<sub>2</sub> levels in a vent gas stream from degassed sulfur. However, the mechanisms to form SO<sub>2</sub> are present and some field data does indicate the potential for much higher levels of SO<sub>2</sub> than H<sub>2</sub>S present in vent gas from degassed sulfur [4]. Therefore, SO<sub>2</sub> in the degassed vent streams should be considered as another factor in recovering and disposing of the vent gas from handling and transport of sulfur.

Finally, elemental sulfur mist, fog, and particulate will generally be present in a vent gas stream from degassed sulfur just as they are for undegassed sulfur. Therefore, accounting for their presence may impact vent gas management decisions (e.g., vent to atmosphere) or design (e.g., prevent molten sulfur accumulation in piping).

The remainder of the paper will focus on the engineering design choices, considerations, and methods to evaluate the management of the vent streams from the storage and handling sources outlined above.

### ***2.3 Estimating Vent Flow Rates and Compositions for Engineering Design***

The flow and composition serve as the central part of the design basis of any engineering evaluation of the vent streams. Vent streams from molten sulfur storage tanks, pits, and loading areas are generally composed primarily of air or nitrogen (or other gas depending on the source of sweep gas), but also contain H<sub>2</sub>S, SO<sub>2</sub>, elemental sulfur (S<sub>8</sub>), sulfur mist/droplets/fog, and possibly also COS and CS<sub>2</sub>. It is important to know the composition of the vent gas beyond just H<sub>2</sub>S as the other components in the vent gas have impacts on any downstream processes where the vent gas is routed and can present health, safety, and environmental concerns. In some cases, it may be possible to sample the vent gas stream directly and analyze for these compounds, especially if the design work is part of an upgrade or retrofit of an existing system. However, if the vent gas stream cannot be sampled (because it is a new process design, or for some other reason), then there are other ways to estimate the composition of the tank vapor space. Different approaches with varying levels of conservatism have been reported in the literature as discussed further in the subsections below. These approaches were also evaluated by Trimeric in papers focused on natural draft ventilation from sulfur tanks and vent streams [8], [1].

#### ***2.3.1 Typical Sulfur Species and Estimation Methods***

The amount of H<sub>2</sub>S that evolves from the molten sulfur at a given point in the process can be estimated from measured H<sub>2</sub>S and H<sub>2</sub>S<sub>x</sub> concentration in the molten sulfur and the liquid sulfur flow rate. There are different locations in the molten sulfur storage and handling process where these measurements can be taken. For example, it may be possible to sample the molten sulfur for H<sub>2</sub>S and H<sub>2</sub>S<sub>x</sub> upstream of the sulfur pit in the rundown lines, in the inlet end of the pit (upstream of an in-pit degasser, if present), downstream of a degassing unit (i.e., final chamber in pit or line leaving an external degassing unit), in the molten sulfur tank or at the sulfur loadout pumps going to loading, and at the truck or rail car loading stations. All of these locations may not be available for sampling at a given site, but they represent a starting point for developing a molten sulfur H<sub>2</sub>S and H<sub>2</sub>S<sub>x</sub> material balance through the storage and handling process. The difference in the H<sub>2</sub>S and H<sub>2</sub>S<sub>x</sub> of any pair of measurements in the preceding sequence gives an indication of the amount of H<sub>2</sub>S that evolves from the molten sulfur in the intervening process step(s). For example, measurements in the pit (undegassed sulfur) and at the sulfur loadout

pumps would give an indication of the H<sub>2</sub>S that evolves in the sulfur tank between the two measurement points. If the molten sulfur cannot be measured upstream and downstream of the process step of interest, it may be possible to use a single measurement upstream and make an assumption for the amount of H<sub>2</sub>S that evolves at each process step. A conservative example of this approach found in the literature is to assume that all the H<sub>2</sub>S present in the initial rundown (e.g., 300+ ppmw) sulfur evolves at each point in the process [3].

Different values for the molten sulfur flow rate can also be used at specific points in the process. The nominal / nameplate capacity of the SRU can be used, or the pump design / actual flow rate, depending on the operating conditions of the specific refinery. For example, the molten sulfur pump (e.g., pit pump) rate to the storage tank is often much higher than the nominal flow, and, when coupled with the measured H<sub>2</sub>S in the molten sulfur, results in a much higher estimated vapor space sulfur load and sweep air requirement. While this would result in a conservative flowrate and design, it may be unrealistically high especially when all of the levels of safety in the assumptions are also considered, for example:

- H<sub>2</sub>S<sub>x</sub> compounds: Since it is known that H<sub>2</sub>S<sub>x</sub> is relatively slow to convert to H<sub>2</sub>S, assuming that the total concentration of both compounds will instantaneously evolve as H<sub>2</sub>S is a conservative overestimation;
- H<sub>2</sub>S evolution: It is unlikely that all of the H<sub>2</sub>S will evolve at a given process step (e.g., storage tank);
- Dilution: The sulfur may enter the tank at a high flowrate, but it does not degas instantaneously, because it is diluted into the tank contents. In many tank designs, molten sulfur often enters through a down-pipe to near the bottom of the tank and mixes with the rest of the sulfur in the tank, which dilutes the entering sulfur and limits the rate at which the sulfur can degas. In both the tank and pit, the residence time of the sulfur in the unit and agitation of the sulfur will play a role, among other factors; and
- LEL values: The LEL (discussed later) for H<sub>2</sub>S is often estimated at conservative temperatures that result in conservatively high amounts of sweep gas being used in the pit and/or tank.

Since a variety of approaches have been reported in the literature for estimating H<sub>2</sub>S evolution, the level of conservativeness and methods required for estimating the amount of H<sub>2</sub>S in vapor space will need to be reasonably rationalized for each specific site and design scenario.

Various literature sources provide vapor-phase analytical data that can be used to estimate the SO<sub>2</sub>, COS, and CS<sub>2</sub> in molten sulfur vapor vent streams (e.g., [4], [9]). It should be noted that the data in the literature show significant variability and their suitability for use in estimating vent gas composition should be reviewed for the particular conditions of the molten sulfur system being evaluated. It may also be possible to measure these other sulfur species alongside H<sub>2</sub>S in vent streams if appropriate sample locations are available.

The amount of elemental sulfur vapor in the vent gas can be estimated by assuming that the gas is saturated with elemental sulfur at the temperature of the molten sulfur and the pressure of the vent stream (generally local atmospheric pressure). Vapor pressure information is available in the literature for elemental sulfur as well as data to distribute the elemental sulfur to  $S_6$  and  $S_8$  at the temperatures in the tank [10].

Finally, sulfur mist or fog may also be present in the vent gas. The amount of sulfur mist in a vent stream may vary significantly and is impacted, in part, by the air sweep rate, molten sulfur temperature, presence of any sources of agitation, steam coil leaks, etc. There is limited data in the literature regarding the amount of sulfur mist ( $S_8$ ) that might be expected in these types of streams [9]. Significant engineering judgment and experience and/or estimation based on measurements are required to arrive at a reasonable value for elemental sulfur mist / sulfur droplet entrainment. However, the presence of elemental sulfur as vapor or mist is important for downstream process as the elemental sulfur i) presents a plugging risk to process equipment [particularly downstream treatment equipment, which may operate at lower temperatures than typical molten sulfur systems], ii) adds to chemical usage (e.g., in a caustic scrubber), and iii) causes other problems such as particulate emissions.

### ***2.3.2 Sweep Gas Flow Requirement***

The vent gas flow rate for sulfur pits, tanks, and for vapor recovery at loading stations can be evaluated by defining an acceptable approach to LEL of  $H_2S$  in the vent gas stream and determining the sweep gas requirement to achieve that  $H_2S$  concentration based on the expected evolution of  $H_2S$  discussed in the preceding section. Using 25% of the LEL is a common industry practice for calculating the sweep air flow rate and is recommended in various literature sources; values as low as 15% [11] and as high as 35% [12] as an upper limit to stop operation have also been reported. The LEL for  $H_2S$  is also sometimes estimated at a conservatively high temperature, because a high temperature gives a conservatively lower LEL for  $H_2S$  and thus a higher sweep rate. A temperature of  $330^\circ F$  is a conservative design choice when determining the required sweep rate.  $330^\circ F$  is higher than a tank would normally be operated, due to concerns with increasing sulfur viscosity at high temperature and increased risks of fires. The sweep rate is estimated by assuming that the  $H_2S$  is combined with enough sweep gas to keep the  $H_2S$  at less than or equal to 25% of the LEL for  $H_2S$  (3 vol% at  $330F^1$ ). Thus, at 25% of the LEL, the target  $H_2S$  concentration is 0.75 vol% (3 vol% divided by 4). It should be noted that there is a chemical reaction in the elemental sulfur which actually consumes the  $H_2S$  and forms  $H_2S_x$  that is favored at higher temperatures (within a range) and this reaction would limit the mass transfer of  $H_2S$  into the gas [13]; however, from an LEL and sweep rate perspective a higher temperature is more conservative.

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<sup>1</sup> LEL condition defined with data from Pahl & Holtappels [16] and personal communication with industry experts.

### **2.3.3 Actual Vent Stream Compositions**

The combination of the H<sub>2</sub>S (and other sulfur species) expected to evolve at each step in the molten sulfur handling process and an estimate of the sweep gas required to maintain a 25% approach to LEL provides a basis to define the vent vapor flow and composition at each vent stream location in the process (i.e., pit vent, tank vent, loading vent). However, it is important to note that the 25% of LEL of H<sub>2</sub>S directly specifies the H<sub>2</sub>S composition in the vent streams and does not reflect an estimate of an actual concentration in the streams due to H<sub>2</sub>S evolution. The purpose of the LEL calculation is to estimate a sweep gas requirement, not represent a realistic H<sub>2</sub>S concentration in the vent gas stream during actual operation. Therefore, after calculating sweep gas requirements, it may be necessary to revisit the estimated concentration of H<sub>2</sub>S, SO<sub>2</sub>, and other sulfur species in the vent gas by making more realistic assumptions about the evolution of the sulfur species at process steps. Analytical measurements of the molten sulfur or vent vapor may also provide a more reasonable estimate of the vent vapor compositions than the LEL basis will provide. This will be important when considering the costs and impact on downstream processes that will handle the vent gas streams.

### **2.4 Options for Collecting Vapors**

While the focus of this paper will be on the disposition of the vent vapor after it is recovered from the storage and handling processes, the vapor collection process is briefly covered in this section. The vent gas streams from molten sulfur pits, tanks, and loading areas will be at or near atmospheric pressure – in fact, pits and tanks will commonly operate at a slight vacuum, requiring some level of driving force to vent to the atmosphere (e.g., tall vent stack or “chimney” to provide natural draft ventilation). Therefore, to send the vent vapors to a downstream destination, there will need to be sufficient motive force to overcome line losses, process pressure drop (e.g., vent gas treatment system), and/or reach the pressure of the vent gas destination (e.g., Claus thermal reactor). Two primary motive devices can be considered for recovering and transporting vapors from the molten sulfur handling system to the vent vapor destination, along with the benefits and limitations of each:

- Ejector
  - More reliable (losing steam or motive fluid system is biggest risk)
  - Consistent sweep gas flow rate provided at source
  - Introduces water if steam is motive (can lead to corrosion, downstream process performance issues - covered later in this paper)
- Blower/compressor
  - Less reliable (risk of corrosion, sulfur plugging)
  - Most flexible (may be able to operate over range of flows)

In addition to the operational and reliability factors highlighted above, cost, site utility availability, and site preferences may impact the selection of motive equipment. Also, the ejector option may impact the performance of the downstream vent gas destination via the addition of a motive fluid to the vent gas stream. This consideration is reviewed further in Section 4.0.

### **3.0 Vent Vapor Destinations**

The molten sulfur vent vapor contains H<sub>2</sub>S and other sulfur species that must be safely and reliably dealt with at the facility. Some of the common vent vapor destinations are discussed in this section. A comparison of the general advantages and disadvantages of the vent vapor destinations is provided at the end of Section 3. The capacity, equipment, cost, and regulatory drivers need to be evaluated specifically for each facility to determine the optimal destination for the vent gas stream on a case-by-case basis.

#### **3.1 Vent to the Atmosphere**

Molten sulfur tank and loading vent vapor can be routed to different destinations in the refinery. The simplest and generally most reliable method is to route the sulfur-containing vent gas directly to the atmosphere. This option, however, has potential safety issues and environmental regulatory concerns given the presence of H<sub>2</sub>S, SO<sub>2</sub>, and sulfur vapor in the gas. Hydrogen sulfide is a combustible gas and also a toxic chemical that can be dangerous to workers in the area. H<sub>2</sub>S has OSHA permissible exposure limits (PEL) of 10 ppmv, 8-hr TWA for construction and maritime industries and 20 ppmv ceiling limit for general industry. H<sub>2</sub>S also has an immediately dangerous to life and death (IDLH) of 100 ppmv [2]. At concentrations above 100 ppmv, a person can lose their ability to smell H<sub>2</sub>S even if it is still in the atmosphere. SO<sub>2</sub> is also hazardous with a PEL of 5 ppmv and an IDLH of 100 ppmv [14]. For these reasons, venting vapors to the atmosphere may require monitoring, and the vent system would need to be carefully designed to minimize personnel exposure (e.g., appropriate stack height, wind direction, etc.) Sulfur condensation can cause acid formation and corrosion [15] of the vent piping and exterior of the equipment. Site specific air regulatory emissions limits for H<sub>2</sub>S and SO<sub>2</sub> would also need to be considered.

Venting to the atmosphere may have been more acceptable in the past but stricter regulations and safety requirements now limit this option. In some cases, natural draft operation to the atmosphere may be put in place as a backup option for when vent system issues occur or when shutdowns occur at the final vapor destination.

#### **3.2 Vent to Incinerator**

Another vent handling option involves thermal or catalytic incineration of the H<sub>2</sub>S to SO<sub>2</sub>. SO<sub>2</sub> emissions will increase with this option since all of the sulfur species in the vent gas react with oxygen to form primarily SO<sub>2</sub> and some H<sub>2</sub>O. Incinerator SO<sub>2</sub> emissions in the United States are typically limited to 250 ppmv maximum on a dry basis with no excess oxygen or a mass limit (pounds/hour or tons/year) of SO<sub>2</sub> [9]. Tail gas incinerators are usually designed to burn H<sub>2</sub>S and are, thus, functionally appropriate destinations.

With this option, the processing capacity of the SRU, TGTU, or sulfuric acid plant (SAP) is not impacted because the vent vapors are sent to a completely separate treating destination (no recycle). Also, the vent gas can still be incinerated even if the SRU, TGTU, or SAP is out of service. There are some differences between the two incinerator types as noted in the literature [11] and summarized below. Catalytic incinerators typically use less fuel, are impacted more by deviations in the vent gas conditions (e.g., flow and composition), and may require preheating to

the ignition temperature. Thermal incinerators (more common) typically require lower vent gas compression than catalytic incinerators. Finally, if an existing SRU/TGTU incinerator is used, then incineration may be an economic option for the plant as long as the SO<sub>2</sub> emissions are maintained within permit limits.

The main capital expenses with this option include the piping to route the molten sulfur vent gas streams to the incinerator (which can be lengthy), and controls to manage/balance the oxygen from the combustion blower air with that in the vent gas stream. The incinerator option will not significantly impact the plot space at the refinery.

### **3.3 *Recycle Vent Vapor***

There are several options for recycling the molten sulfur vent vapors to other parts of the refinery, including but not limited to:

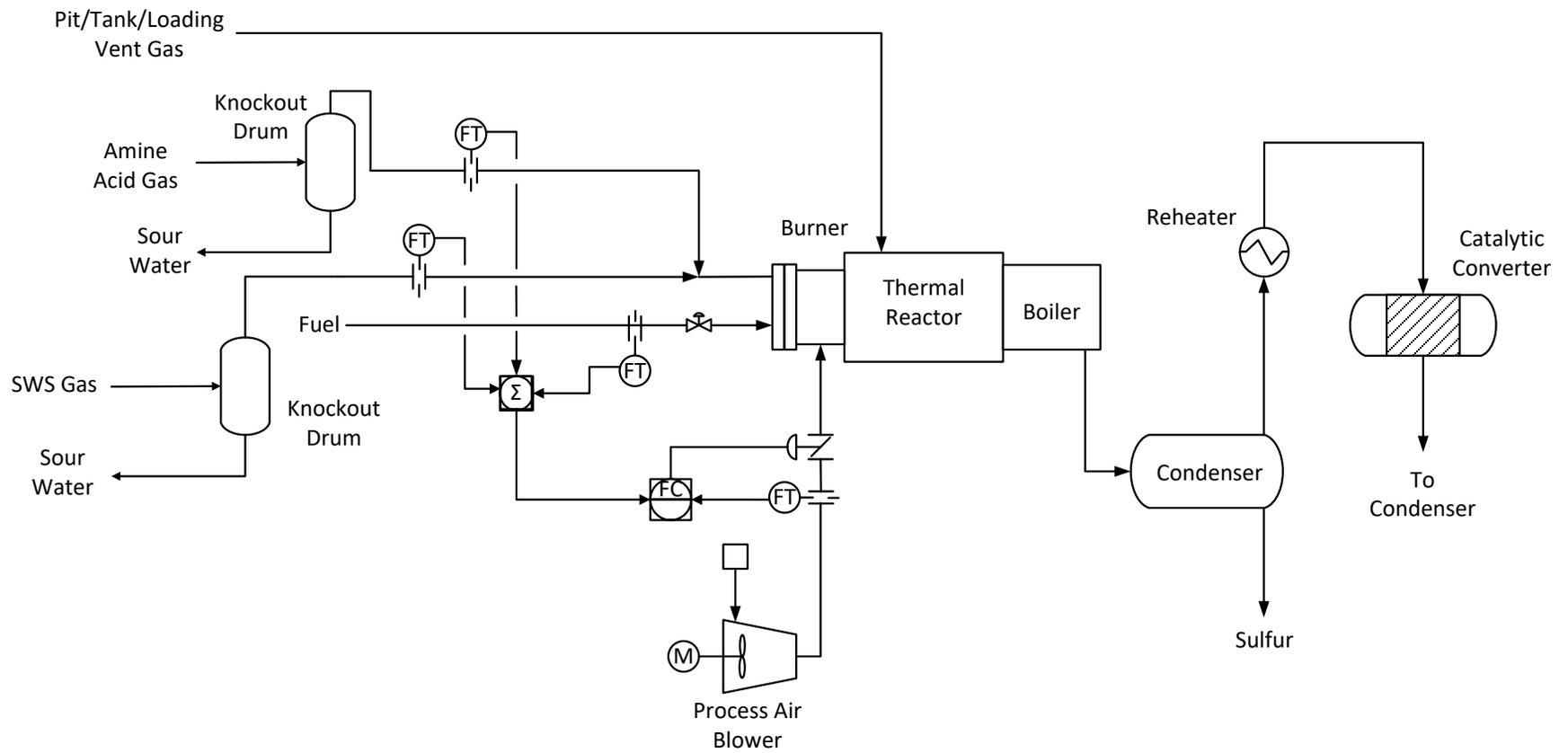
- Recycle to the front of the Claus sulfur recovery unit (SRU) thermal reactor;
- Recycle to the tail gas unit (TGU) reducing gas generator (or in-line heater); and
- Recycle to a sulfuric acid plant (SAP) thermal section.

The H<sub>2</sub>S-rich vent vapors typically only account for a small fraction of the overall H<sub>2</sub>S load to the units. None of the recycle options cause significant emission increases of SO<sub>2</sub> from the SRU incinerator. It may be prudent, however, to use the incinerator as a backup destination in case the SRU, TGU, or SAP goes down. Changes to the facility to implement the recycle options are often reasonable in scope, with little impact on plot space; they can also be implemented in a relatively short period of time. Additional details of these options are discussed in the subsections below.

#### **3.3.1 *SRU Recycle***

This option is most often used when there is an existing Claus plant that has room for additional gas flow. Figure 3-1 shows an example of routing pit/tank/loading vent gas to the thermal reactor. Routing to the thermal reactor may impact the processing capacity of the SRU; the extent of which depends on how much vent gas flow needs to be handled in contrast to the capacity of the unit. The vent air could be a significant fraction of the combustion air (particularly if the SRU utilizes O<sub>2</sub> enrichment) [15]. The controls and operation of the combustion air (and oxygen enrichment) for a specific SRU and the operating cases for that SRU must be evaluated to determine when there is “too much vent gas” relative to the combustion air. For example, the turndown of the combustion air blower may be limiting in one plant but not another depending on the configuration of the blower controls and the operating cases for the plant. If an ejector is used to send the vent gas to the SRU, the motive fluid impact on the SRU performance and operation should be evaluated.

SRU recycle likely requires higher vent gas compression compared to incineration. This will result in a larger motive fluid requirement or blower power demand. However, fuel consumption is expected to be lower than with incineration [11]. The main capital expenses include the motive device, piping to the SRU thermal reactor, and controls that are believed to need to be more robust than the incinerator controls.



**Figure 3-1. Addition of Molten Sulfur Pit/Tank/Loading Vent Gas to SRU Thermal Reactor**

Some other issues have been reported in the literature when recycling molten sulfur vent gas to the SRU [15], [16]. The first issue is the accumulation of solid sulfur in the air plenum that required melting out by temporarily minimizing the main air. The second issue is increased backpressure on the vent gas blowers that resulted in higher blower operating temperature from the compression heat and additional blower maintenance. Care should be taken to manage these concerns with SRU recycle.

### ***3.3.2 Tail Gas Recycle***

Figure 3-2 shows an example of routing the sulfur pit vent gas to the tail gas unit reducing gas generator (RGG). As indicated in the literature [11] and summarized below, directing the sulfur-laden vent vapor to the inline heater/ RGG is not often done because it is hard to control the process with the extra oxygen in the vent gas from the sweep air - oxygen will poison the hydrogenation reactor catalyst. In addition, the vent gas may be a significant portion of the air/oxygen required in the inline heater/RGG, creating additional operational/control challenges. [11].

Vent gas recycle to the RGG could potentially be used if nitrogen is the sweep media (instead of air) since the risk of contaminating the hydrogenation catalyst is reduced. However, an issue with nitrogen-only (or other inert gas) blanketing / purging is that it is common to form pyrophoric iron species on the walls of the equipment, and much care is required to prevent these species from causing a fire if air ever enters the system.

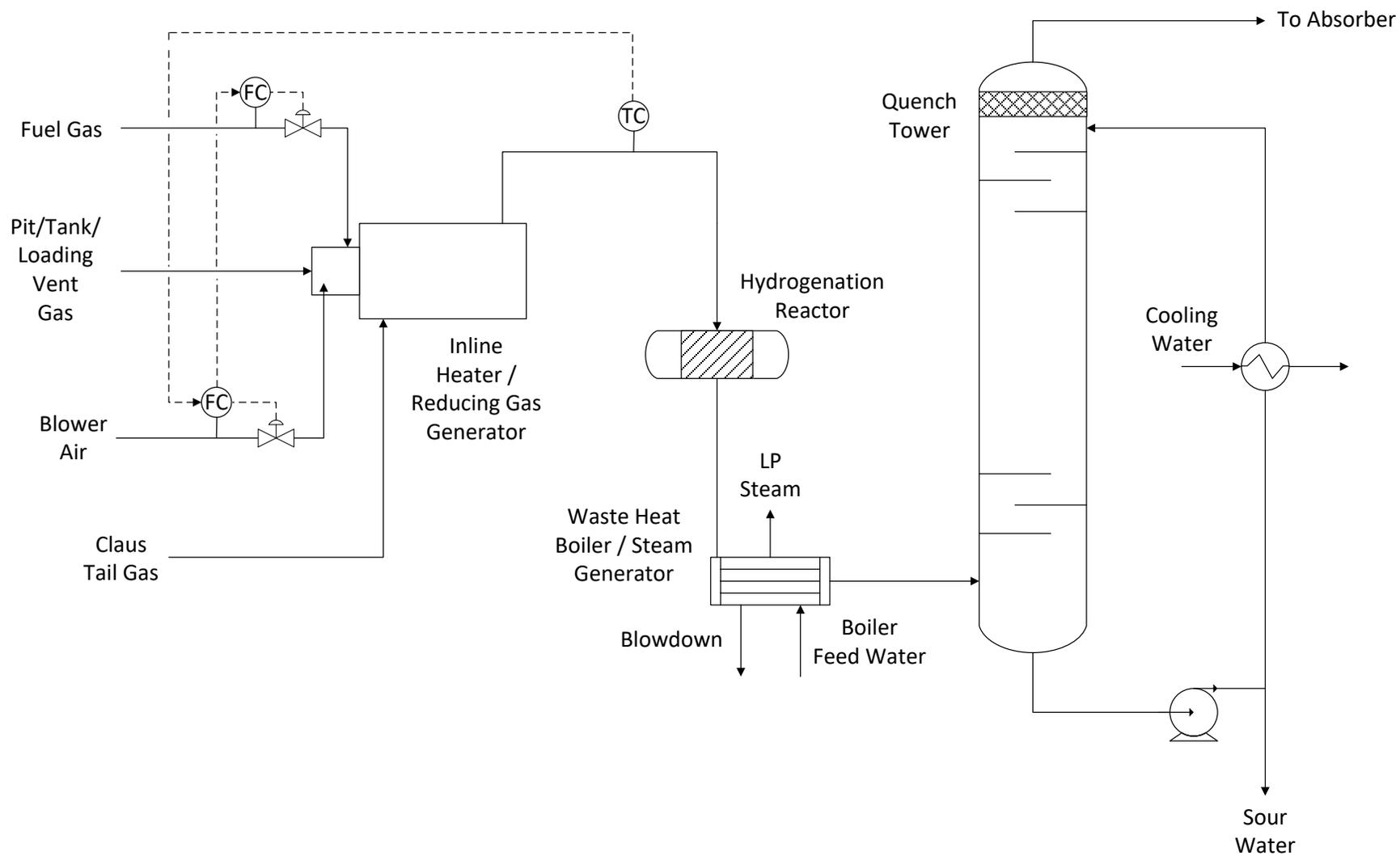
As with the SRU recycle option, tail gas recycle likely requires higher vent gas compression (than incineration) but lower fuel consumption than incineration. Similar modifications and new equipment are also required. There may also be additional demands to the quench tower and downstream TGU, depending on the stream composition and motive fluid.

### ***3.3.3 Sulfuric Acid Plant Recycle***

As with the other recycle options, routing the molten sulfur vent gas to the sulfuric acid plant (SAP) combustion chamber can impact the processing capacity of the plant. The type of motive device and motive fluid can affect conversion, specifically with steam ejectors. Similar equipment modifications and operating expenditures are anticipated with routing to the SAP.

### ***3.3.4 Recycle via Steam Sweep with Vent Stream Condensation***

There are a few sites that use or have used steam to sweep molten sulfur tanks. As with nitrogen-swept (inert-gas-swept) tanks, the tank usually operates at a small positive pressure. The practice of using steam introduces water into the vessel being swept/blanketed, which, along with the exclusion of air / oxygen, can lead to buildup of pyrophoric iron sulfide and potentially severe corrosion. However, if the walls of the tank are kept warm enough, then it may be theoretically possible to prevent liquid water formation and perhaps reduce corrosion rates. The steam is sometimes vented to atmosphere. However, one variant of this approach completely condenses the vent stream exiting the tank. For example, a venturi eductor with liquid water as the motive fluid could be used to condense / absorb the entire vent stream. Then, once the vent stream is condensed into the motive fluid, the resulting liquid stream (which will also contain



**Figure 3-2. Addition of Molten Sulfur Pit/Tank/Loading Vent Gas to TGTU Reducing Gas Generator**

solid elemental sulfur particles) may be sent to a sour water system, waste water treatment plant, or other wastewater system. Thus, this is a type of “recycle” to an upstream process (e.g., the sour water system). However, compared to the other recycle options discussed above, this approach should have no effect on the upstream SRU, TGTU, or SAP. Expenses for this option may be related to steam usage, specially designed heating systems to avoid water condensation at any point, piping, and sour water system modifications to handle the produced sulfur-laden water.

### **3.4 Scrub / Treat Vent Vapor**

Another option is to remove the H<sub>2</sub>S (and SO<sub>2</sub>, molten sulfur, and potentially other species) from the molten sulfur vent vapor, then vent to atmosphere. This can occur through use of different vent gas treatment technologies including caustic scrubbing, scavengers, and liquid redox. Since the vent gas stream is treated directly with these technologies, there is no impact on the SRU, TGTU, or SAP processing capacity. Likewise, if the SRU, TGTU, or SAP goes down, it will not impact the operation of the vent gas treatment processes. These treatment options are discussed below, although other processes could also be considered.

#### **3.4.1 Caustic Scrubbing**

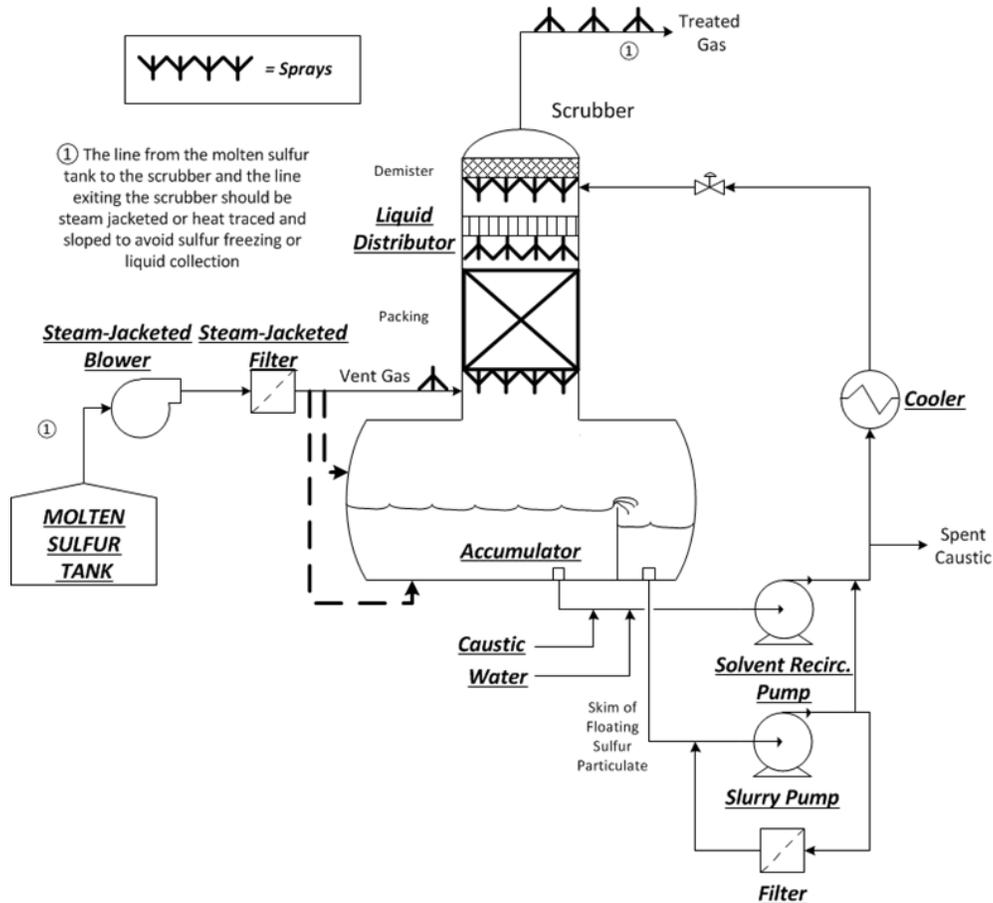
Caustic scrubbing is a vent stream treatment technology that has been applied in a number of oil refineries and other locations outside of oil refining. While caustic scrubbing is an established technology that can readily remove H<sub>2</sub>S and SO<sub>2</sub>, its use on molten sulfur vent streams is complicated by the presence of elemental sulfur that can plug different areas of the processing equipment. The elemental sulfur in the vent gas and in the associated caustic scrubber system may be in various forms (vapor, aerosols/fog, sulfur sols, and solid particulate) so that plugging can occur in the piping from the source and in the scrubber itself. The risk of plugging is usually the primary operating issue with caustic scrubbers in this service. Minimizing sulfur plugging can be accomplished by including certain design features in the equipment and by managing the dissolution of elemental sulfur into the caustic solution. Figure 3-3 shows a generic caustic scrubbing process flow diagram with sulfur deposition mitigation strategies shown in bold font.

Some strategies to mitigate sulfur plugging in caustic scrubbers are discussed below and additional details and methods can be found in the literature [17].

- **Improved Gas / Liquid Contact** –The system should be designed to get elemental sulfur out of the gas and into the liquid where it can be dealt with more easily. Once in the liquid, it is important to keep the solids suspended in solution or as a slurry until they dissolve or reach an appropriate point for removal. The liquid circulation rate can be increased to remove elemental sulfur from the gas. Liquid spray designs could be used to remove solids at the scrubber entry, and the gas entry could be submerged in the sump to remove solids from the gas. Intermittent spray washes could keep the mist eliminator from plugging and wash the piping.
- **Removal of Elemental Sulfur Solids** – Dissolution of elemental sulfur into the caustic solution is the ideal approach to manage elemental sulfur. If dissolution is not

possible, then suspended sulfur solids can be removed from the liquid phase by allowing them to settle in a separator for removal or filtering the liquid.

- Alternate Equipment and Process Flow Schemes – venturi contactors have been used with caustic and a high circulation rate to provide the needed contact between the gas and liquid phases. Cross-flow (horizontal) scrubbers may offer improved operation and longer run times. Redundant scrubbers could be implemented so that one can be cleaned while the other continues to operate.



**Figure 3-3. Generic Caustic Scrubber Process Flow Diagram**

Caustic scrubbing can remove  $H_2S$  and  $SO_2$  from the vent gas, so there should be negligible increase in refinery-wide emissions. (The treated gas from the caustic scrubber would vent to the atmosphere and not be sent to the incinerator.)

Major operating expenses are related to makeup  $NaOH$  and waste disposal of blowdown since the process is not regenerable. Higher vent gas compression may be required compared to incineration and the recycle options. Because of the potential for sulfur plugging, the process requires high operation attention and frequent maintenance. Capital expenses can be either higher or lower than the incinerator and recycle options. Significant equipment (scrubber, exchangers, pumps, tanks) needs to be purchased for the caustic scrubber, but this may be justified

if the vent stream (e.g., tank vent) is a long ways from any other destination. Finally, a moderate amount of additional plot space is required for the equipment.

### ***3.4.2 Liquid and Solid Scavengers***

“Scavengers” refer to non-regenerable chemicals or processes that remove a constituent (e.g. H<sub>2</sub>S), and then the spent chemical goes to disposal. Examples of scavengers include iron-oxide solids, some activated-carbon-based systems, and others. Liquid and solid scavengers are sometimes proposed for molten sulfur vent streams and occasionally used. However, the operating costs (primarily chemical costs) per pound of sulfur removed are higher than other options, and plugging may be more problematic with scavenger systems than others. Thus, scavengers are not reviewed further in this paper.

### ***3.4.3 Liquid Redox***

Liquid redox processes (e.g., LO-CAT, SulFerox) have also been applied on the vent streams from molten sulfur operations. As shown in Figure 3-4, liquid redox processes use a chemical (usually chelated iron) in aqueous solution to absorb H<sub>2</sub>S from gases, converting it directly to elemental sulfur. The chemical is regenerated to its reactive state using oxygen (air). The elemental sulfur must also be filtered from the liquid and disposed of. Under ideal conditions, it may be possible to capture elemental sulfur vapor by condensing / freezing it into the liquid redox circulating solution so that it can be filtered out. SO<sub>2</sub> will be removed by liquid redox processes, but may cause higher than desired salt formation or chemical degradation.

Some vendors claim experience with liquid redox processes in molten sulfur vent gas service. The elemental sulfur in the vent gas may plug the liquid redox equipment. Operator attention is considered to be high for this technology.

The main operating costs are associated with makeup chemicals, solid sulfur disposal (sold or landfill), and high vent compression compared to incineration. The liquid redox process is much more expensive than some options (e.g., caustic scrubbing) due to all of the necessary equipment (absorber, separators, exchangers, pumps, sulfur filtration) and the lead time can be long. The process requires the most plot space of the technologies presented here.

## ***3.5 Vent Vapor Destination Comparison***

Table 3-1 through Table 3-3 show a comparison of the molten sulfur vapor destinations discussed in the previous sections for incineration, recycle to other portions of the plant, and vent treating. The tables provide a “quick glance” comparison of the options. Refer to other sources in the literature ([11], [15]) for additional comparisons of the advantages and disadvantages of the destination options.

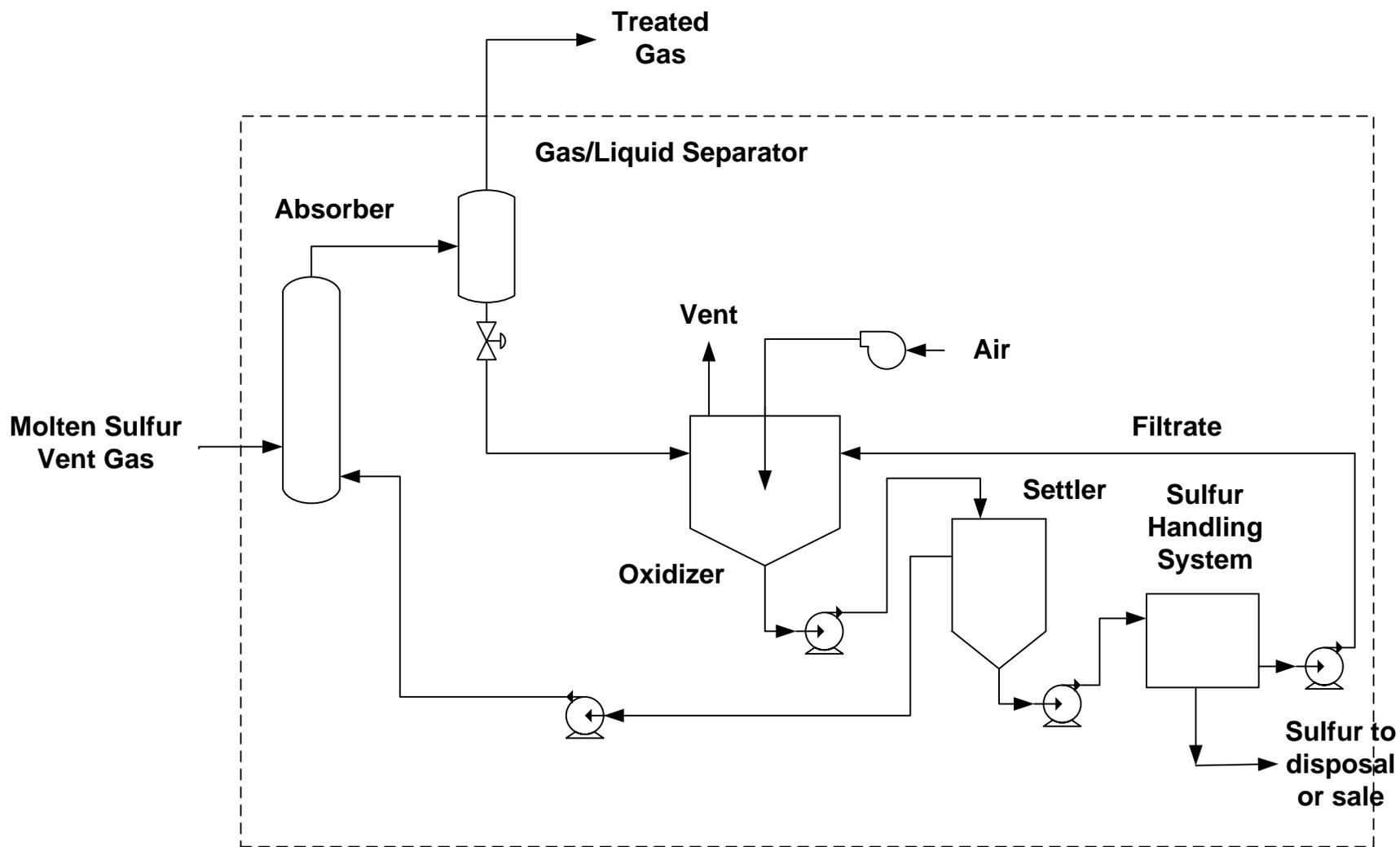


Figure 3-4. Generic Liquid Redox Process for Vent Gas Treatment

**Table 3-1. Comparison of Base Case (SRU Recycle) and Incineration Destinations for Molten Sulfur Vent Vapor [11], [15]**

Parameter	Recycle to SRU Claus Thermal Section		Thermal Incineration		Catalytic Incineration	
	Advantages	Disadvantages	Advantages	Disadvantages	Advantages	Disadvantages
Emissions	No increase			SO2 increase		SO2 increase
Sweep Gas	Air sweep allowed		Air sweep allowed		Air sweep allowed	
Motive Device Compression		Moderate	Lowest		Low	
SRU, TGTU, SAP Impact		Yes	No		No	
Reliability / Operations	Low operator attention	<u>Needs:</u> <ul style="list-style-type: none"> <li>• Backup treatment</li> <li>• Combustion controls for vent/sweep air</li> </ul>	Low operator attention		Low operator attention	Affected by deviations in flow and composition
Capital and Operating Expenses	Decreased fuel (compared to thermal incinerator)	<ul style="list-style-type: none"> <li>• Moderate capital (motive device and robust controls)</li> <li>• Moderate ejector motive fluid or blower power</li> </ul>	<ul style="list-style-type: none"> <li>• Low capital if existing incinerator used (motive device and controls)</li> <li>• Low motive fluid or blower power</li> <li>• No preheating</li> </ul>	Increased fuel	<ul style="list-style-type: none"> <li>• Low capital if existing incinerator used (motive device and controls)</li> <li>• Lower fuel (compared to thermal incinerator)</li> <li>• Low motive fluid or blower power (but more than thermal)</li> </ul>	<ul style="list-style-type: none"> <li>• Preheat vent gas to ignition temperature</li> </ul>
Plot Space	No plot impact		No plot impact		No plot impact	

**Table 3-2. Comparison of Base Case (SRU Recycle) and Other Recycle Destinations for Molten Sulfur Vent Vapor [11], [15]**

Parameter	Recycle to SRU Claus Thermal Section		Recycle to TGTU Reducing Gas Generator		Recycle to SAP Combustion Chamber	
	Advantages	Disadvantages	Advantages	Disadvantages	Advantages	Disadvantages
Emissions	No increase		No increase		No increase	
Sweep Gas	Air sweep allowed			Air sweep may not be possible	Air sweep allowed	
Motive Device Compression		Moderate		Moderate	Low	
SRU, TGTU, SAP Impact		Yes		Yes		Yes
Reliability / Operations	Low operator attention	<u>Needs:</u> <ul style="list-style-type: none"> <li>• Backup treatment</li> <li>• Combustion controls for vent/sweep air</li> </ul>	Low operator attention	<u>Needs:</u> <ul style="list-style-type: none"> <li>• Backup treatment</li> <li>• Combustion controls for vent/sweep air</li> <li>• Sulfur equipment positive pressure</li> </ul>	Low operator attention	<u>Needs:</u> <ul style="list-style-type: none"> <li>• Backup treatment</li> <li>• SAP combustion controls for vent/sweep air</li> </ul>
Capital and Operating Expenses	Decreased fuel (compared to thermal incinerator)	<ul style="list-style-type: none"> <li>• Moderate capital (motive device and robust controls)</li> <li>• Moderate ejector motive fluid or blower power</li> </ul>	Decreased fuel (compared to thermal incinerator)	<ul style="list-style-type: none"> <li>• Moderate capital (motive devices and robust controls)</li> <li>• Increased quench demand (w/ steam)</li> <li>• Moderate ejector motive fluid or blower power</li> </ul>	<ul style="list-style-type: none"> <li>• Decreased fuel (compared to thermal incinerator)</li> <li>• Low ejector motive fluid or blower power</li> </ul>	<ul style="list-style-type: none"> <li>• Moderate capital (motive devices and robust controls)</li> </ul>

**Table 3-3. Comparison of Base Case (SRU Recycle) and Vent Gas Treatment Destinations for Molten Sulfur Vent Vapor [11], [15]**

Parameter	Recycle to SRU Claus Thermal Section		Caustic Scrubber		Liquid Redox	
	Advantages	Disadvantages	Advantages	Disadvantages	Advantages	Disadvantages
Emissions	No increase		Minimal H <sub>2</sub> S/SO <sub>2</sub> increase		Minimal H <sub>2</sub> S/SO <sub>2</sub> increase	
Sweep Gas	Air sweep allowed		Air sweep allowed		Air sweep allowed	
Motive Device Compression		Moderate		High		High
SRU, TGTU, SAP Impact		Yes	No		No	
Reliability / Operations	Low operator attention	<u>Needs:</u> <ul style="list-style-type: none"> <li>• Backup treatment</li> <li>• Combustion controls for vent/sweep air</li> </ul>	Some molten sulfur experience	<ul style="list-style-type: none"> <li>• Elemental S plugging (incorporate design features)</li> <li>• High operator attention</li> <li>• Frequent maintenance</li> </ul>	Claim experience with molten sulfur gas	<ul style="list-style-type: none"> <li>• Elemental sulfur may plug equipment</li> <li>• High operator attention</li> </ul>
Capital and Operating Expenses	Decreased fuel (compared to thermal incinerator)	<ul style="list-style-type: none"> <li>• Moderate capital (motive device and robust controls)</li> <li>• Moderate ejector motive fluid or blower power</li> </ul>	Moderate capital of 2 H <sub>2</sub> S removal technologies	<ul style="list-style-type: none"> <li>• High capital (motive device, controls, and new equipment)</li> <li>• Makeup caustic costs and waste disposal</li> <li>• High ejector motive fluid or blower power</li> </ul>	Highest capital of 2 H <sub>2</sub> S removal technologies	<ul style="list-style-type: none"> <li>• High capital (motive device, controls, and new equipment)</li> <li>• Long lead time</li> <li>• Makeup chemicals</li> <li>• Disposal of solid sulfur (sold or landfill)</li> <li>• High ejector motive fluid or blower power</li> </ul>
Plot Space	No plot impact			Moderate plot space		High plot space

## **4.0 Factors that Impact Performance of Molten Sulfur Vapor Destinations**

The type of motive device and motive fluid has a significant impact on the performance of the process at the molten sulfur vapor destination. The sulfur load and type of sweep gas used also affects operations. Methods to check the effects of these factors are also discussed below.

### ***4.1 Motive Device and Motive Fluid***

Ejectors and blowers are the two most common motive devices used to transfer the molten sulfur vent vapors to their final destination. Ejectors require a motive fluid (steam, air, N<sub>2</sub>) to increase the pressure of the discharge gas. The type of motive fluid used can have a significant influence on the performance of the downstream process, especially if this refers to recycle to the SRU, TGTU, and SAP, but the motive fluid may also influence any vent stream treating process. Because of this, the refinery should carefully evaluate the vent system hydraulics (plot area and pipe distances) to understand the pressure requirements and motive fluid conditions (flow and feed pressure) and blower needs to transport the vent vapors.

#### ***4.1.1 Ejector versus Blower***

Blowers offer the advantage in that they add no additional fluid that could impact the SRU, TGTU, or SAP performance. However, blowers are typically more expensive than ejectors, they require electricity to operate, and plugging or fouling may sometimes be a bigger concern than with ejectors. The use of a blower could also present some operating issues that would need to be considered. Blowers are used with satisfactory experience in molten sulfur vapor service at some locations, but blowers are reputed to be problematic at other locations. It is also thought that most blowers used in this service are centrifugal type, not positive displacement type. If a blower is used, the type of blower should be carefully considered and the design should be carefully implemented to avoid plugging and other issues. The rotating parts of the blower may make this option somewhat more difficult given the concerns with plugging and corrosion in the vent lines. The blower also needs to be elevated and the lines to and from it sloped (similar with an ejector). Blowers may become a more economic choice for applications with high vent gas compression requirements.

Ejectors have advantages over blowers because ejectors have no moving parts and are more reliable in general. Ejectors are simple and less costly motive devices. Ejectors, however, increase the amount of material sent to the SRU, TGU, or SAP because of the need for motive fluid. Depending on the motive fluid and operating conditions at the vent gas destination, this could negatively impact plant capacity.

#### ***4.1.2 Impacts of Ejector Motive Steam***

For all of the molten sulfur vent gas destinations, the use of steam as the motive fluid increases the chances of corrosion in the piping due to the potential for condensation of acid species (e.g., sulfurous) from the vent gas and the possibility of condensed water at cool spots. For this reason, the piping to and from the ejector needs to be kept hot and well insulated (steam jacketed or ControTraced), and sloped to avoid pooling of liquids in the line. Liquids and solids could accumulate in pockets / low point areas, and the piping could plug or fail due to solids

buildup or solid sulfur accumulation [1]. Motive steam of the right pressure, however, has the benefit that it maintains or elevates the temperature of the ejector discharge gas, which helps to keep sulfur species in the vapor phase and prevent solids plugging. Using motive steam can also potentially impact how the processes at the final destination operate.

For the SRU, motive steam can decrease the SRU thermal reactor temperature. The motive steam could also adversely affect the Claus conversion since steam is a reaction product. For the TGTU, motive steam may add to the load in the quench tower, requiring additional cooler duty and pumparound pump power [11].

Likewise for the SAP, motive steam can decrease the temperature in the combustion chamber [11]. The presence of water in the vent gas can also decrease conversion to sulfuric acid. Cold startup or turndown can result in steam condensation that can damage the refractory of the gas combustion chamber [11]. Finally, the capacity of the SAP declines by roughly the same mass rate of vent gas introduced to the system [11].

For the vent gas treatment processes, the water vapor in the ejector discharge gas will condense at the cooler operating temperatures of the vent gas treatment processes, increasing blowdown and disposal volumes. With caustic scrubbers, a blower is often used to avoid this problem.

With the incinerator options, there is no significant impact expected due to the additional water vapor, other than it contributing to the thermal mass of the feed gas. There may also be additional precautions that need to be taken to minimize corrosion where the vent gas line enters the burner or incinerator. Corrosion in the stack itself is not expected since the temperature is significantly hotter than the acid dewpoints. In fact, many stacks are made of carbon steel in similar applications and do not experience significant corrosion.

#### ***4.1.3 Impacts of Ejector Compressed Air***

If the ejector uses compressed air as the motive fluid, and if the amount of ejector compressed air is less than that required in the SRU thermal reactor, then there may be no negative effect on plant capacity. The vent air simply reduces the amount of air supplied by the combustion air blower. However, proper controls would be needed to regulate the air flow from the two sources (vent vapor and blower) and the blower turndown would need to be evaluated. The refinery needs to have a sufficient supply of compressed air, and the compressed air may also need to be heated prior to the ejector [11].

As discussed with the sweep air present in vent gas, sending air to the TGU RGG is generally not desirable (see section 3.3.2 for discussion) and therefore compressed air is not an ideal motive fluid for recycle to the TGU RGG.

Similar to the SRU, if air is the motive fluid, then the SAP blower and incinerator air demand can be decreased by the same rate as air is added via the vent gas. The combustion air controls and instrumentation would also need to be checked for proper operation.

The use of compressed air is not expected to negatively impact the H<sub>2</sub>S treating options (caustic scrubbing and liquid redox). The CO<sub>2</sub> present in air will consume additional caustic to some extent.

#### ***4.1.4 Impacts of Ejector Nitrogen***

As discussed previously, the use of nitrogen should be considered carefully given the concerns with pyrophoric iron formation and fires. The refinery would also need a source of potentially significant and expensive nitrogen. For these reasons, nitrogen as a motive fluid is generally less common. Nitrogen should not significantly impact the performance of the vent gas treatment options for H<sub>2</sub>S removal.

#### ***4.2 Sweep Gas, Sulfur Load, Capacity***

The choice of sweep gas (air, N<sub>2</sub>, steam, etc.) will have similar impacts on the vent gas destination as discussed in Section 4.1 for the different ejector motive fluids.

The amount of sulfur (sulfur load) in the vent gas should be a small fraction of that being processed in the existing SRU, TGTU, and SAP so that its impact on performance should be minimal. The vent gas treatment processes will be designed specifically to handle the H<sub>2</sub>S in the vent gas stream so there should be no issues with sulfur load.

The other items that could impact performance of the downstream units (e.g., SRU, TGTU, SAP) are the operating conditions (temperature and pressure) and flow rate. The existing equipment needs to be evaluated for performance and size to handle the extra vent gas. System hydraulics, heat exchanger duties, and reactor loads, etc. will need to be evaluated for performance issues. If the capacity of the existing equipment is inadequate, then other technologies could be considered, or oxygen enrichment could be implemented.

#### ***4.3 Checks to Evaluate Suitability of Vent Destination***

While the methods described in Section 2 can be used to estimate a worst case H<sub>2</sub>S content in the vent gas stream for LEL and sweep gas flow determination, the actual content of H<sub>2</sub>S and other sulfur species is often much lower. In one example from Trimeric's work, the actual measured H<sub>2</sub>S content in the tank vent vapor was a little less than an order of magnitude lower than that estimated by assuming all of the H<sub>2</sub>S evolved from the molten sulfur. In order to verify the suitability of sending the vent gas to its final destination, it may be prudent to perform sampling of the vapors in existing systems that are being considered for modification. This will give a more accurate estimate of the impacts on emissions from incinerators and the performance of the recycle options (SRU, TGTU, or SAP) and vent gas treatment units with additional sulfur load. The vent vapor destination for completely new molten sulfur systems may need to be based on other site specific data or more realistic estimation assumptions for H<sub>2</sub>S evolution from the liquid.

The impact of the molten sulfur storage and transfer vents on the sulfur recovery equipment at the refinery should be modeled with process simulation software. Modeling can

provide a relatively easy indication of how the sweep gas, motive device (e.g., presence and type of motive fluid, if any) and/or operating conditions affect performance.

## 5.0 Molten Sulfur Pit, Tank, and Loading Vent Routing Options and Configurations

The preceding sections have focused on the source of the vent streams produced by molten sulfur handling and transport, the motive equipment used to transport the recovered vent streams, and the options for the final destination of the vent stream. The routing and configuration of the vent streams from the source to the destination may appear to be details (e.g. piping hydraulics) unrelated to the overall vent system design choices. However, when vent streams from multiple sources (e.g., pit, tank, loading) are present at a single site, there are many options for configuring the vent system that may significantly impact the cost, safety, efficacy, and operability/flexibility of the entire vent vapor system. These options are not simply theoretical – refiners are known to apply the varying configurations in practice. Understanding the vent stream routing options, therefore, represents a design choice that should be part of any molten sulfur vent recovery evaluation. For the purposes of this paper, three specific configurations will be reviewed:

- Configuration #1: Individual Sweep and Motive Device per Source
- Configuration #2: Single Motive Device and Inter-Connected Sweep
- Configuration #3: Hybrid of Configuration #1 and #2

Each option is reviewed below, including a schematic and review of benefits and disadvantages of each option. In addition, to facilitate comparison of each option, the following assumptions are made for calculating a sweep air requirement:

- 300 ppmw  $H_2S + H_2S_x$  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.
- The sulfur make rate for the Claus unit is 500 LTPD, and this will also be the sulfur flow design basis used at each point in the process. (Higher pump flow rates may be used in actual design calculations – the sulfur make rate is used for the entire process in this case for simplicity.)
- All of the  $H_2S$  can evolve at any point in the system (conservative assumption).
- 25% approach to LEL of  $H_2S$  at 330°F (i.e., target 0.75 vol%  $H_2S$  in vent gas).

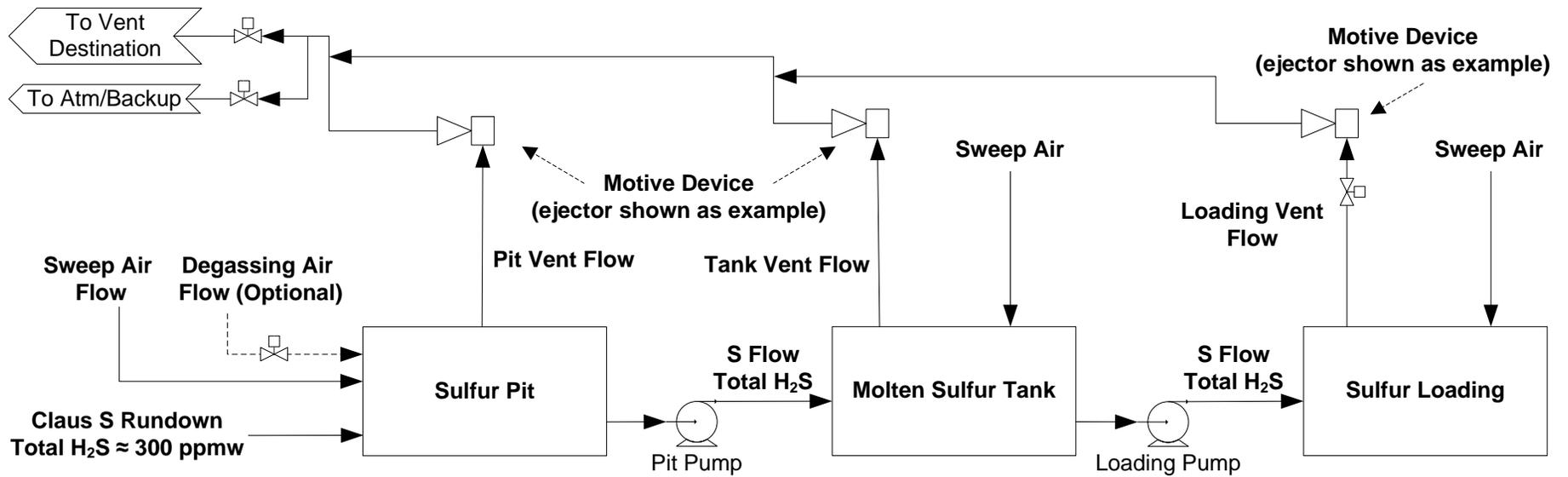
Based on the assumptions above, the sweep air requirement at any single point in the process will be approximately 55 lbmol/hr (1,580 lb/hr). This basis will be used to calculate total sweep air requirements for each of the system configurations that follow.

Figure 5-1 depicts Configuration #1, which is the default option for the vent system configuration. This option provides a single motive device for each source (in this example, separate ejectors for each of the pit vent, tank vent, and loading vent). The vent gas streams are then combined downstream of the each ejector discharge and upstream of the vent vapor destination. The general benefits of this configuration include the following:

- Sweep air is provided, controlled, and designed for each source in the system. There is no inter-dependence on piping system hydraulics elsewhere in the process.
  - For loading operations, there may be a desire to only provide sweep air when loading operations commence.
- If process conditions change or sweep air requirements must be modified for part of the system, the motive device for each individual source can be modified / replaced to accommodate the change.
- Each vent stream can be isolated from the vapor destination if necessary and may allow future modification to send each source to a separate destination, if needed.

The potential drawbacks of Configuration # 1 include the following:

- Additional capital cost, maintenance costs, etc. of motive devices for each source.
- For the specific case of routing to the thermal reactor of the Claus unit, multiple paths for flashback / flame propagation exist that must include the proper isolation / safety measures and controls. Frequently, the sulfur pit is an in-ground concrete structure, which makes it generally more robust in the event of flashback from the Claus thermal reactor. By contrast, the tank and loading areas represent a more significant risk to personnel and property if flashback occurs, so additional isolation/safety requirements may be needed for these vent sources.
- Sweep air requirements must be estimated at each point in the process. Since the H<sub>2</sub>S evolution at each step may not be known, a conservative approach to estimate sweep air (as described in Section 2.2) is often used. In this example evaluation, all of H<sub>2</sub>S is assumed to evolve at each point in the process, which requires that 1,580 lb/hr of sweep air is provided at each point. **For the system, that means a total of 4,740 lb/hr sweep air (plus vapors picked up at each source and any motive fluid if ejectors are used) that would go to the vent destination.**



**Figure 5-1. Molten Sulfur Vent Vapor Routing Configuration #1 (Individual Sweep and Motive Device per Source)**

Figure 5-2 represents Configuration #2, which is the other extreme of vent routing options. Rather than managing each vent stream source separately with individual motive devices and piping, all vent vapors are routed back through the pit (the source that is the furthest upstream in the system). A single ejector (or other motive device) is located on the pit vent to draw vapors through the entire system. The general benefits of this configuration include the following:

- All vent streams pass through the pit before entering a combined vent line that will go to the vapor destination. When the final destination is the Claus thermal reactor, this has the specific benefit of ensuring that only one path exists for flashback (one set of isolation / safety / control devices for the vent lines) and ensuring that the pit is the first location impacted (as noted previously, the pit is a generally more robust structure and probably safer location for flashback than the tank or loading area).
- Only one motive device (not considering spares) is required for the entire system.
- Sweep air requirements only need to be estimated for one, worst case location in the system. This is because all of the vent systems are interconnected, so assumptions about H<sub>2</sub>S evolution at each point are not important – the full volume of sweep air for the maximum H<sub>2</sub>S evolution case will be available at every point in the system. In this example evaluation, it was assumed the sulfur flow at every point is identical (the sulfur make rate) for simplicity. Therefore, the worst case is to assume all of the 300 ppmw of H<sub>2</sub>S + H<sub>2</sub>S<sub>x</sub> will evolve at a single location in the system and provide that sweep air flow continuously from the loading area through the tank and then pit. **For the example system in this paper, that means a total of 1,580 lb/hr sweep air (plus vapors picked up at each source and any motive fluid if ejectors are used) that would go to the vent destination. This is 1/3 of the sweep air required for Configuration #1 (under the assumptions of this example).**
  - The sweep air can be provided through the tank headspace when sulfur is not being loaded into trucks, in the event that the loading area sweep is to be operated only intermittently.
  - If the actual H<sub>2</sub>S evolution at each point in the process could be known exactly, the sweep air at each point in Configuration #1 could be defined specifically to the H<sub>2</sub>S present at each step, and the benefit a reduced sweep air requirement for Configuration #2 would disappear. However, in practice, the H<sub>2</sub>S evolution is not known at each step, and this uncertainty necessitates the conservative assumptions which make a single, inter-connected sweep system potentially attractive.

The potential drawbacks of Configuration # 2 include the following:

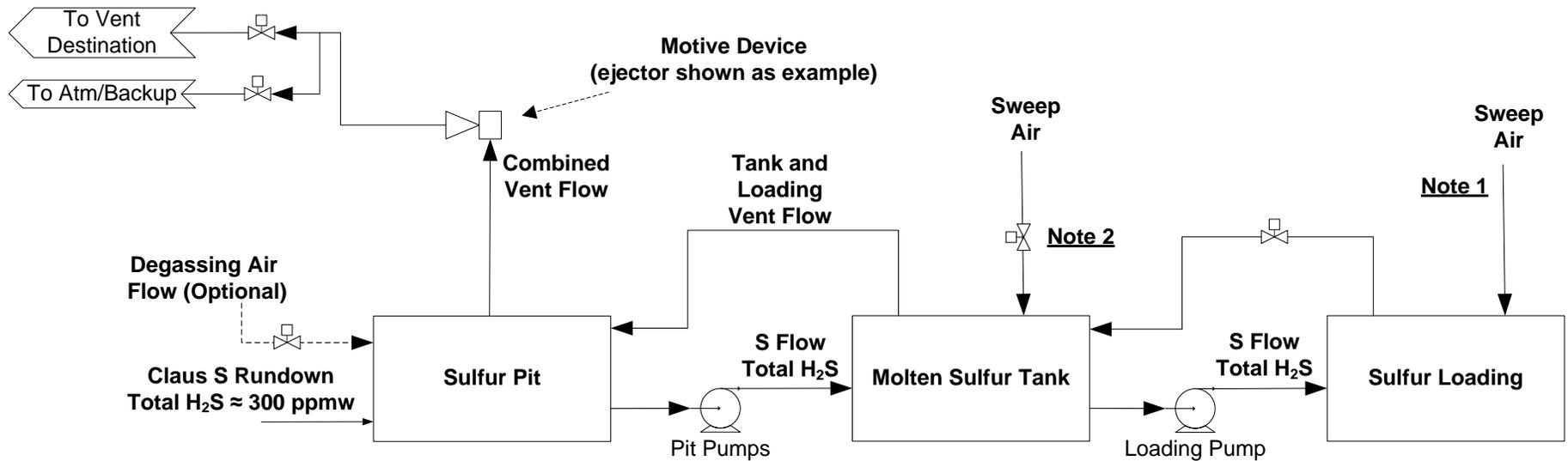
- The sweep air at any given point in the system cannot be controlled and may be impacted by system hydraulics. This creates a risk where a localized issue in one part of the vent system (e.g., plugging) reduces the sweep air flow at all points in the system, creating a potentially dangerous situation (possible explosion risk if H<sub>2</sub>S rises beyond design levels in head spaces).

- If this system is implemented with an existing pit, the sweep air from the downstream processes entering the pit headspace may displace existing pit sweep air or impact degassing performance. A careful analysis of the pit headspace conditions may be required.
- The design of the tank sweep / vent system may require special considerations. Air intakes cannot be open at all times (as they might be in a typical tank design) because the sweep air may be originating from downstream at the loading area. If air intakes are open, it may “short-circuit” the sweep flow.

Finally, there are many intermediate options that represent some combination of the systems represented in Figure 5-1 and Figure 5-2. All of these combinations are not reviewed in this paper. Rather, one intermediate example is presented in Figure 5-3 to facilitate discussion and comparison of the vent gas routing options. Configuration #3 provides an individual motive device for the pit and loading areas, but routes the tank vent through the pit and pit vent ejector. Since this system is a hybrid of the first two configurations, it has a combination of the benefits and drawbacks of each preceding option. Specifically, Configuration #3 balances the number of individual sweep locations against having independent control at specific locations (e.g., loading, which may be operated intermittently). All three configurations are compared side-by-side in Table 5-1. Configuration #3 is depicted in Figure 5-3.

**Table 5-1: Comparison of Vent Routing Configurations**

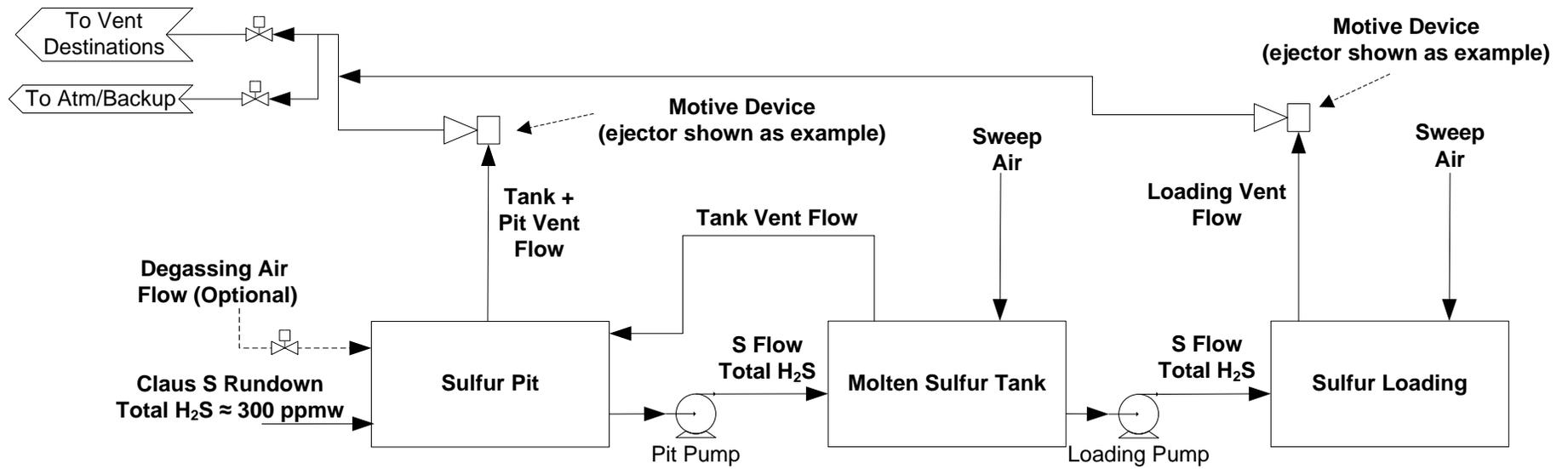
	<b>Configurations</b>		
	<b>#1: Individual Sweep and Motive Device per Source</b>	<b>#2: Single Motive Device and Inter-Connected Sweep</b>	<b>#3: Hybrid of Configuration #1 and #2</b>
<b>Motive Devices</b>	3	1	2
<b>Number of Paths for Flashback (i.e., relative number of control/safety devices required to isolate vents from destination)</b>	3	1	2
<b>Sweep Air Flow Required</b>	4,740 lb/hr	1,580 lb/hr	3,160 lb/hr
<b>Sweep Air Control at Each Vent</b>	Yes	No	Partial
<b>Flexibility (future re-route, changes in vent requirements, etc.)</b>	Best	Worst	Intermediate
<b>Challenge as Retrofit Design (Difficulty/Risk of Retrofit Implementation)</b>	Least	Most	Most



**Notes**

1. Sweep air flow is calculated based on the highest possible H<sub>2</sub>S evolution at any single point in the system, not necessarily at loading. This ensures that adequate sweep air is present at all points in the system.
2. Normally closed. Only open when loading vapor recovery is not operational (no sweep air from loading).

**Figure 5-2. Molten Sulfur Vent Vapor Routing Configuration #2 (Single Motive Device and Inter-Connected Sweep)**



**Figure 5-3. Molten Sulfur Vent Vapor Routing Configuration #3 (Hybrid Configuration)**

As the table indicates, the options result in different safety, economic, and operational considerations. Therefore, to select a vent routing design or approach would require evaluation for a specific site in the context of their priorities. As noted, the examples represent a range of configurations used in the field by refiners and therefore, might represent practical choices for other operators as well.

### **5.1 Other Options/Considerations**

The preceding discussion does not cover all options and scenarios that might be present at a given site. The following list represents some of the situations that may dictate different routing choices for a given facility:

- The options listed in the preceding discussion assume that all vent stream sources will be routed to the same destination. In some cases, a single destination may not be able to accommodate all of the vent stream sources (e.g., hydraulic limitations preventing return to the Claus unit), economics may dictate that combining the vent gas streams is not practical, or the site may have a preference to manage the vent streams separately for flexibility. In that case, some of the vent stream sources may need to be handled individually. For example, if the tank and loading stations are located remotely from the SRU, then it may be advantageous to treat the tank and truck loading vapors in one system (local to the tank and loading area) while separately managing the pit vent vapor in the SRU (e.g., thermal reactor or incinerator).
- At some sites, an existing system may already be in place to deal with some of the vent vapor sources (e.g., caustic scrubber for a tank vent), and the existing equipment and vent routing may create limitations for integrating all vent gas streams for disposition or may dictate that one configuration is superior to others based on the configuration of existing equipment.
- Specific sites may have varying tolerances for emissions events due to a failed primary option for vent disposition. Therefore, the system design may need to include backup vent destinations that change the considerations for vent routing configurations.

## **6.0 Conclusions**

Molten sulfur vent streams contain  $H_2S$ ,  $SO_2$ ,  $S_6$ ,  $S_8$ , sulfur mist, and other sulfur species that make handling the gas challenging. The vent gas streams can be routed to different destinations including: i) venting to the atmosphere, ii) incineration, iii) recycling to the SRU, TGTU, or SAP, iv) condensing the stream [requires steam sweep], and v) treating with caustic scrubbing or liquid redox technology among others technologies. The vent gas streams can also be transported to their final destination with different motive devices and fluids (ejectors with steam, air,  $N_2$  or blowers). The type of motive fluid used can have a significant impact on the performance of the downstream process and could represent a potential source of corrosion (steam) or pyrophoric iron fires ( $N_2$ ). The vent gas streams can also be transferred with different flow schemes (single, individual, or hybrid sweep) and motive devices. The optimal approach needs to be evaluated on a site-by-site basis to meet each plants level of conservatism for safety, environmental regulations management, and operational philosophy.

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