DESIGN CONSIDERATIONS FOR NATURAL DRAFT VENTILATION IN MOLTEN SULFUR STORAGE TANKS

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Abstract

Refineries with Claus sulfur recovery units (SRUs) often store molten sulfur in tanks prior to loading in rail car or trucks for delivery to customers. The molten sulfur contains dissolved H_2S that will desorb into the gas phase to varying levels depending on the source of the molten sulfur and the handling conditions. In the modified Claus process in oil refineries, undegassed molten sulfur can contain several hundred ppmw H_2S. If the head space in the storage tank is stagnant, then the H_2S can accumulate in the vapor space above the liquid sulfur to dangerous levels (tens of volume percent) if undegassed. H_2S is extremely toxic (10 ppmv OSHA PEL, 8-hr TWA) and can also cause a significant explosion concern in the storage tank as well. Because of this, sweep gas is often used to keep the H_2S concentration in the head space below a maximum of around 25% of the lower explosive limit.

To prevent a potential explosion, an air-swept tank must be designed to accommodate the necessary sweep air flow. Some refineries use ejectors or blowers to pull vapors through the tank to a downstream Claus furnace, tail gas treater, incinerator, or treating system (e.g., caustic scrubber) during normal operation, while utilizing natural draft flow for backup operation. The basis for natural draft air flow in the tank is the "stack effect". This is the movement of air into and out of the tank from the buoyant force created by the pressure differential from the outside ambient air (colder, more dense) and the vapor in the tank head space (hotter, less dense). Many factors can impact the natural draft flow in the tank including the atmospheric and tank vapor temperatures, the physical properties of the gases, wind effects, and the tank stack and peripheral vent characteristics, among others. This paper reviews calculation methods for the natural draft flow in the headspace of a molten sulfur tank and describes the impacts of some of the underlying parameters. In addition, other tank design evaluations for unloading (inbreathing with vacuum conditions) and out-breathing with positive-pressure (during tank filling or through use of snuffing steam) are also presented, as well as optional monitoring and control features to ensure safe tank operation.

1.0 Introduction

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 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 will desorb into the gas phase. The molten sulfur flowing into the pit (or first receiving vessel) from a Claus SRU is often assumed to contain 300 ppmw[1,2,3] H_2S and H_2S_x, although oxygen enrichment and subdewpoint operation can produce higher levels, e.g. 450 ppmw[4].

The sulfur from the Claus unit often flows to a sulfur pit. The sulfur may be degassed, either in the pit or in separate equipment, to remove H_2S down to about 10 ppmw. Even if the molten sulfur is not degassed while in the pit, some H_2S will evolve from the pit (on the order of 50%[2]), 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. The molten sulfur then often flows to a tank where it is stored until it can be loaded into railcars or trucks for transportation to customers. 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[2], which could cause an explosion and/or pose a significant exposure hazard to personnel. (The OSHA permissible exposure limits[5] 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.) Even with degassed sulfur (e.g., to 10 ppmw H_2S), it is theoretically possible that additional H_2S could evolve during the residence time in the storage tank leading to dangerous concentrations of H_2S in the tank vapor space (hundreds of ppmv to low volume percent levels)[2]. While some literature sources[3] suggest low H_2S in the tank vapor space of degassed sulfur, presumably due to the oxidation of the residual H_2S to SO_2, 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.

Other sulfur species are also present around molten sulfur operations. Sulfur dioxide (SO_2) is generally also found in the head space of sulfur storage equipment with both undegassed and degassed molten sulfur and, in some situations, may be present at significantly higher concentrations than H_2S. Some of the SO_2 originates from the elemental sulfur entering the storage equipment from the Claus SRU, although SO_2 is believed to also come from the reaction of elemental sulfur with oxygen from the air in the storage tank and loading areas[2]. SO_2 is not flammable, but it is toxic at similar levels to H_2S. Elemental sulfur vapor in various forms (S_2, S_4, S_6, S_8 and even with larger molecules to S_{12}) have been reported in the literature[6]. Although small sulfur molecules exist at higher temperatures, primarily S_8 is expected at the conditions of sulfur tank vent gas (250-300^{o}F)[6]. Finally, sulfur species such as carbonyl sulfide (COS) and carbon disulfide (CS_2) may also be in the vent streams from molten sulfur systems[7].

Because H_2S is flammable, sweep air is often used to keep the H_2S content in the tank vapor space below 25% of the lower explosive limit (LEL), although other percentages have been reported in the literature[7,8,9]. Air is often used but other gases such as fuel gas, N_2, or other inert gas purge are sometimes considered to blanket / sweep sulfur tanks.

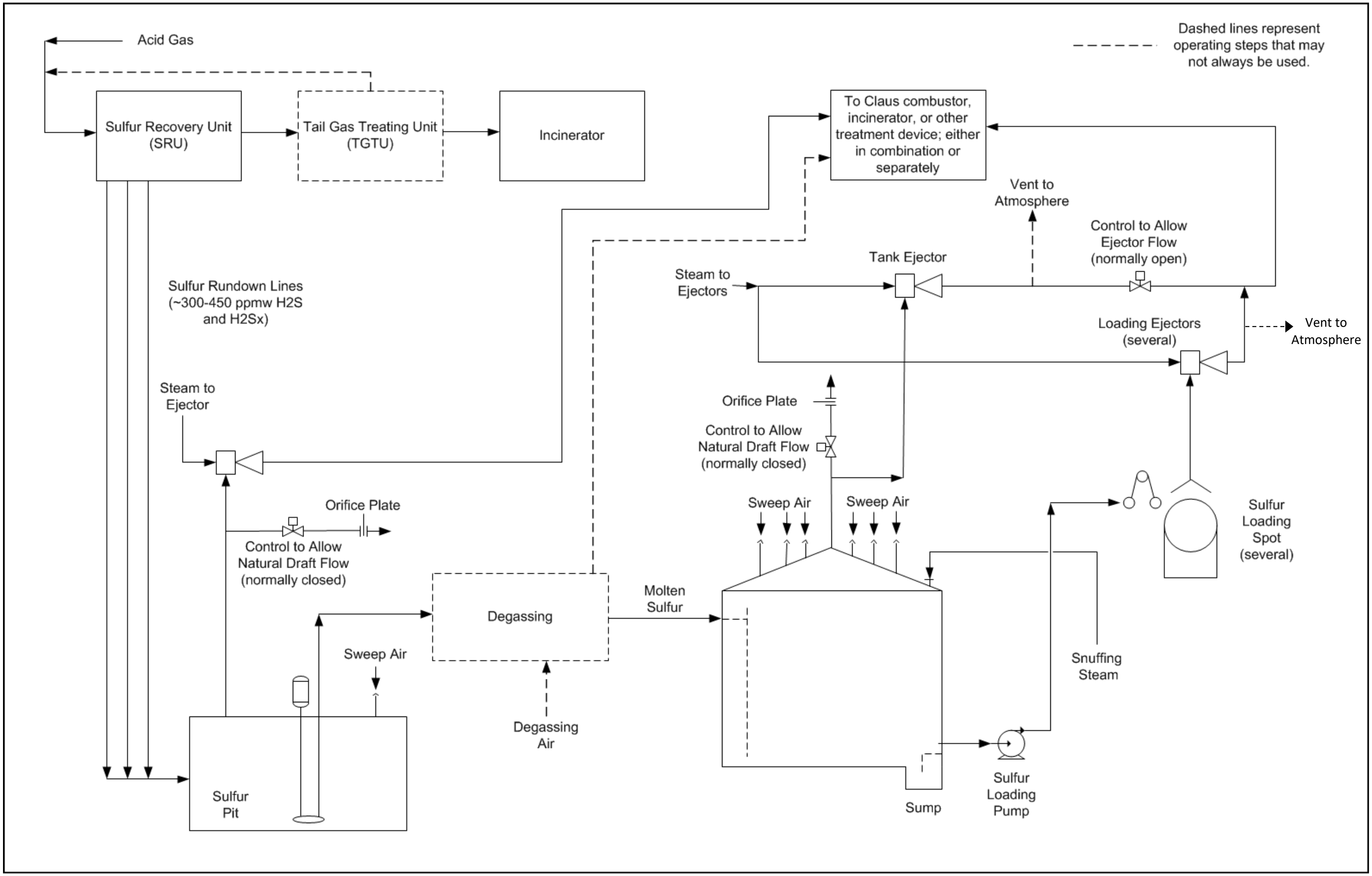

Figure 1. Molten Sulfur Storage and Handling System

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. Many options exist for this including but not limited to: sending the tank vapors to the Claus reaction furnace, to a tail gas treater, to the SRU incinerator, or treating the tank vapors in a particulate control device and/or caustic scrubber or other H_2S removal process. Often times, steam ejectors or blowers are used to pull air through the storage tank vapor space and route the vapors to the downstream treating system. While ejectors or blowers may be used during normal operation, storage tanks are often designed for natural draft air ventilation during emergency or backup operation. In other cases, where it is allowed by permit conditions, natural draft ventilation may be the only source of vapor flow into and out of the tank.

Consider a tank with a central stack at a higher elevation and a number of other lower nozzles around the perimeter (air inlets or vents). Natural draft air flow through the tank is based on the temperature difference between the outside air and the internal tank vapor. Because the vapor temperature in the tank is hotter than the outside air temperature, the density of the tank vapors is less than the outside air density causing the tank vapors to flow up and out of the central stack of the tank. The colder outside air will be drawn into the lower peripheral air inlets. This is often referred to as the "stack effect", where the stack in this case is represented by the headspace of the tank and the central stack on the tank.

This paper presents some methods for designing a molten sulfur storage tank for natural draft flow based on the "stack effect" model. In this model, it is important to balance the maximum flow area of the central stack and peripheral vents (to increase the sweep air rate) while maintaining sufficient pressure drop across the inlets to prevent reverse flow. Parameters that can impact the natural draft flow in the tank are also discussed including: the atmospheric and tank vapor temperatures, the physical properties of the gases, wind effects, and the tank stack and peripheral vent characteristics, among others. Other tank design evaluations for unloading and positive pressure during out-breathing are also presented, as well as optional monitoring and control features to ensure safe tank operation.

Lastly, while the "stack effect" approach to designing for natural draft flow is based on sound engineering principles, additional detailed computational fluid dynamic (CFD) analyses or comparisons to other well-proven tank designs may be warranted for a new tank construction.

2.0 Molten Sulfur Storage Tank Vent Gas Characteristics

Vent streams from molten sulfur storage tanks are generally composed primarily of air or nitrogen (depending on the source of sweep gas), but also contain H_2S, SO_2, elemental sulfur (S_8), sulfur mist/droplets, and possibly also COS and CS_2. It is important to know the composition of the vent gas in the tank because, although the sulfur species may be at low levels, they can impact the physical properties (molecular weight and density) of the gas used in the natural draft flow calculations. In some cases, it may be possible to sample the vent gas stream directly and analyze for these compounds, especially if the tank design is for a replacement or upgrade of an existing tank. However, if the vent gas stream cannot be sampled (because of a new tank design or for another reason), then there are other ways to estimate the composition of the tank vapor space. Different approaches with varying levels of conservativism have been reported in the literature as discussed further in the subsections below.

2.1 *Typical Sulfur Species and Estimation Methods*

The amount of H_2S that evolves from the molten sulfur into the tank vapor space can be estimated from measured H_2S and H_2S_x 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 and used. For example, the molten sulfur can be sampled for H_2S and H_2S_x in the pit (prior to the tank) and possibly also in the tank or at the truck or rail car loading stations. The difference of these two measurements gives an indication of the amount of H_2S that evolves from the molten sulfur into the storage tank headspace. If the molten sulfur cannot be measured at both locations, it may be possible to use only the pit molten sulfur H_2S and assume some safe percentage (e.g., 100% or other) evolves in the storage tank. Another even more conservative approach found in the literature is to assume that all the H_2S present in the initial rundown (e.g., 300+ ppmw) sulfur evolves at each point in the process[2].

Different values for the molten sulfur flow rate can also be used. 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. The molten sulfur pump rate to the storage tank is often much higher than the nominal flow, and, when coupled with the measured H_2S in the molten sulfur, results in a much higher estimated vapor space sulfur load and sweep air requirement. In one previous application, using the actual pump rate and 75% H_2S evolution resulted in a vent gas flow and sulfur content that was 7 times greater than that estimated with the SRU nameplate capacity and 100% H_2S evolution. While this would result in a conservative natural draft tank 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_2S_X compounds: Since it is known that H_2S_x is relatively slow to convert to H_2S, assuming that the total concentration of both compounds will evolve as H_2S is a conservative overestimation;

- H_2S evolution: It is unlikely that all of the H_2S will evolve from the tank;

- Sulfur degassing: The sulfur entering the tank does not degas instantaneously, in part because the sulfur in many tank designs 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 limits the rate at which the sulfur can degas; and

- LEL values: The LEL (discussed later) for H_2S is often estimated at conservative temperatures that result in conservatively high amounts of sweep gas being used in the tank.

Since a variety of approaches have been reported in the literature for estimating H_2S evolution, the level of conservativeness and methods required for estimating the amount of H_2S in vapor space will need to be reasonably rationalized for each specific storage tank design.

Various literature sources provide vapor-phase analytical data that can be used to estimate the SO_2, COS, and CS_2 in the tank vapor space. Molar ratios of 1:1 SO_2 to H_2S have been reported in the literature for undegassed sulfur[10]. CS_2 has been reported in the literature to be on average (0.15:1 molar CS_2:H_2S)[3] and past experience with COS shows a molar ratio of 0.02:1 COS:H_2S. It should be noted that the data in the literature show significant variability and their suitability for use in estimating the vent gas composition should be reviewed for the particular conditions of the tank design.

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 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[11].

Finally, sulfur mist may also be present in the vent gas. The amount of sulfur mist in the 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 ratio of sulfur mist (S_8) to H_2S that might be expected in these types of streams[10]. Significant engineering judgment and experience and/or estimation based on measurements is required to arrive at a reasonable value for elemental sulfur mist / sulfur droplet entrainment.

2.2 Sweep Gas Source and Flow Requirement

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%[8] and as high as 35%[9] as an upper limit to stop operation have also been reported. The LEL for H_2S is also sometimes assumed for a conservatively high temperature, because a conservatively high temperature gives a conservatively lower LEL for H_2S and thus a higher sweep rate. A temperature of 330°F is a conservative design choice when determining the required air rate. 330°F is higher than a tank would normally be operated, due to concerns with increasing sulfur viscosity at high temperature. At this temperature, the LEL is 3.4 vol%[2] so at 25% of the LEL the target H_2S concentration is 0.85 vol% (3.4 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[12]; however, from an LEL and sweep air rate perspective a higher temperature is more conservative.

Even though both H_2S and sulfur are flammable, the general practice in the industry is to use air as the sweep gas. The presence of oxygen keeps the atmosphere in the tank in an oxidizing state, which helps prevent the formation of pyrophoric iron sulfides on carbon steel surfaces. (Air is also readily available and generally less expensive than other inert gases such as nitrogen, CO_2, or fuel gas.) Iron sulfide only forms in significant amounts under the reducing (without oxygen) conditions found in unvented tanks or tanks swept/blanketed with nitrogen. Once formed, iron sulfide poses a safety risk if it is subsequently exposed to the atmosphere – e.g., for maintenance or cleaning – because the iron sulfide could spontaneously combust in the presence of oxygen, causing a sulfur fire or, if the vapor space is in the flammable range, an explosion. Lastly, any flammability concerns with air can be mitigated by utilizing safe approaches to the LEL and installing proper monitoring equipment on the tank.

The water content of the sweep gas should also be considered to arrive at the overall storage tank vapor space composition. It can be determined by the assuming air is saturated with water at atmospheric conditions.

3.0 Fundamentals of Natural Draft Flow for Tank Ventilation

The air sweep rate needed in order to maintain no more than, for example, 25% of LEL for H_2S serves as the basis to design a tank for natural draft air flow. Natural draft flow utilizes the inherent temperature difference between the vapors in the molten sulfur tank headspace and the ambient conditions outside of the tank to create a natural air flow pattern to sweep the headspace of the tank. Since natural draft flow does not rely on an external motive force (blower/ejector) to move the air, it should serve as a more reliable source of sweep air. However, the sweep air rate will vary with ambient conditions and operating conditions of the tank, so it is critical to design the tank to ensure that sufficient natural draft flow occurs at all relevant operating and ambient conditions the tank will experience. The following sections will describe the fundamentals of natural draft air flow in the tank, the important design and operating conditions/parameters that impact the air sweep rate, and the impact of these conditions on the natural draft flow rate.

3.1 Theory of Natural Draft Flow – "Stack Effect"

Natural draft air flow is sometimes described as the "stack effect" or "chimney effect" referring to the buoyancy-driven flow that occurs in a flue gas stack or chimney. The principles governing flow in these systems are the same as those in the natural draft flow in a tank and can serve as the basis to develop a simplified model and equations used to calculate draft flow in a tank. A "stack" model is depicted in Figure 2 below.

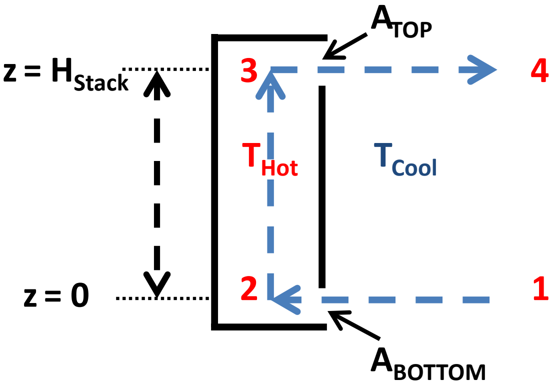

Figure 2. Natural Draft Flow or "Stack Effect".

Figure 2 includes a proposed path for air flow – the air flow path is depicted as flowing from station 1 where ambient air enters the stack, warms up and rises in the stack, exits the stack to station 4. In addition, a mechanical energy or pressure balance (i.e., Bernoulli equation) can be written for the path from station 1 to station 4.

Point 1 and 2

The pressure difference across the air inlet at the bottom of the stack represents the frictional losses due to gas entry and should represent the specific inlet device (e.g., orifice, nozzle, etc.). Equation 1 represents the pressure difference across the entry (after simplification) and uses a discharge coefficient to account for frictional losses. Alternatively, fitting or loss coefficients could be used to evaluate frictional losses. The used of a single discharge coefficient for the inlet (and the outlet in the following equations) implies that the discharge coefficient is accounting for all frictional losses at these points (e.g., orifice at the inlet). If a specific design includes additional fittings or a specific design, the discharge coefficient may need to be modified accordingly.

$$P_1 - P_2 = \frac{1}{C_{D,BOTTOM}^2} \frac{\dot{m}_{BOTTOM}^{\;2}}{2\rho_{Cold} A_{BOTTOM}^2} \qquad (1)$$

Where:

C_D = Discharge Coefficient;
$\dot{m}_{BOTTOM}$ = Mass flow rate through the bottom stack opening;
ρ_{Cold} = Mass density of “cold” or ambient air;
A_{BOTTOM} = Cross-sectional area of bottom stack opening.

Point 3 and 4

The pressure difference from points 3 to 4 represents frictional losses at the exit of the stack and can be represented by Equation 2 (analogous to Equation 1 at the entry):

$$P_3 - P_4 = \frac{1}{C_{D,TOP}^2} \frac{\dot{m}_{TOP}^{\;2}}{2\rho_{Hot} A_{TOP}^2} \tag{2}$$

Where:

$\dot{m}_{TOP}$ = Mass flow rate through the top stack opening;
ρ_{Hot} = Mass density of “hot” exiting air;
A_{TOP} = Cross-sectional area of top stack opening.

Point 2 and 3

The pressure difference between points 2 and 3 represents the weight of the column of hot air in the stack between the points (hydrostatic head). Equation 3 is a simple hydrostatic equation that is used to estimate the pressure difference based on the hydrostatic head between these points:

$$P_2 - P_3 = \rho_{Hot} g H_{Stack} \tag{3}$$

Where:

H_{Stack} = Stack height = (Height of the top stack gas opening) - (Height of the bottom stack gas opening) (reference height)[I].
g = Gravitational acceleration (in appropriate units).

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Point 4 and 1

The pressure difference between points 4 and 1 represents the weight of the column of cold air outside of the stack between the points. Equation 4 is a simple hydrostatic equation that is used to estimate the pressure difference based on the hydrostatic head between these points:

$$P_1 - P_4 = \rho_{Cold} g H_{Stack} \tag{4}$$

[I] Alternative derivations can be developed using a reference height known as the “neutral stack height”. At this height, the pressure inside of the column is equal to the pressure outside of the column (i.e. point at which the stack changes from operating at negative pressure to positive pressure relative to the ambient condition). An analogous set of equations can be developed around this reference height, providing the same resulting mass flow.

Deriving the Mass Flow Rate of Natural Draft Circulation

The driving force for the circulation of the air is the difference in the hydrostatic head inside of the stack vs. outside of the stack (Equations 3 and 4). The weight of the column of hot air in the stack is less than that of the equivalent height of cold air outside of the stack due to the difference in density of the two columns of air. Therefore, a new expression can be written to quantify this driving force for flow by subtracting Equation 3 from Equation 4:

$$(P_1 - P_4) - (P_2 - P_3) = \rho_{Cold} g H_{Stack} - \rho_{Hot} g H_{Stack} \tag{5}$$

Equation 5 relates the pressure driving force for the flow to the density difference of the two columns of air. Equation 5 can be re-arranged to a more convenient form:

$$(P_1 - P_2) + (P_3 - P_4) = (\rho_{Cold} - \rho_{Hot}) g H_{Stack} \tag{6}$$

The left hand side of the Equation 6 now represents the pressure difference across the openings where the gas flows into and out of the stack. Equations 1 and 2, respectively, can be substituted into this equation to relate the mass flow rate of the air to the hydrostatic pressure difference. After substitution and rearrangement (recognizing that at steady state, $\dot{m}_{BOTTOM} = \dot{m}_{TOP}$), the natural draft mass flow rate can be determined from Equation 7:

$$\dot{m} = \sqrt{\frac{2(\rho_{Cold} - \rho_{Hot}) g H_{Stack}}{\left(\frac{1}{\rho_{Hot} C^2_{D,TOP} A^2_{TOP}} + \frac{1}{\rho_{Cold} C^2_{D,BOTTOM} A^2_{BOTTOM}} \right)}} \tag{7}$$

The mass flow rate of natural draft circulation is related to the height of the stack, density difference between the gas inside and outside of the column, and the size/frictional losses of the opening of the stack[II]. This simplified model (and associated derivation) will serve as the basis for natural draft flow in a molten sulfur tank.

3.2 Stack Model for Molten Sulfur Tank Vent

As the discussion of the stack effect illustrates, if a height difference is provided between the point of air ingress (cooler air) and the point of air egress (warmer air) for a molten sulfur tank, a density-based pressure difference (or buoyant force) will exist and provide the driving force necessary to move air through the "stack". In this case, the headspace of the tank and a central stack vent on the tank (described in following sections) represent the "stack" for the air flow. Based on this description, a simplified model can be developed to represent the tank stack-effect flow, as represented by Figure 3.

[II] This derivation implicitly neglects skin friction losses through the air inlet piping and through the central stack. In practice, these losses are expected to be small compared to the losses across the inlet and outlet orifices – this should be verified on a case by case basis, however.

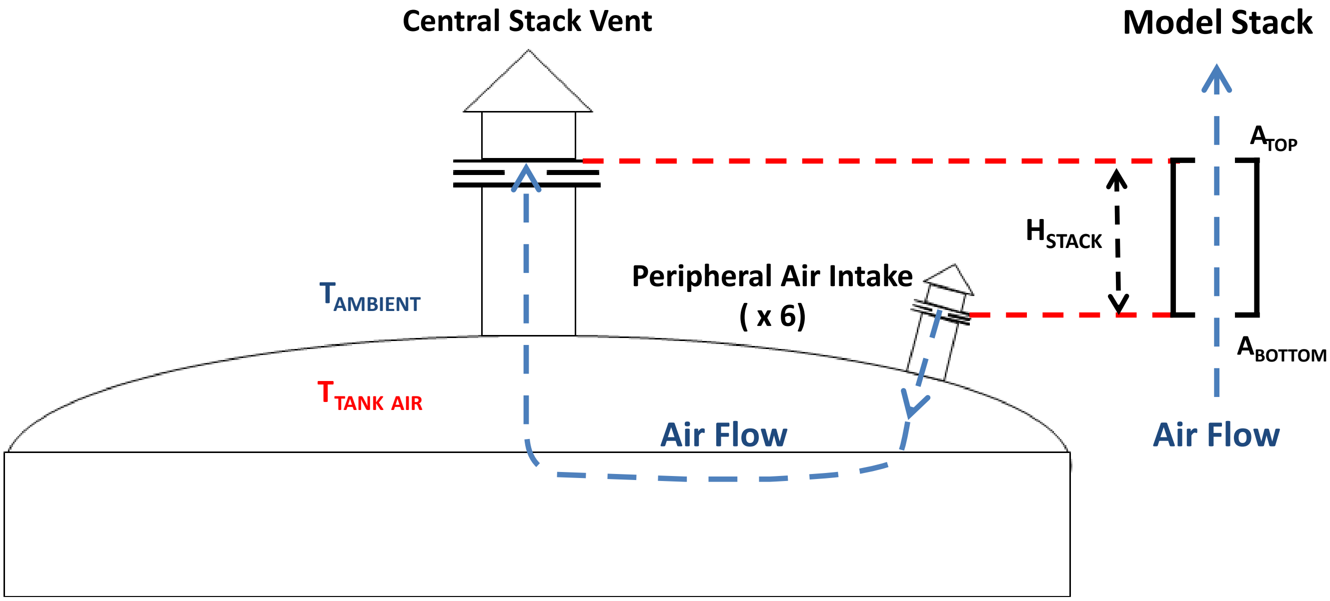

Figure 3. Modeling Natural Draft Air Flow in a Molten Sulfur Tank Headspace

The total height of the stack includes the vertical distance from the inlets of the peripheral air intakes to the top of the central stack.

For design calculations, the air sweep flow rate required to maintain the tank headspace H_2S concentration below 25% of LEL (or other safe level) can be used to size the air intake and central stack vent via Equation 7. Key assumptions and information for the calculation include (but are not limited to) the following:

- The temperature of the molten sulfur tank;
- The temperature distribution of the air in the headspace above the molten sulfur;
- Pressure losses (frictional losses) into and out of the tank and losses to be considered along the flow path;
- The molecular weight of the air coming into the tank and the vapor leaving the tank; and
- The atmospheric temperature and pressure for relevant design conditions.

The density of the ambient air and tank vapor are a function of the respective temperature and molecular weight of each gas, so accurate representation of the temperature and composition of the gas is critical to the design of a tank with natural draft circulation.

Equations 1 and 2 can be used to evaluate the pressure drop across the air inlets. This is an important aspect of the design of the molten sulfur tank as it should operate at a slight vacuum condition at the air inlet to prevent reverse flow through the air inlets[13]. The vacuum requirement provides a further constraint to limit the variables that must be considered when designing the tank ventilation.

3.3 Natural Draft Flow Sensitivity Studies

As noted in the bulleted list in the preceding section, several assumptions or pieces of data are required as part of the natural draft circulation design process. As part of the design process, it is critical to understand the impact of the operating conditions and assumptions on the natural draft flow performance of the tank. As an example, Figure 4 illustrates the impact of the assumption (or measurement) of the tank headspace temperature that is required to estimate the sweep air flow rate.

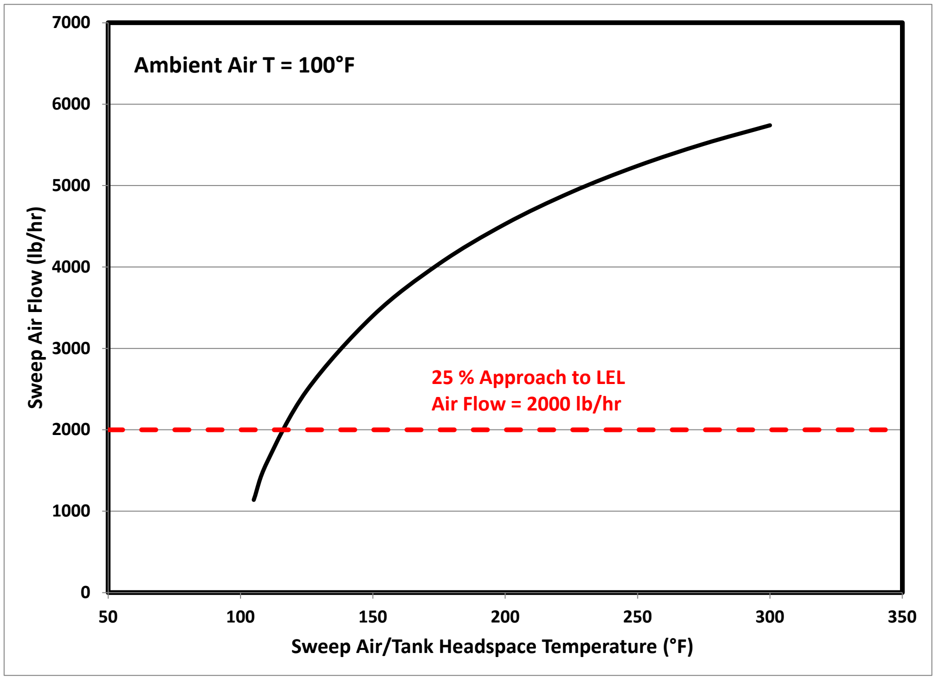

Figure 4. Modeling Natural Draft Air Flow in a Molten Sulfur Tank Headspace

Figure 4 illustrates the strong variation in the sweep air flow rate with the tank headspace temperature. The tank headspace temperature, in turn, may be impacted by many other variables: the molten sulfur temperature in the tank, heat transfer rate from the molten sulfur and the tank walls and roof to the vapor in the headspace, the turbulence/mixing in the tank headspace, conditions of the ambient air sweeping the headspace, etc. The problem may be further complicated by the fact that the air sweep rate itself may impact the tank headspace temperature, leading to a complex relationship between the temperature in the tank and the headspace temperature that provides the driving force for natural draft flow. Ultimately, as illustrated in Figure 4, the tank headspace temperature will impact the ability of the natural draft sweep design to provide sufficient air to stay above a 25% approach to LEL for H_2S. Therefore, understanding the molten sulfur tank system, making appropriate simplifying assumptions, and experience with the design and operation of molten sulfur tanks is essential to designing a molten sulfur tank with natural draft flow.

As an extension to this sensitivity analysis, the ambient conditions for a given operating site for a molten sulfur tank may vary widely across the seasons. As Equation 7 indicates, the density of the ambient air also strongly impacts the natural draft flow through the tank. The limiting condition for natural draft flow (lowest natural draft flow) is the highest ambient temperature experienced by the tank (e.g., maximum summertime temperature). This will produce the lowest driving force for natural draft flow (all other conditions fixed). However, it is not sufficient to consider the maximum ambient temperature case alone. The minimum ambient temperature case is important for the design of the tank heating system (e.g., steam coils, external tank heating system, etc.). This condition sets the maximum heat loss for the tank and is the basis for the sizing of the tank heating elements. However, this minimum temperature condition leads to the ***largest*** natural draft flow rate that the tank will experience. Therefore, both scenarios must be explicitly evaluated during the design of the tank. Table 1 illustrates the 99.6% high and 0.4% low dry bulb temperatures for a generic site (based on Midland, Texas in this case) and the corresponding sweep air rates for a specific molten sulfur tank.

Table 1. Impact of Seasonal Ambient Temperature Variation on Sweep Air Rate under Natural Draft Flow Conditions (all other conditions are identical between the cases).

	Temperature (°F)	Sweep Air Flow (lb/hr)
99.6% Annual High (dry bulb)[14]	100.4	1960
0.4% Annual Low (dry bulb)[14]	19.9	3600

As Table 1 illustrates, in the transition from the high ambient temperature design point to the low temperatures the tank might experience, the air sweep rate increases by more than 80%. This maximum sweep rate will increase the heat loss from the tank significantly, driving up the costs to heat the tank and will require an optimization between the tank designer and heating medium supplier.

Finally, temperature is not the only parameter that impacts the density of the circulating sweep air. The composition of the gas in the headspace of the tank (sweep air plus volatile/entrained components from the molten sulfur) impacts the density via the molecular weight of the gas. Measuring the composition of this gas is not always realistic, and, as discussed in Section 2, the composition often must be estimated. Table 2 illustrates the impact of assuming humid, but otherwise pure, normal air for both the inlet and outlet gas density versus accounting for an estimated vent gas composition that includes H_2S, sulfur vapor/mist, and other compounds.

Table 2. Impact of the Tank Headspace Vapor Molecular Weight Estimation on Sweep Air Rate under Natural Draft Flow Conditions (all other conditions are identical between the cases).

	MW of Tank Headspace Vapor	Sweep Air Flow
Assume Moist Air Only	28.5	2590
Estimated Full Vent Gas Composition	30.5	2050

Table 2 illustrates that underestimating the vent gas molecular weight by ~7% (i.e., assuming moist air only) leads to > 25% over estimation of the sweep air rate; that is, the actual sweep air rate will be 25% lower than estimated. This can have potentially serious consequences for the expected performance of the molten sulfur tank vent system and would not necessarily be covered by adding a general margin or safety factor to the design.

3.4 Other Considerations

The analysis and design approach above does not consider wind effects on the tank. Wind effects are complex, site-specific, and highly variable as the impact of the wind will be determined by the average / maximum velocities of the wind, prevailing direction of the wind, and obstructions to the flow path of the wind, among other factors. A concern for the design of molten sulfur tanks is the potential for wind to force reverse flow of air out of the inlets on the roof of the tank by lowering the air pressure around the air intakes. The height of the air intakes, geometry of the roof, cap design for air intakes, and other parameters may impact an evaluation of wind effects. The details of wind effects are beyond the scope of this paper.

Furthermore, as detailed in the following section, the conceptual design of a tank to operate with natural draft flow must be followed with a detailed design of the equipment itself that is consistent with the assumptions and conditions of natural draft flow (e.g., air intake design to provide expected frictional losses at all times).

4.0 Additional Tank Evaluations

Additional tank evaluations are necessary to make certain that the tank is designed to handle vacuum conditions from inbreathing and to handle the positive pressure that occurs during out-breathing or situations where snuffing steam for fire suppression is necessary. A brief description of the design cases and reference sources for tank design guidance are presented below.

4.1 Tank Inbreathing/Vacuum Design Case

API 2000 outlines tank design criteria for inbreathing (vacuum) for atmospheric tanks, such as molten sulfur tank[15]. In the case of the molten sulfur tank, rapid condensation of vapors is not a limiting design case. The inbreathing case is generally defined by maximum outflow of liquid (e.g., during truck or rail car loading). The volume of air replacing the displaced molten sulfur must be calculated, and the pressure drop across the air intakes must be evaluated to determine the vacuum generated in the tank. In API 650 Section 5 guidance on the maximum allowable vacuum for atmospheric storage tanks is provided[16].

4.2 Tank Out-breathing/Positive-pressure Design Case

API 2000 also outlines tank design criteria for out-breathing or positive pressure in atmospheric storage tanks[15]. As with inbreathing, the relevant case for molten sulfur tanks is due to movement of air due to the transfer of sulfur. In this case, as the molten sulfur tank is loaded, air is displaced through the vents and central stack. The corresponding pressure drop through the existing air intakes (which are may operate in reverse flow under worst case conditions) and through the central stack represent the maximum pressure developed during sulfur transfer.

In the case of molten sulfur tanks, a second scenario must be considered for out-breathing/over-pressure. Snuffing steam is commonly used to suppress fires that may develop in the molten sulfur tank headspace, and is probably the largest out-breathing case. NFPA-655 recommends 2.5 lb/min snuffing steam flow per 100 $ft^3$of tank volume for fire suppression[9]. All of this steam must exit the headspace of the tank, creating an alternate overpressure scenario that should be evaluated in the design of the tank.

5.0 Tank Design Features

An example molten sulfur tank design is shown in Figure 5, although many variations exist to store molten sulfur. The molten sulfur storage tank should also incorporate design features to maintain and monitor operations for proper natural draft ventilation as depicted in the bold text in Figure 5. The important elements of the tank design are discussed more below.

The air intake nozzles should be sized appropriately (see Section 3) with an adequate number of vents distributed appropriately throughout the periphery of the tank. This will ensure even distribution of the sweep air and adequate mixing of the vapor space so that the H_2S is kept below 25% of the LEL in all areas of the tank head space. The air intake nozzles and central stack (if available) must also be sized to relieve snuffing steam without exceeding the tank pressure rating and with a reasonable exit velocity.

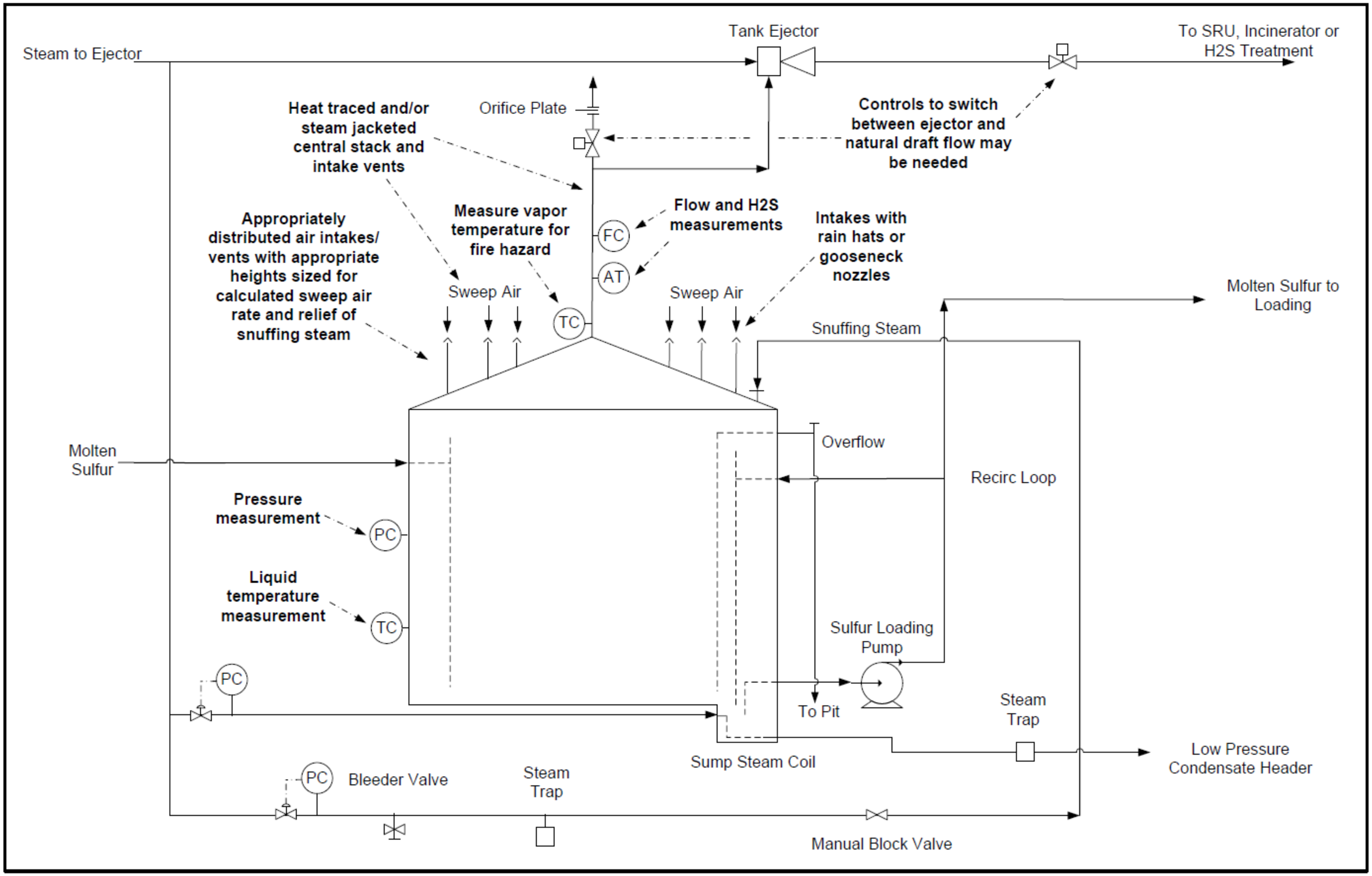

Figure 5. Example Molten Sulfur Tank Design Features for Natural Draft Ventilation

The height of the intake nozzles relative to operator-accessible areas should be considered as well to limit operator exposure to high H_2S during potential upset reversal of flow.

The central stack and peripheral air intakes should be steam jacketed or otherwise heated and insulated to maintain uniform temperatures along the air flow path and to prevent sulfur build-up on the surfaces. The intake vents and exhaust stack should be regularly inspected to confirm that they are not plugged off with sulfur solids. The air intake nozzles should have rain hats or, alternatively, goose-neck nozzles could be also used. Goose-neck nozzles may be better at preventing water infiltration from rain blown in by wind; they are also reported to be easier to heat trace and thus probably less likely to collect sulfur deposits, although potentially more difficult to inspect.

Pressure transmitters with chemical seals (e.g., remote diaphragm elements) can be tied into shutdowns on the inlet and exiting streams from the tank to monitor the internal tank pressure and help prevent rupture or collapse of the tank. The temperature of the vapor space in the tank should be routinely monitored to aid in evaluate of the natural draft flow and to monitor for potential sulfur fire (high temperature) and need for snuffing steam or inert gas to cool the system.

Air flow meters can be installed on the tank air inlets or possibly in the stack to monitor the flow of vent gas through the tank head space. Low air flow could be a sign of backflow through the intake vents and plugging of the vents, which could result in uneven vapor distribution in the tank and pockets of gas with high H_2S content. Excessively high air flow could strip additional sulfur species from the molten sulfur.

H_2S analyzers can also potentially be installed to monitor the H_2S content of the vapors in the central stack.

6.0 Summary

This paper summarized the principles of natural draft flow in molten sulfur storage tanks. The required natural draft flow rate is based on achieving 25% (or other safely low percentage) of the LEL for H_2S in the tank vapor space. Natural draft flow through the tank is based on the differences in temperature and density of the cold ambient air and the hot tank vapors, causing cold air to be pulled into the tank and hot air to rise and exit the top of the stack. Design of the air intake and outlet stack vents is achieved based on the mechanical energy or pressure balance of the Bernoulli equation around this system. The density of the tank vapors is an important parameter in the design of natural draft flow in the tank, so it is important to know the composition of this stream. If the tank vapors cannot be directly measured (because of a new tank design vs. a retrofit of an existing tank), the estimation methods and literature sources referenced in this paper could be used to assess the tank vent composition. Seasonal and daily variations in ambient air temperature also need to be considered due to the effect on the density of the inlet air. The physical design of the tank also needs to be consistent with the assumptions used to estimate natural draft flow in the tank. For example, the impact of wind could cause reverse flow through some air inlets, and design of the vents to prevent this should be considered. Situations of tank in-breathing and out-breathing due to filling and unloading of the tank and due to snuffing steam also need to be evaluated. Finally, several design features (flow meters, H_2S analyzers, goose-neck nozzles, etc.) are also reviewed to ensure uniform natural draft flow and safe H_2S levels of the vent gas for the protection of refinery operators.

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