

Preventing or Extinguishing Molten Sulfur Tank and Pit Fires

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Abstract

Fires are known to occur in sulfur storage pits and tanks somewhat frequently due to the presence of both flammable material and air, so methods for preventing and extinguishing these fires are critical. This paper reviews some of the fire suppression methods used in the industry including: snuffing/sealing steam, rapid sealing, water mist, and inert gas blanketing. Unique industry experiences for several of the methods are presented, including blanketing with post-combustion gas to below the limiting oxygen concentration as well as mechanical sealing of inlets and vents, among others. The benefits and limitations, design considerations, and recommended guidance for each fire suppression approach will also be discussed. Protective tank design features and other safe operating practices that can be implemented to reduce the likelihood of a sulfur fire are also reviewed.

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 removed before emitting gases to the atmosphere. A modified Claus sulfur recovery unit (Claus SRU) is one common method for converting the removed H_2S to molten elemental sulfur. The molten sulfur produced in a Claus SRU is stored and handled in a number of steps as depicted in the example in Figure 1.

The sulfur from the Claus unit often flows to a sulfur pit. The molten sulfur flowing into the pit (or first receiving vessel) from a Claus SRU is often assumed to contain 300 ppmw H_2S and H_2S_x ([1], [2], [3]) although oxygen enrichment and subdewpoint operation can produce higher levels, e.g. 450 ppmw [4]. The sulfur may be degassed, either in the pit or in separate equipment, to reduce H_2S concentrations down to about 10 ppmw. Undegassed sulfur is common and generally must be considered in any molten sulfur handling design in the event the degassing system is not functioning. 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.

The molten sulfur in the tanks and pits and the associated headspace vapors contain multiple sulfur species that must be considered when evaluating the risks and hazards of the system. As noted,

H₂S will be present as a residual from the upstream Claus process (present as molecular H₂S or as the polysulfide H₂S_x in molten sulfur, which is in temperature-dependent equilibrium with H₂S). H₂S is both toxic and flammable and represents a significant hazard in molten sulfur handling. The OSHA permissible exposure limits for H₂S in the atmosphere are: 10 ppmv, 8-hr TWA, for construction and maritime industries; and 20 ppmv ceiling limit for general industry [5].

Sulfur dioxide (SO₂) 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 H₂S. Some of the SO₂ originates from the elemental sulfur entering the storage equipment from the Claus SRU, although SO₂ is believed to also come from the reaction of elemental sulfur with oxygen from air in storage tanks and loading areas [1]. SO₂ is not flammable, but it is toxic at similar levels to H₂S. Elemental sulfur vapor in various forms (S₂, S₄, S₆, S₈ and even with larger molecules to S₁₂) have been reported in the literature [6]. Although small sulfur molecules exist at higher temperatures, the primary elemental sulfur species present in the vapor is expected to be S₈ at the conditions of sulfur tank vent gas (250-300°F) [6]. Finally, sulfur species such as carbonyl sulfide (COS) and carbon disulfide (CS₂) may also be in the vent streams from molten sulfur systems [7].

Figure 1 also illustrates the handling of vent vapors from the pit, degassing unit, and storage tank. There are many disposition options for the vapors from these storage and handling systems that depend on site and system specific considerations – a more detailed review is available in other papers [8]. The figure also assumes the use of sweep air, which is discussed briefly in this paper as an approach to manage explosion hazards but is also covered in detail elsewhere [9].

Several points in the process represent places where fire and explosion risks exist, particularly in the storage areas (pit, tank) where explosive vapors may accumulate and other hazardous conditions may develop as part of the operating conditions of the system [10]. This paper focuses on the hazards associated with sulfur fires in molten sulfur storage applications. Approaches to preventing or suppressing sulfur fires and identifying the merits and shortcomings of each approach are reviewed. A summary of industry guidance, standards, and/or common practices is also presented.

While this paper reviews a variety of approaches for fire prevention and suppression, operators may choose to follow the applicable industry standards (e.g., NFPA standards) directly for some of the following reasons:

- The site may be required by insurance to comply with specific standards.
- A regulatory authority (referred to as an “Authority Having Jurisdiction, AHJ, in NFPA) may require that a specific standard (or group of standards) be followed at a site.
- The site’s process and equipment may mirror a reference design, which complied with specific standards.

Many sites do not or cannot comply fully with the standards, e.g., due to limited utilities on site. The goal of this paper is to review the various approaches and practices objectively and allow the reader to use judgement on approaches that might be applicable to their specific situation. The paper is divided into three sections: fire and explosion hazards, fire prevention, and fire suppression.

Other hazards exist with molten sulfur handling and storage including health and safety hazards from the toxicity of components associated with (or generated from) the molten sulfur, such as H₂S and SO₂. These hazards (and others) are covered along with methods to manage the risks elsewhere in the literature on molten sulfur (e.g., [7] [1]).

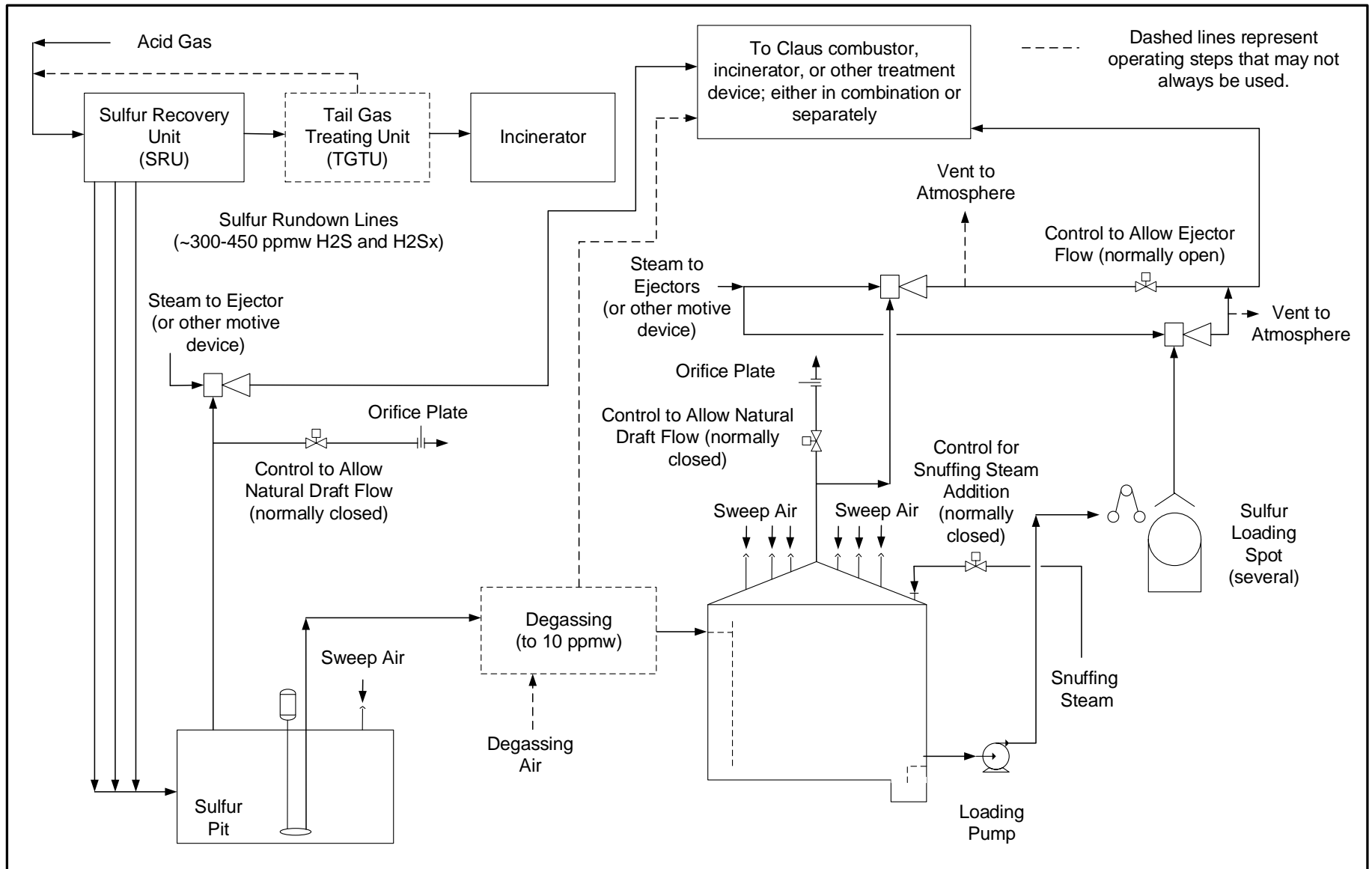


Figure 1: Molten Sulfur Storage and Handling System

2.0 Fire and Explosion Hazards in Molten Sulfur Storage

2.1.1 Flammable Components

H₂S will be present in the molten sulfur itself and ultimately in the vapor space of storage and handling equipment as the H₂S evolves from the molten sulfur into the vapor phase. H₂S is flammable and its flammability window is commonly denoted by upper and lower explosive limits (UEL and LEL). In molten sulfur handling applications, the LEL is of practical concern since concentrations approaching the UEL are not expected based on the equilibrium concentrations of H₂S in the vapor. Figure 2 depicts the LEL of H₂S as a function of temperature.

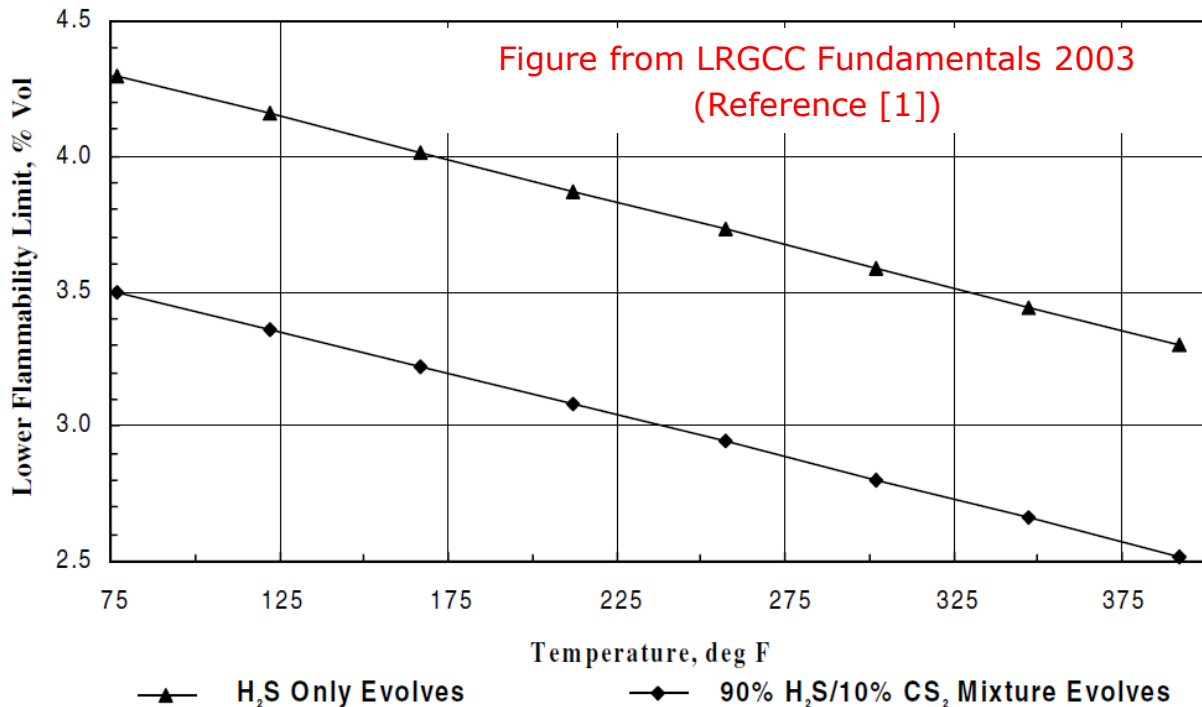


Figure 2: LEL of H₂S as a function of temperature.
Source: Johnson, J and Hatcher, N., LRGCC Fundamentals 2003 [1].

The LEL of H₂S decreases with temperature. Higher temperatures have larger flammability windows and require more stringent design choices to avoid the flammability window. Note that there is more recent data in the literature that differs slightly in estimated LEL of H₂S compared to the data in the figure (e.g., at 330°F, the newer literature data indicates the LEL of H₂S is ~3 vol% H₂S) [11].

In addition to H₂S, the molten sulfur itself is flammable. Once a fire is ignited, the molten sulfur can serve as the fuel for the fire. In addition, elemental sulfur vapor in the headspace of storage vessels has a flash point value as low as 334°F reported in the literature [1]. Therefore, if the sulfur handling equipment is operated above the flash temperature, the risk of fires increases significantly. Furthermore, the auto-ignition temperature of elemental sulfur is as low as 450°F [12]. While this is well-above the normal operating temperature of molten sulfur storage systems, which are typically designed to avoid the pure-sulfur viscosity transition temperature

(~318°F), localized hot spots approaching the auto-ignition temperature could be a source of fires. Figure 3 shows the potential operating window for molten sulfur given its unique properties.

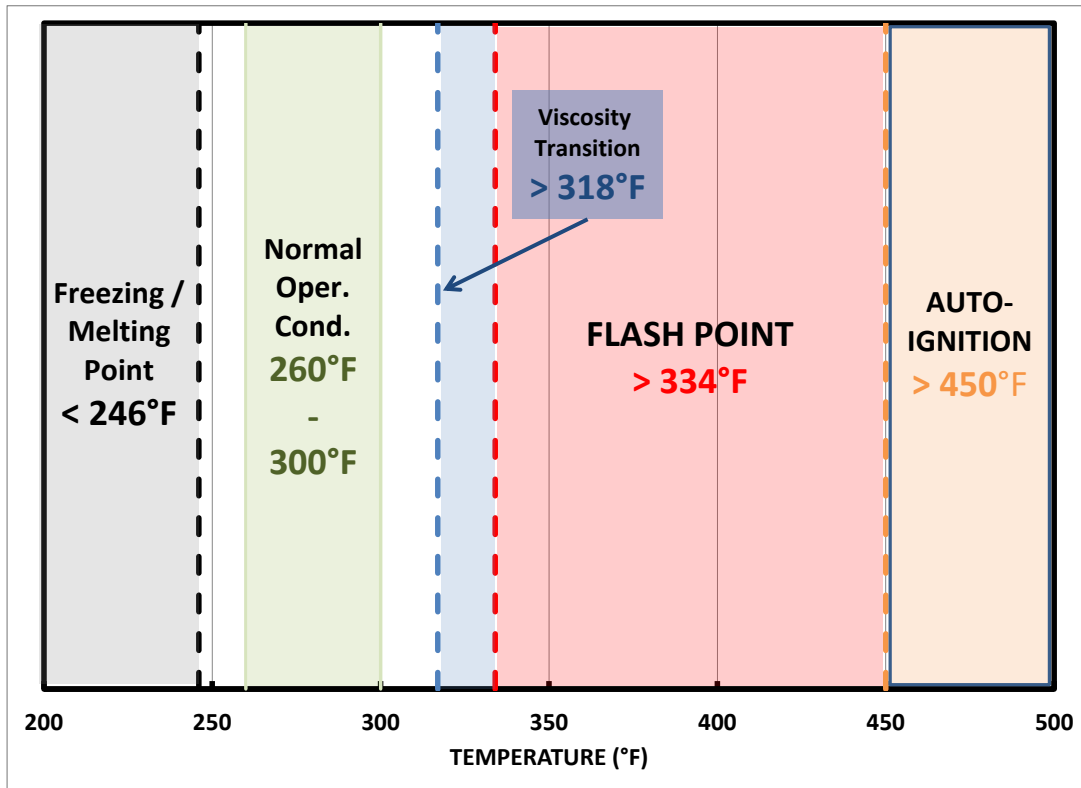


Figure 3. Key Sulfur Property Temperatures

Finally, NFPA-655 cites 309°F as a transition temperature for the design of molten sulfur storage equipment. Above this temperature, additional design requirements apply (e.g., deflagration vents) [13]. Field experience reported in the literature [14] and in Trimeric’s first-hand knowledge of operator experience supports the implication that temperatures above 309°F, but still below the sulfur vapor flash point, are associated with increased frequency of sulfur fires. An operating window, as depicted in Figure 3, can be defined based on the aforementioned property data, the freezing temperature of elemental sulfur, and leaving adequate margins between the operating window and temperature limits.

2.1.2 Ignition Sources

Unless the molten sulfur is above its auto-ignition temperature, in addition to being in the flammable region, fires in sulfur tanks and/or pits nominally require an ignition source. Ignition sources can span a broad range of general sources (hot surfaces, open flames, sparks, electrical discharge, etc.). In molten sulfur applications, potential ignition sources include the following:

- Static discharge accumulated by free-falling sulfur¹ [1],[14]: Molten sulfur is an electrical insulator, and therefore can accumulate static charge when falling through air. This leads to a risk of electrostatic discharge that can serve as an ignition source for fires.
- Hot surfaces in equipment: Rotating equipment may be particularly susceptible. For example, pump bearings that are failing may lead to increased friction and localized hot spots.
- Improper operating temperature: This can occur due to improper temperature design targets (e.g., selecting operating temperatures above 309°F) or improper use of heating medium in storage application (e.g., using saturated steam above the flash point of sulfur [>80 psig]).

In addition to the sources above, general ignition sources in an operating facility, such as sparks generated by maintenance work, pose a risk and must be considered as part of work performed in molten sulfur handling areas. Several of these ignition sources are discussed in additional detail later in the paper.

2.1.3 Pyrophoric Iron Sulfide Formation

The formation of pyrophoric iron sulfide is a unique risk that exists in carbon steel equipment where H₂S and/or elemental sulfur and water are present in an anaerobic or reducing environment [15]. For example, in a carbon steel molten sulfur tank that is purged or blanketed with an inert gas (e.g., nitrogen), iron sulfide can form on internal tank surfaces. Iron sulfide can also form in air-swept tanks underneath any accumulations of solid sulfur, due to the fact that the air is blocked from contacting these areas. This is depicted in Figure 4. When water is present (e.g., via steam leaks), corrosion of the carbon steel vessel occurs yielding iron sulfide on the tank surface (see [16] for detailed discussion of the chemistry). The iron sulfide does not present a risk on its own. However, if iron sulfide is exposed to oxygen (e.g., via air during tank maintenance), a pyrophoric reaction can proceed leading to fires and/or explosions. In molten sulfur handling systems where air is continually introduced (e.g., sweep air), any iron sulfide that is formed is generally oxidized quickly in a controlled manner, preventing accumulation to levels where the pyrophoric reactions can occur. However, even in systems with continuous air sweep, if significant deposits of solid sulfur accumulate on tank surfaces, it may limit access of the oxygen to the tank surface, allowing iron sulfide to form and accumulate. Therefore, as discussed later, internal tank surfaces that accumulate solid sulfur deposits are a safety concern.

¹ Note that, while the authors are not aware of any incidents where air moving over a stagnant molten sulfur surface (e.g., sweep air in a tank) have led to sulfur fires, the mechanism for static charge generation is similar to free-falling sulfur (i.e., there is a relative velocity and associated friction between the air and the molten sulfur). Therefore, some have hypothesized that air sweeps over molten sulfur could pose a static discharge risk [14].

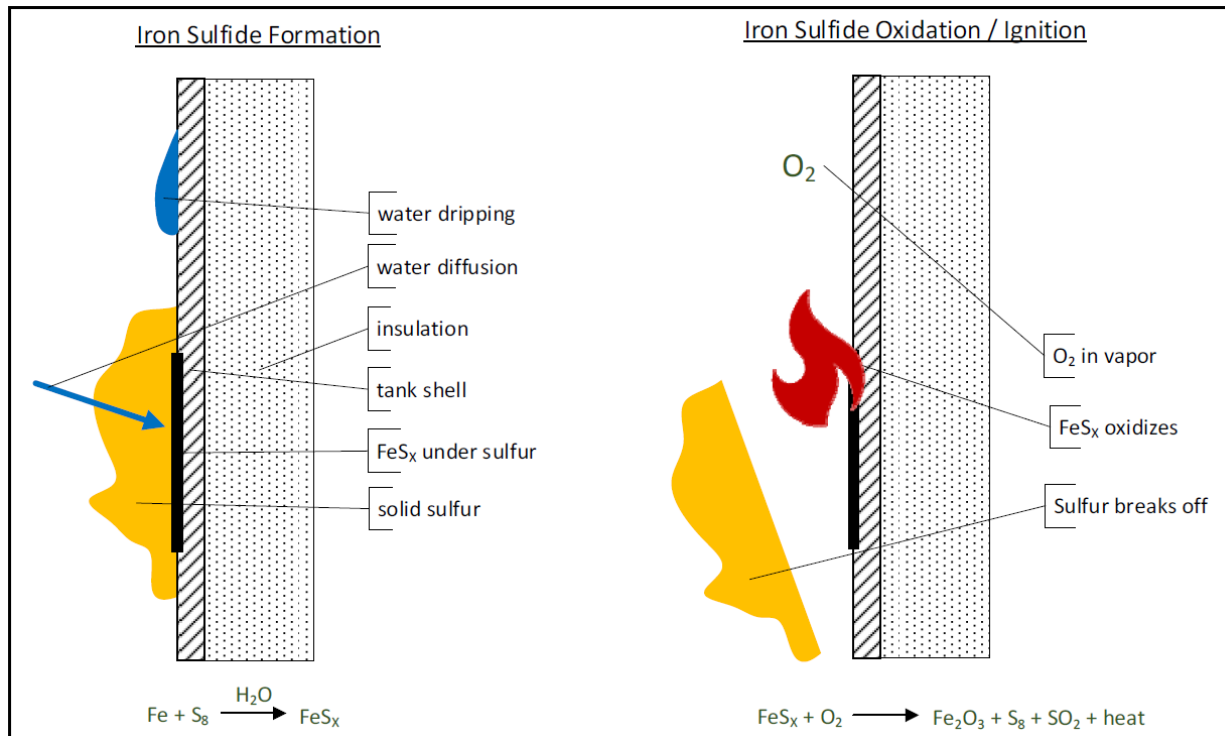


Figure 4. Formation of Pyrophoric Iron Sulfide

Source: B. Forbes, D. Cipriano, Controls Southeast/ AMETEK, 2020 [17]

3.0 Fire Prevention

3.1 Industry Standards and Guidance

NFPA-655 ("Standard for Prevention of Sulfur Fires and Explosions") is a primary industry reference for fire prevention in molten sulfur handling applications. The standard covers both fire prevention and suppression. Chapters 5 and 6 (in the 2017 edition) are specifically related to molten ("liquid") sulfur handling. Chapter 5 applies to what NFPA defines as normal handling temperatures (246°F - 309°F). Chapter 6 applies to handling sulfur above 309°F. Regarding fire prevention, NFPA-655 includes guidance on the following preventative measures:

- Design for normal handling temperatures (Fire Prevention)
 - Detection of Unsafe Conditions: Covers the monitoring of H_2S concentration in molten sulfur storage headspace.
 - Notably, the guidance indicates that "operations shall be discontinued" when the H_2S concentration in the vapor headspace exceeds 35% of LEL at the designated temperature and that "operations shall not be resumed" until the H_2S concentration is below 15% of LEL.
 - Equipment Design: Covers tank feed/fill line design to minimize free-fall and agitation of sulfur upon feeding sulfur to the tank (via a line extending below the liquid level towards the bottom of the tank).

- Vent Systems: Provides general guidance on vent systems (specifically focused on heated vent system design to prevent molten sulfur solidification).
- Bonding and Grounding: Provides guidance on bonding and grounding of sulfur lines, tanks, loading trucks/cars alongside guidance for electrical wiring², and the need to keep steam coils covered with molten sulfur.
- Open Flames and Sparks: Covers general guidance regarding activities that may introduce flames or sparks in the vicinity of molten sulfur handling activities.
- Design for handling temperatures above 309°F
 - All of the guidance for normal handling temperatures apply.
 - Equipment Design: Recommends design of equipment to be “closed as tightly as possible to prevent escape of vapor and to exclude air”, signaling a different approach to fire prevention than sweeping with air to stay well below the LEL.
 - Deflagration Venting: Refers to NFPA 68 for deflagration venting design and covers other design considerations associated with deflagration vents (heating of vents/ducts, need for an inerting agent, etc.).

In addition to NFPA-655, NFPA-68 is relevant for deflagration venting (if required) and NFPA-69 (Standard on Explosion Prevention Systems) includes information on preventing and managing explosions/deflagrations. Specifically, NFPA-69 identifies two approaches to prevent combustion: i) Combustible concentration reduction, ii) Oxidant concentration reduction. The standard provides an extended discussion on each approach (Chapter 7, 8, and Annex B in 2018 Edition).

The preceding discussion is not meant to serve as a proxy or interpretation of NFPA standards. The reader should consult the standards directly for guidance on design for fire prevention. While NFPA provides guidance on approaches to prevent fires and explosions, it generally does not provide detailed design recommendations for the specific process or equipment. Therefore, the following sections reviews some approaches to fire prevention in more detail.

3.2 Minimizing Combustible Component Concentration – Use of Sweep Gas³

Sweep gas is often used to dilute the H₂S concentration in the vapor space of storage equipment. Different sweep gases have been used including air, nitrogen, fuel gas, steam, combustion product gases, and CO₂. Many molten sulfur storage tanks are swept with air. Because oxygen is introduced with the air, it is imperative that enough air be supplied to dilute combustible components such as H₂S a safe margin below the LEL. Ejectors, blowers, or natural draft effects are used to pull air through inlets on the tank roof and out of a vent. The vent gas is emitted to the atmosphere or sent to another process (e.g., H₂S removal process, recycle to Claus reaction furnace, etc.). Sweeping with air produces a continuous flow of vent gas, and the tank generally operates under a slight vacuum (whereas tanks with inert gases fed to them tend to operate under a slight positive pressure). Air is a common sweep gas because:

- Air is readily available and inexpensive to use;

² Refers to NFPA 70 on this topic as well.

³ The reader may also refer to other recent articles covering sweeping and blanketing of gases in more detail [32].

- The presence of oxygen keeps the atmosphere in the tank in an oxidizing state, which helps prevent the formation of pyrophoric iron sulfides (FeS) on carbon steel surfaces;
- Flammability concerns with air (oxygen) can be mitigated by maintaining a safe margin below LEL and installing monitoring equipment; and
- Sweep air can be handled by a number of downstream technologies that treat the H₂S in the vent gas.

Considerations for other sweep gases (e.g., nitrogen, fuel gas, steam) include:

- Increased risk of pyrophoric iron sulfide formation;
- If the gas is not available on site, it may need to be produced or purchased, which may not be cost effective for the large quantities required to continuously sweep the head space of the tank;
- If fuel gas is used it introduces additional combustible material into the tank vapor space;
- Downstream treatment technology sensitivity to oxygen (e.g., poisoning of hydrogenation reactor catalyst with tail gas recycle) may favor sweep gases other than air (e.g., nitrogen) [8].

A few sites use steam to sweep molten sulfur tanks. As with inert-gas-swept tanks, the tank usually operates at a small positive pressure. Using steam introduces water into the vessel, which, combined with the exclusion of oxygen, can lead to the buildup of pyrophoric iron sulfide. Any condensed water on the metal surfaces can also lead to corrosion. However, if the walls and roof of the tank are kept warm enough, it is possible to prevent liquid water formation, reducing corrosion rates. The steam is sometimes vented to the atmosphere, but one variant of this approach condenses the steam exiting the tank. A venturi eductor with liquid water as the motive fluid can be used to condense steam and absorb volatiles including some of the H₂S. The combined effluent from the eductor can be sent to a sour water system, wastewater treatment plant, or other wastewater system. This provides an alternative disposition route that is not available with the other sweep gases.

3.2.1 Sweep Gas Flow Requirement

Using 25% of the LEL is a common industry practice for calculating the sweep air flow rate requirement and is recommended in various literature sources; values as low as 15% [18] and as high as 35% [13] as an upper limit to stop operation have also been reported. The LEL for H₂S is sometimes assumed for a conservatively high temperature, because as noted in Figure 2, the LEL for H₂S is lower at the elevated temperature necessitating a higher sweep rate. A temperature of 330°F is a conservative design choice when determining the required air rate. As discussed previously, 330°F is higher than a tank would normally be operated, due to concerns with increasing sulfur viscosity at high temperature and increased fire risks. At this temperature, the LEL is 3 vol% [11], so 25% of the LEL for H₂S is 0.75 vol%.

The chemistry of H₂S equilibrium with the molten sulfur is complex. There is a chemical reaction in the elemental sulfur favored at higher temperatures which consumes the H₂S and

forms H_2S_x , and this reaction would limit the mass transfer of H_2S into the gas phase [19]. However, this complication is typically ignored in the calculation of the equilibrium concentration of H_2S in the gas phase using this conservative higher temperature assumption.

3.3 Minimizing Oxidant Concentration - Inert Gas Blanketing

Another method to prevent fires and explosions in sulfur tanks is to blanket the tank with inert gas to limit the oxygen content in the vapor space by preventing air ingress. As shown in Figure 5, the blanket gas (e.g., nitrogen) is fed to or removed from the tank to maintain a constant slightly positive pressure as inbreathing or outbreathing occur (primarily via liquid movement). As such, the flow of N_2 in “blanket” mode is intermittent and typically less than the gas requirement in “sweep” mode. The blanketing method may be used if a site does not have the means to handle and/or treat the large continuous sweep gas flow. However, inert gas blanketing can result in a significant amount of H_2S accumulating in the vapor space. This represents an explosion hazard if oxygen were to be subsequently unintentionally introduced to the tank. Inert gas blanketing also results in increased formation of pyrophoric iron sulfide, and special procedures for maintenance would be required to prevent auto-ignition when tanks are opened to air. A source of the inert gas is also required. For these reasons, the use of inert gas blanketing to prevent molten sulfur tank explosions is less common than the use of air sweeps.

An alternative to inert gas blanketing is to utilize an inert gas with some oxygen in it, such as post-combustion (e.g., exhaust or flue) gas. The gas would need to have enough oxygen to prevent pyrophoric iron sulfide formation but not enough oxygen to exceed the limiting oxygen concentration (LOC) for combustion of sulfur or H_2S . The appropriate oxygen range would need to be determined with a safe margin applied. The tank generally must be operated at positive pressure to prevent air ingress as uncontrolled air flow entering the headspace could pose a risk of exceeding the LOC. Instrumentation and gas-phase analytical measurements may be required to ensure proper oxygen levels. Exhaust gas has been reported privately to Trimeric to have been successfully implemented in a molten sulfur tank. Blanketing with exhaust gas is also documented to have been practiced in the transportation industry for various cargos [20], [21]. Further, other cases have been identified where inert gas with some oxygen has been used for similar purposes in Sulfur Recovery Units (SRU) and other equipment where the formation of pyrophoric iron sulfide under a reducing atmosphere is a risk [18], [22].

A summary table comparing the sweep and blanket gas options is presented in Table 1. The selection of sweeping or blanketing and the type of gas used is site specific. Many factors need to be considered including: i) the sulfur load and associated volume of gas needed; ii) whether the downstream H_2S treatment technology can handle the exiting H_2S -containing sweep gas, iii) the availability/cost of the gas; and iv) the site risk tolerance and degree of safety measurements in place to control issues with pyrophoric iron sulfide and hazardous tank vapor space environments.

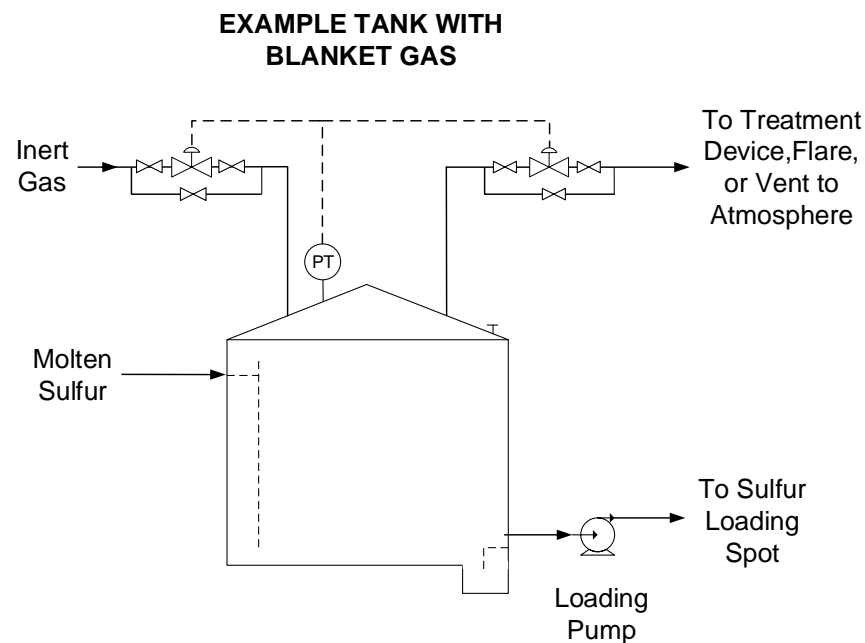
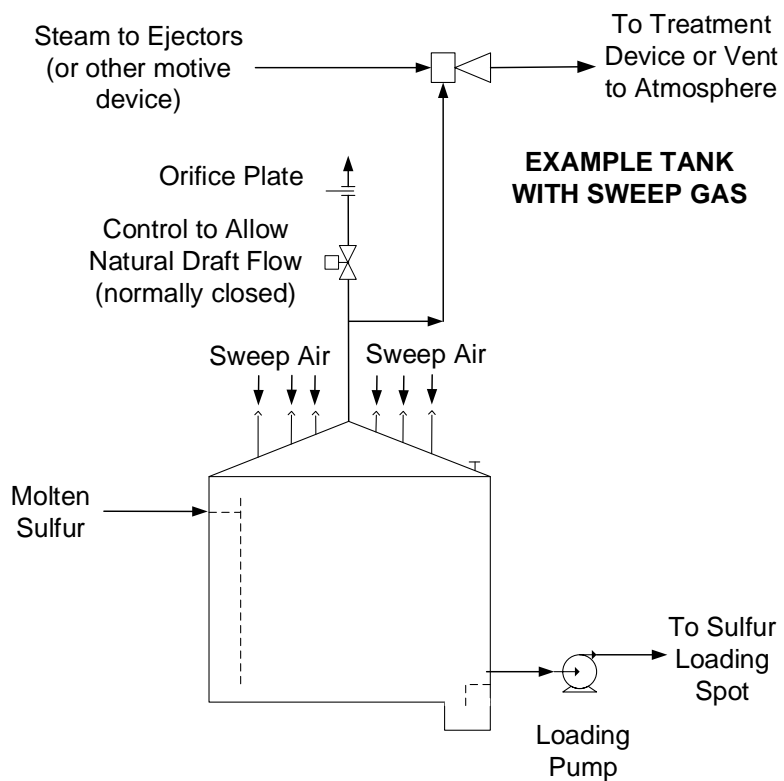


Figure 5. Example Molten Sulfur Tank Configurations with Sweep Air and Inert Gas Blanket

Table 1: Molten Sulfur Tank Sweep and Blanket Gas Summary

	Air	Inert Gas (e.g., Nitrogen)	Inert Gas with O₂ (e.g., combustion gas)
Tank Use	Sweep	Sweep and/or Blanket	Sweep and/or Blanket
Flammability	Introduces oxygen, creates risk for ignition.	No air present during normal operation.	Introduces oxygen at low concentration (below the LOC).
Explosion Risk	Maintaining adequate sweep air (H ₂ S < 25% of LEL) mitigates risk.	FeS formation in reducing environment. Pyrophoric material increases risk if air enters vessel.	Maintaining adequate oxygen concentration can limit or eliminate FeS / pyrophoric accumulation.
Tank Pressure	Operates at slight vacuum.	Operates under slight positive pressure.	Operates under slight positive pressure.
Cost	Readily available. Some cost may be required for heating.	Tie into existing system or add new source of inert gas. Usually higher cost option.	Tie into existing system (e.g., flue/exhaust gas) or add new source of inert gas, both with appropriate oxygen content.

Sweep gas and blanket gas are used to prevent fires and explosions in molten sulfur tanks. Both approaches can be designed successfully, but sweeping with air appears to currently be considered best practice in some industries, such as petroleum refining.

3.4 Fire Prevention and Detection Design Features

The design of the molten sulfur pit or tank should also include features to mitigate, detect, and handle sulfur fires. Important elements of the design for this equipment are discussed below.

3.4.1 Vapor Space Temperature Measurement

The temperature of the vapor in the headspace of the tank or pit should be monitored for indication of a sulfur fire. Multiple temperature measurements of the vapor space may be needed to detect localized fires that could potentially form in different locations in the vessel. High vapor-space temperatures could alert operators of a potential fire and the need for snuffing / sealing steam or inert gas to cool the system, purge air from the headspace, and prevent air ingress. A high vapor-space temperature could be used to shut down a motive device (ejector or blower) to prevent more air from entering a pit or tank that could supply the fire with oxygen. In this instance, a literature source [23] recommends i) installing a thermocouple near the suction line of the motive device to monitor the temperature of the vapor leaving the vessel and ii) locating additional temperature measurements in areas in the tank headspace with the potential for low velocity (determined by CFD or other means) so temperature rises can be observed.

In Trimeric’s experience, some parties use a rate-of-temperature-increase as an alarm, rather than (or in addition to) an alarm based on a temperature set point. Literature showing

vapor-space temperature measurements suggests temperature increase rates in the range of ~2 F/min to ~5 F/min have been experienced [23] during a fire.

3.4.2 Molten Sulfur Temperature Measurement

Thermocouples in the molten sulfur liquid may not detect a fire burning at the surface. However, monitoring the liquid temperature is important to ensure the temperature stays within critical sulfur operating ranges. It is important to avoid temperatures above 309°F (due to higher fire danger and additional NFPA-655 requirements) and maintain appropriate viscosity for handling as discussed previously.

3.4.3 SO₂ and H₂S Analyzers

An SO₂ analyzer in the pit or tank vapor space can also provide an indication of a sulfur fire. Because there will likely always be some SO₂ in the vapor space, the presence of SO₂ does not necessarily indicate a fire; rather a swift, large increase in SO₂ in the vapor space would be indicative of a fire. It has also been reported in the literature [23] that SO₂ measurements in an SRU incinerator stack have been used as an indication of sulfur pit fires. In this case, the ejector remained operational so that the SO₂ generated during the fire could be routed to the incinerator and monitored. Upon high SO₂ emissions, operators would commence steam injection to the pit for 15 minutes. When the steam was turned off, the SO₂ incinerator levels would often go back to normal. Vapor space temperature measurements were also taken in the pit, which indicated an increase of only 50-60°F likely because of localized fire. Thus, installing temperature measurement in the ejector suction line itself was recommended so that an average temperature of the gas flowing through the vapor space could be obtained [23].

H₂S analyzers or LEL monitors could also potentially be installed to monitor the H₂S content of the vapors to ensure that the concentration is below 25% of LEL.

3.4.4 Air Flow Measurement

For tanks or pits that utilize sweep air, air flow meters can be installed on the tank air inlets or 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 indicate potential for plugging of the vents, which could result in uneven vapor distribution in the tank and pockets of gas with high H₂S content resulting in a flammable mixture.

3.4.5 Visual Detection

Depending on the tank configuration, a sulfur fire can also sometimes simply be detected by a yellow plume emitted from the vent of the tank [23].

3.5 Other Safe Operating Practices

It is important to operate a molten sulfur tank and pit in ways to avoid the potential for a fire and to be able to alleviate the fire should one occur. In addition to those mentioned previously, several other safe operating practices are discussed below.

3.5.1 Preventing Static Discharge

Liquid sulfur is a nonconductive material and thus can build up a significant electrostatic charge that, if discharged, can result in ignition under the right circumstances. Incidents have been reported where static buildup was identified as the source of a sulfur fire or explosion [24]. There are several ways to accumulate a static charge within a sulfur tank or pit. Free falling sulfur streams tend to build up static electrical charges that should be avoided. Thus, free fall of sulfur entering storage vessels should be averted. This can be done by extending fill pipes to below the lowest liquid level in the storage tank or pit. This also minimizes agitation and release of H₂S from the molten sulfur. Spray nozzles, as well as sulfur loading arms and other transfer devices, should all be grounded [1].

Another possible source of static charge generation may be the sweep air used to reduce the concentration of H₂S in the pit or tank. One CFD study [14] showed that in a particular pit configuration a jet of air caused several square feet of molten sulfur surface to have flow velocities above 4 ft/s, which is higher than the velocity limit of 3 ft/s for free falling hydrocarbons per API standards [25]. It was hypothesized (but not proven) that this flow was enough to create a static charge in the sulfur vapors leaving the surface of the molten sulfur [14]. A good design for air inlets to prevent excessive velocities in contact with the surface of the liquid sulfur is prudent.

Because of the concerns with static electricity, instrumentation should also be designed with explosion proof housing that meets the area electrical classification [1]. All sulfur pipe, metal parts of tanks / pits, and buildings must be bonded and grounded as well.

3.5.2 Heat Tracing and Insulation

Heating with jacketed pipe or engineered bolt-on heat tracing and insulation is imperative to safe and proper operation of a molten sulfur handling system. It is desired to maintain a temperature above the melting temperature of sulfur (~246°F) to avoid solid sulfur plugging in unwanted areas. For example, the inlet and outlet vents from a pit or tank 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 metal surfaces. This includes not only the vent pipe but also the rain hat or goose-neck nozzle. Plugging of the vents could result in inadequate air flow and subsequent accumulation of explosive quantities of hydrogen sulfide in the pit or tank. It is also important to heat trace and insulate relief devices to avoid sulfur plugging and possibly rendering the devices inoperable. Key instrumentation and controls require appropriate heat management as well.

The tank itself must also be properly heat traced and insulated to avoid the formation of solid sulfur on the tank inner walls and roof, which could lead to fires in the tank due to pyrophoric iron sulfide formation.

For these reasons, it is critical that equipment and instrumentation in a molten sulfur handling system be periodically inspected for proper heat tracing and insulation. When possible, normally inactive valves should be opened and closed to verify they have not been plugged with sulfur and can operate effectively when needed.

3.5.3 Steam Pressure

The appropriate steam pressure should also be used for steam jacketing and tracing. To prevent sulfur solidification, a minimum steam pressure of 35-40 psig should be used. However, using steam that is too hot can cause safety issues. Generally, no higher than 80 psig steam should be used for jacketing and tracing since this temperature is approximately the same as the flash point for sulfur (334°F). Several incidents have been reported where high pressure steam was believed to have started a sulfur fire. In one case, a site observed relatively frequent tank fires over several years. Several mitigating actions were taken (e.g., sweep changes, minimum operating levels, etc.) but they were all ineffective. It was later realized that the site had been letting roughly 400+ psig steam (447°F) down to approximately 75 psig, with no de-superheating (390°F). The frequency of fires was reduced when the site stopped using the superheated 75 psig steam.

3.5.4 Operating Temperature

To avoid the possibility of increased fire danger, the temperature of the molten sulfur should not exceed 309°F, per NFPA-655. This is because higher temperature, even when below the flash point (334°F), is associated with more fires. An industry example of this is for a facility that observed persistent fires in a sulfur pit [14]. The pit operated at a temperature of 315 to 320°F. Many changes, such as reducing static discharge, were implemented to reduce the likelihood of a fire, without success. The fires were only eliminated when the operating temperature was reduced to 290 to 300°F. Therefore, care needs to be taken to operate molten sulfur tanks and pits in the appropriate temperature range.

3.5.5 Pressure Protection

Should a fire event occur, appropriately-heated pressure transmitters (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. Alternately, a pressure relief device can be used for overpressure protection during a tank sealing event in a fire. A vacuum relief device is also recommended because as the tank cools down after a fire is extinguished, it is possible that a vacuum may form.

3.5.6 Other Practices

It is also recommended that the sulfur level in pits and tanks be kept above any heating coils used in these vessels. When heating coils are exposed to air, ignition can occur from the pyrophoric iron sulfide that can form in this area.

4.0 Fire Suppression

4.1 Industry Standards and Guidance

As with fire prevention, NFPA-655 is a primary standard for fire suppression in molten sulfur handling operations. In the 2017 edition [13], Chapter 5 (normal handling temperatures, 246°F - 309°F) and Chapter 6 (applies to handling sulfur above 309°F) contain relevant information on fire suppression. NFPA-655 should be consulted directly for guidance and for

specific language used in the standard. The following is a summary of some of the fire suppression topics covered in the standard (2017 edition) [13]:

- Firefighting methods (see section 5.5 in NFPA-655) referenced for covered liquid sulfur storage tanks, pits, and trenches include the following:
 - Inert gas system designed according to NFPA 69.
 - Steam extinguishing system capable of delivering a minimum of 2.5 lb/min of steam per 100 ft³ of volume. In this paper, this will be referred to as “snuffing steam”.
 - In the Annex of the standard ((Annex A, Section A.5.5.1(2)), a design recommendation that the snuffing steam “should be preferably introduced near the surface of the molten sulfur” is included based on NFPA 86, Section F.3. This is discussed further in the following section of this paper.
 - Rapid sealing of the enclosure
 - The only rapid sealing method explicitly discussed in the current NFPA-655 standard is the application of sealing steam. Sealing steam is covered in an Annex section of NFPA-655 (Annex A, Section A.5.5.1(3)).
 - Note, although sealing steam is the only sealing method explicitly mentioned in the current NFPA-655, it also does not specifically exclude sealing a vessel by closing off its inlets and outlets.
 - Some prior versions of NFPA-655 apparently did explicitly refer to “..closing the container to exclude air;..”; there was also apparently language referring to small sizes for this practice [26].
 - In the authors’ opinion, extreme caution is advised regarding mechanical sealing of a vessel as a fire mitigation technique (see later section of this document).
 - Sealing steam is applicable to enclosed sulfur tanks or pits designed with sweep air systems that are designed to meet the requirements of NFPA 69. Sealing steam delivered at a minimum rate of 1 lb/min per 100 ft³ of tank or pit volume is “expected to develop a positive pressure in the enclosure, thereby sealing the sulfur tank or sulfur pit and preventing air ingress and extinguishing the fire.”
 - The standard includes guidance on the design and application of sealing steam and references the original literature that developed the concept of sealing steam and includes more detailed guidance on design considerations for sealing steam [23].
- For open containers, fine water sprays are deemed acceptable for fire extinguishing.
- For storage equipment operating above 309°F, the standard indicates that storage equipment should be designed to exclude air under normal operation, so sealing methods are not applicable as with storage tanks or pits at lower operating temperatures that may include air sweeps, etc. The standard does indicate, however, that an “adequate” supply of an inerting agent, such as steam, must be available “at all times for blanketing and purging equipment.”

4.2 Snuffing and Sealing Steam

As noted in the preceding section, NFPA-655 makes a distinction between snuffing and sealing steam. Snuffing steam is steam used to directly extinguish a fire by displacing air at the fuel-fire interface with steam, removing the oxygen needed for combustion. Sealing steam, on the other hand, flows out of all tank air inlets, effectively sealing the tank by preventing additional air ingress, allowing the fire to consume any remaining oxygen prior to burning out.

The distinction and specification of both snuffing steam and sealing steam in NFPA-655 was necessary based on an analysis of the steam requirements for fire suppression and the overpressure risk for typical air-swept tank and pit designs subject to the snuffing steam requirement [23]. The analysis indicated that the snuffing steam requirement of 2.5 lb/min/100 ft³ of tank volume was not required for adequate fire suppression and did not reflect a practical steam flow to be vented from air swept tanks (and some pits) while balancing the overpressure risk from the steam (large vents required) against the normal air venting (smaller vents, maintain sufficient tank vacuum pressure to prevent reverse flow from tank vents). Snuffing steam design requirements were originally adopted from other NFPA standards for ovens and furnaces (e.g., NFPA 86) and testing for gasoline fire suppression, and updated over time for NFPA-655. Therefore, the snuffing steam requirement apparently did not originally consider the additional design constraints of molten sulfur tanks and pits. The authors of the analysis proposed a lower sealing steam rate (1 lb/min/100 ft³) based on industry feedback and steam flow evaluation via CFD.

4.2.1 Design and Operating Considerations

Sealing and snuffing steam systems have several considerations outside of the fire suppression function/flow requirements. All of these topics will not be considered in detail in this paper. However, some of the key design considerations include:

- Location of the Steam Activation Valve: This valve is often a manual valve, and industry practice is that the valve should be at least 50 ft from the tank (radially) to ensure the person operating the valve is safely removed from the hazard area [23] [2]. In addition, the valve should be located in a place where the operator has a clear line of sight from the valve to the tank vent(s) to verify steam activation.
- Verification of Dry Steam: The design should include provisions for blowdown of steam prior to activation to ensure only dry steam is present in the line. Wet steam can create a tank rupture risk as the mass of water (liquid and vapor) reaching the tank may be much higher than with dry steam and, upon entering the tank and vaporizing/expanding, the steam may risk over-pressuring the tank. (Trimeric's industry contacts indicate that this has indeed happened. Further, there are examples of the same overpressure phenomenon happening in furnaces / heaters where wet snuffing steam entered the equipment.) The steam system design should also include a drip leg and steam trap upstream of the valve to ensure condensate does not accumulate in the line and the line stays warm [23].
- Minimize the Risk of Plugging: To prevent plugging of the steam line with elemental sulfur, the line may have rupture disks at the tank (there is mixed industry experience with rupture disks, which do, in Trimeric's understanding). The line may alternately have a small purge gas flow to prevent back flow of sulfur vapor and/or be thoroughly

steam jacketed or traced to prevent plugging. In addition, the sealing steam line operation should be proven periodically to ensure plugging has not occurred.

- Note that some references also indicate that sealing steam should be introduced close to air inlet nozzles⁴ so that the sealing steam rapidly exits via the air inlets, sealing the tank or pit (preventing air from entering) [13], [23]. However, in practice, if sufficient steam is introduced to generate positive pressure in the tank (i.e., force tank vapor out of the air inlets), the sealing effect of the steam should still be effective, even if the vapor that initially flows out of the inlets is headspace vapor (rather than steam). However, benefits of having the steam leave rapidly to form the “seal” may include:
 - Limiting the rapid expulsion of the toxic headspace vapors to the atmosphere and immediate tank vicinity as the steam enters (though some headspace vapor will always be entrained with steam leaving the tank).
 - Quick visual verification that the steam has reached the tank (operator can verify steam is exiting from air inlets and/or stack).

In addition, while the NFPA guidance for sealing or snuffing steam flow can be used directly as the basis for a steam fire suppression system design, several independent engineering checks can be performed to validate the steam rate used in the design (either the NFPA recommended value or another steam rate):

- Verify with engineering calculations that the positive pressure generated by the steam is sufficient to “seal” the tank/pit across a range of operating conditions (e.g., normal air sweep flow, air forced into the tank by wind effects, etc.).
- The over-pressure risk should be checked carefully once the maximum possible steam flow is finalized.
- CFD analysis could be used to confirm adequate performance of sealing steam.

Other analyses not covered here may also be prudent as part of the new sealing steam system design.

In Trimeric’s experience, many sites do not have enough steam to supply the 1 lb/min/100 ft³ sealing steam as recommended in NFPA-655. For example, a site that receives sulfur from various sources and then ships it out to other destinations (that is not associated with a large process plant) may only have enough steam capacity to provide all the heating and melting requirements. If such a site has a large tank, then the available steam may be much lower than 1 lb/min/100 ft³. In such cases, one may have to work with the available steam supply and perform analyses that show that the available steam rate and tank design result in a positive pressure sufficient to exclude air, when the steam is turned on. Literature suggests that fires can be suppressed, even if the steam rate is much lower than in NFPA-655 [23], and Trimeric’s contact with molten sulfur handling and logistics parties also indicate that lower steam rates are successfully used to put out fires.

⁴ It is important to distinguish between sealing steam, where it is recommended to introduce the steam near the air inlet nozzles and snuffing steam, where it is recommended (in NFPA-655) to introduce the steam close to the molten sulfur surface (see Section 4.1). The difference in the primary mechanism to extinguish the fire for each application explains the different recommendations for steam introduction.

Another consideration is how quickly the steam should be turned on after a fire is detected in order to prevent tank or vessel damage. This cannot be answered definitively, as far as the authors are aware. However, both the authors' experience and some of the available literature [23] [27] suggest that operators have activated snuffing steam within ~4 to ~10 minutes of detecting a sulfur pit or tank fire. The data also suggest that the pits and tanks often suffered no known damage, sometimes in spite of multiple fires. So, a reaction time of maybe 5-10 minutes might be a reasonable assumption to put out a tank fire and prevent tank damage. A bit more information from the two literature references follow.

One document gives some data from 4 sites that had fires (3 in pits and one in tanks) [23]. Rough reaction times from detection of a fire to application of snuffing steam can be assessed by interpreting the figures (e.g., vent temperatures) and text together. This document also shows that a fire in a tank may be detected by a temperature increase in the vapor exiting the tank (e.g., near the bottom of the central stack), or more commonly, by observation of a yellow plume coming from the tank (e.g., from the central stack). The document also gives the length of time that steam was applied for specific events, although the length of time one may need to run steam (in order to ensure the fire is out) may vary greatly site to site depending on many factors.

Another document presented at the 2017 Brimstone Sulfur Recovery Symposium had one more bit of data regarding operator response time in a response dated "2-16-17" which says: "Operators typically diagnose the source and have snuffing steam started within 5-10 minutes [27]." This indicates a probable operator response time of 5-10 minutes after the fire is detected.

4.3 Mechanical Sealing

Another approach to mitigating a molten sulfur pit or tank fire is to mechanically close / seal off all vents and air inlets [28], [29]. This can be done using control valves that are activated remotely by an operator or automated as a response to a measured operating parameter (e.g., high vapor space temperature) that indicates a fire in the system. By stopping air ingress into the pit or the tank, the fire will consume the limited available oxygen, producing SO₂ in the process. The fire will put itself out once the oxygen level in the tank or pit reaches its lower limiting oxygen concentration (LOC) for combustion of sulfur.

The 2017 NFPA-655 guidance includes "rapid sealing of the enclosure to exclude air" as a fire fighting method for covered storage tanks and pits [13]. Thus, mechanical sealing appears to comply with the guidance. This method may be considered if not enough snuffing or sealing steam is available at the site. However, a concern with mechanical sealing is that the pit or tank may become very hot before the fire goes out.

Estimating the temperature and pressure that could be produced by a fire burning in a sealed tank is complicated. The combustion of sulfur can be rather slow. There is also a large amount of thermal mass from the molten sulfur in the tank and the tank walls that can absorb the heat generated from combustion reactions. In an extremely fast fire, the heat of combustion may only impact the headspace of the tank. In a very slow fire, the heat generated by combustion may be dispersed through the tank and its contents at the same temperature. Trimeric conducted a simple analysis to evaluate the total potential heat-up to consume oxygen below the LOC and extinguish a fire for the two extremes. It was not attempted to characterize the rate of the

combustion reaction and the mechanisms that heat would be distributed throughout the tank. The results of this cursory evaluation for an example tank are shown below.

- Fast Combustion (all combustion heat absorbed by tank headspace and impacting gas temperature only): Tank headspace heats to >2,000 F with >30 psig increase, if not relieved; and
- Slow Combustion (all combustion heat absorbed by entire tank and all contents at equal temperature): Temperature of all contents rise by ~10 F with a pressure increase of 0.1 psi.

The two combustion scenarios display a wide range of outcomes from a fire that could occur in a mechanically sealed vessel. The impact on temperature and pressure may fall between the two extremes depending on the specific operating conditions in the tank or pit and the mechanisms of the fire, which can vary with each occurrence. Thus, it may be prudent to consider the potential for these extremes to occur and take the necessary measures needed to prevent these risks. Damage to the tank could be severe, resulting in a loss of mechanical integrity or even an entire collapse of the structure or roof. Overpressure and vacuum relief devices are important to relieve the buildup of pressure from heating and the vacuum that could occur with cooling. Explosion hatches may also be warranted. Finally, the system will need to be allowed to cool below 309°F before reopening.

(Note: Trimeric has some experience with large sulfur tanks designed [by others] with mechanical sealing, and, in Trimeric's experience, some such tanks have suffered overpressure and/or vacuum {upon cooling} resulting in major tank damage; extreme caution is advised.)

In general, if steam can be used, it is thought to be a more effective and lower risk means to extinguish a fire [28], [29].

4.4 Water Mist

Spraying a solid stream of water onto a fire may cause the generation of a large amount of steam or cause sulfur (perhaps burning sulfur) to be splashed wildly as the water hits the surface of the hot sulfur. The sudden generation of steam in an enclosed space may also result in over pressurization of the tank or pit and is generally not recommended.

However, there have been cases where a water mist is used for fire suppression in molten sulfur tanks. Water spray methods have reportedly been used to control sulfur fires on merchant sulfur vessels [30] and in sulfur production and manufacturing industries [31]. Also, NFPA-655 recognizes the use of a fine water spray to extinguish liquid sulfur fires stored in *open* containers. In this situation, high-pressure water streams (as opposed to fine sprays) are to be avoided and the quantity of water used minimized. Although Trimeric knows from experience that water sprays have been used to suppress fires in enclosed tanks, NFPA-655 does not mention using a water spray in enclosed tanks [13].

In theory, if the proper amount of water is used, the water mist option should function similar to sealing steam because the water would vaporize to make steam. The water should be provided in a fine mist form to avoid splashing and to provide good dispersion. In addition, it is

important to prevent any nozzles and spray headers used to supply the water in mist form from plugging. There are no known widely accepted or published engineering standards or guidelines for this molten sulfur fire suppression method, and careful consideration would be required to provide water to the tank or pit in a suitable spray or mist form.

In summary, designing for a fine water mist may be an option at sites with molten sulfur storage vessels that do not have enough utilities to use steam. But, careful consideration must be given to the design or application of a water mist to avoid problems.

5.0 Conclusions

Many different methods can be used to prevent and suppress molten sulfur tank and pit fires and explosions. The most common methods to prevent explosions involve maintaining the pit or tank vapor space below 25% of the LEL of H₂S, either through use of sweep air or with inert gas blanketing. The tank and pit can be designed with special features to detect and mitigate a sulfur fire and safe operating procedures can be used as well. If a fire occurs, the most common method used is to extinguish the fire is to provide snuffing or sealing steam to the tank. Snuffing steam is used to eliminate a fire by supplying a high rate of steam to displace air from the area where a fuel source may be located. The steam may also carry away some heat as well. Sealing steam is used at a lower rate than snuffing steam to provide positive pressure and effectively seal the vents and inlets to prevent air ingress. Over-pressuring the tank or pit with these methods is a concern that needs to be addressed in the design of the equipment. Rapid sealing of the tank by mechanically closing the vents is another method that has been used historically, but it can result in high temperatures without a means to release heat from the tank or pit, and can result in overpressure or vacuum conditions in the tank, with tank damage, unless properly relieved. Direct contact with a solid stream of water is not recommended, but the use of a fine water spray has been successfully used to suppress fires; the water mist evaporates and effectively serves as sealing steam. The choice of fire suppression method may be impacted by the available utilities at the site. Of these approaches, NFPA-655 recognizes the use of steam and rapid tank sealing.

6.0 References

- [1] J. Johnson and N. Hatcher, "Hazards of Molten Sulfur Storage and Handling," in *Proceedings of the 53rd Annual Laurence Reid Gas Conditioning Conference*, Norman, OK, 2003.
- [2] K. McIntush et al., "Molten Sulfur Storage Tank, Loading, and Vapor Ejection Systems Review," in *Brimstone Sulfur Symposium*, Vail, 2015.
- [3] J. Lagas, C. Butlin, E. Fitzpatrick, M. Wetzels and W. Kijlstra, "Understanding the Formation of and Handling of H₂S and SO₂ Emissions from Liquid Sulphur During Storage and Transportation," in *Sulfur Seminar*, Amsterdam, 1999.
- [4] S. Fenderson, "D'GAASS Sulfur Degasification Sulfur Update," in *Brimstone Sulfur Recovery Symposium*, Vail, Colorado, 2005.
- [5] "US Depart of Labor Occupational Safety and Health Administration," [Online]. Available: <https://www.osha.gov/SLTC/hydrogensulfide/hazards.html>. [Accessed 5 September 2019].

- [6] R. Steudel, Y. Steudel and M. W. Wong, "Speciation and Thermodynamics of Sulfur Vapor," in *Elemental Sulfur and Sulfur Rich Compounds I*, Berlin, Springer Berlin Heidelberg, 2003, pp. 117-134.
- [7] Ken McIntush, Darryl Mamrosh, Darshan Sachde, Carrie Beitler, "Use of Caustic Scrubbers on Vent Streams from Molten Sulfur Storage and Shipping Equipment," in *Brimstone Sulfur Recovery Symposium*, Vail, CO, 2017.
- [8] K. E. McIntush, D. Sachde and C. A. M. Beitler, "Molten Sulfur Vent Stream Disposition - Vent Stream Routing, Managing Emissions, and Impact of Process Conditions/Equipment," in *Brimstone Sulfur Recovery Symposium*, Vail, Colorado, 2019.
- [9] K. E. McIntush, K. Fisher, D. Sachde and C. A. M. Beitler, "Design Considerations for Natural Draft Ventilation in Molten Sulfur Storage Tanks," in *Brimstone Sulfur Symposium*, Vail, CO, 2018.
- [10] AFPM, "AFPM Process Safety Bulletin: Flammability Hazards of Hydrogen Sulfide (H₂S) Accumulation in Sulfur Tanks," American Fuel & Petrochemical Manufacturers (AFPM), Washington D.C., 2018.
- [11] R. Pahl and K. Holtappels, "Explosions Limits of H₂S/CO₂/Air and H₂S/N₂/Air," *Chemical Engineering & Technology*, vol. 28, no. 7, pp. 746-749, 2005.
- [12] Conoco Phillips, *Sulphur, Liquid (Canada) - Safety Data Sheet*, Calgary: Conoco Phillips, 2012.
- [13] National Fire Protection Association (NFPA), "NFPA 655: Standard for Prevention of Sulfur Fires and Explosions," NFPA, Quincy, MA, 2017.
- [14] P. Bisila, "ABPG Lessons Learned: Molten Sulfur Reliability Issues and Solutions," in *Brimstone Sulfur Recovery Symposium*, Vail, CO, 2014.
- [15] AFPM, "AFPM Process Safety Bulletin: Hazards of Purged Tanks - Formation of Pyrophoric Iron Sulfide in Low Oxygen Environments," American Fuel & Petrochemical Manufacturers, Washington D.C., 2014.
- [16] P. D. Clark and N. Dowling, "Corrosion Due to Elemental Sulfur in Sour Gas Production and Claus Sulfur Recovery Systems," in *MESPO 2016*, Abu Dhabi, United Arab Emirates, 2016.
- [17] B. Forbes and D. Cipriano, "Case Study of Corrosion Rates of an Externally-Heated Sulfur Storage Tank," in *Brimstone Sulfur Symposium*, Vail, CO, 2018.
- [18] Thomas Chow and Teresa Flood, "Emissions Reduction: Handling Sulfur Pit Vents and Sulfur Storage Tank Vents," in *Brimstone Sulfur Recovery Symposium*, Vail, CO, 2006.
- [19] R. Marriott, P. Clark, P. Davis, E. Fitzpatrick and K. Lesage, "A Re-examination of H₂S Solubility in Liquid Sulfur," in *Brimstone Sulfur Recovery Symposium*, Vail, CO, 2007.
- [20] W. Affens, "Can Pyrophoric Materials Form in Oil Tankers with Inert Gas Fire Protection Systems?," NRL, 1977.
- [21] A. Wankhede, "Marine Insight," 2020. [Online]. Available: <https://www.marineinsight.com/marine-safety/protection-against-explosion-the-i-g-system>. [Accessed 14 8 2020].
- [22] B. Welch, "ABPG Lessons Learned: Understanding Iron Sulfide and its Pyrophoric Nature," in *Brimstone Sulfur Recovery Symposium*, Vail, CO, 2016.
- [23] A. D. Mosher, S. M. McGuffie and D. H. Martens, "Molten Sulfur Fire Sealing Steam

- Requirements: Proposed Modifications to NFPA 655," in *Brimstone Sulfur Symposium*, Vail, CO, 2015.
- [24] J. Donovan, "Safe Handling of Molten Sulfur," *Chemical Engineering Progress*, vol. 58, no. 1, 1962.
- [25] American Petroleum Institute, "API Recommended Practice 2003: Protection Against Ignitions Arising Out of Static, 6th Ed.," American Petroleum Institute, Washington D.C., 1998.
- [26] Texas Gulf Sulphur Company, TGS (Texas Gulf Sulphur Company) Sulphur Manual, New York: Texas Gulf Sulphur Company, 1959.
- [27] L. Stern, "ABPG - Brimstone Sulfur Symposium, Vail - 2017," in *Brimstone Sulfur Recovery Symposium*, Vail, CO, 2017.
- [28] DKL Engineering, Inc., "Sulphuric Acid Plant Safety," 2 November 2003. [Online]. Available: <http://www.sulphuric-acid.com/>. [Accessed 2 September 2020].
- [29] Occupational Safety and Health Service, "Approved Code of Practice for the Prevention of Sulphur Fires and Explosions," Department of Labour, Wellington, New Zealand, 1993.
- [30] L. Johnson, "Sulphur Vessels," in *Gulf Coast Section Meeting of the Society of Naval Architects and Marine Engineers*, Houston, 1972.
- [31] Georgia Gulf Sulfur Corporation, "Sulfur Fires," 2015. [Online]. Available: <https://georgiagulfsulfur.com/safety/sulfur-fires>. [Accessed 2 September 2020].
- [32] D. Sachde, C. Beitler, K. McIntush and K. Fisher, "Preventing explosions in molten sulphur tanks," *Sulphur Magazine*, September/October 2020.