MOLTEN SULFUR FIRE SEALING STEAM REQUIREMENTS PROPOSED MODIFICATIONS TO NFPA 655

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Brimstone Sulfur Symposium
Vail, Colorado
September 14-18, 2015

Abstract

National Fire Protection Association (NFPA) 655, *Standard for Prevention of Sulfur Fires and Explosions* (current edition: 2012), Chapter 5, Handling of Liquid Sulfur at Normal Handling Temperatures, Section 5.5, Fire Fighting, states that protection of covered liquid sulfur storage tanks, pits and trenches shall be by one of the following means: (1) inert gas system, (2) steam extinguishing system capable of delivering a minimum of 2.5 pounds per minute (lb/min) (1.13 kilograms per minute [kg/min]) of steam per 100 cubic feet (ft^3) (2.83 cubic meters [m^3]) of volume, or (3) rapid sealing of enclosure to exclude air. The NFPA snuffing steam rate stated in the standard results in a large steam rate being fed to sulfur tanks and sulfur pits that typically have a low design pressure. The sulfur tanks and sulfur pits are typically designed with air sweep systems to prevent the accumulation of hydrogen sulfide (H_2S) in the vapor space, thereby eliminating the flammable mixture. The air intake and exhaust systems are typically designed with very low pressure drops for normal operation. If snuffing steam is fed to sulfur tanks and sulfur pits at the rate specified in NFPA 655, the built-up back pressure typically far exceeds the design pressure of the enclosure. For these reasons, the refining and gas plant industry has tended to choose not to follow the NFPA 655-specified snuffing steam rate. Actual operating data from sulfur fires in sulfur tanks and sulfur pits indicate that a lower sealing steam rate is adequate to extinguish the fire by sealing the sulfur tank or sulfur pit from air ingress and purging some of the air as the fire is extinguished by lack of oxygen. Some computational fluid dynamics (CFD) modeling has been completed that supports the field data showing that a lower steam rate is adequate to extinguish the fires. This paper focuses on the potential problems caused by the current NFPA 655 snuffing steam rate, analysis of actual field data for fires in sulfur tanks and pits, and a recommendation for the NFPA 655 committee to consider regarding a steam rate to seal the enclosure and extinguish the fire in a sulfur tank and sulfur pit. The paper also includes comments on good engineering practice resulting from the calculations and CFD analyses that were completed. NFPA 655 is currently being updated and will be reissued in 2017. This paper was initially prepared to document issues with the current NFPA 655 snuffing steam rate for molten sulfur and to recommend a reduced rate to NFPA during the first public comment period that ended on January 5, 2015.

Executive Summary

On the basis of the data collected and analysis performed for this paper, in December 2014 the authors recommended the following changes **(text in red)** to National Fire Protection Association (NFPA) 655, *Standard for Prevention of Sulfur Fires and Explosions* (current edition: 2012), Chapter 5, Handling of Liquid Sulfur at Normal Handling Temperatures:

5.5 Fire Fighting.
5.5.1 Protection for covered liquid sulfur storage tanks, pits, and trenches shall be by one of the following means:
(1) Inert gas system in accordance with NFPA 69, *Standard on Explosion Prevention Systems*
(2)*Steam extinguishing system capable of delivering a minimum of 2.5 lb/min (1.13 kg/min) of steam per 100 ft^3 (2.83 m^3) of volume.
~~(3) Rapid sealing of the enclosure to exclude air~~
(3)*Rapid sealing of the enclosure to exclude air. For sulfur tanks and sulfur pits, the use of a steam rate of 1.0 lb/min (0.45 kg/min) of steam per 100 ft^3 (2.83 m^3) of total tank or pit volume is expected to develop a positive pressure in the enclosure, thereby sealing the sulfur tank or sulfur pit, preventing air ingress, and extinguishing the fire.
5.5.2 Snuffing Steam and Sealing Steam Precautions.
5.5.2.1 The vent systems on enclosed sulfur tanks and sulfur pits must be designed to allow the required snuffing steam rate or sealing steam rate to vent without overpressuring the enclosure. The vent systems must also be designed for proper operation during normal operation.
5.5.~~2~~**3** Water Extinguishing Precautions.
5.5.~~2.1~~**3.1** Liquid sulfur stored in open containers shall be permitted to be extinguished with a fine water spray.
5.5.~~2.2~~**3.2** Use of high-pressure hose streams shall be avoided.
5.5.~~2.3~~**3.3** The quantity of water used shall be kept to a minimum.
5.5.~~3~~**4** Dry Chemical Extinguishers. Where sulfur is being heated by a combustible heat transfer fluid, dry chemical extinguishers complying with NFPA 17, *Standard for Dry Chemical Extinguishing Systems*, shall be provided.

A.5.5.1(3) For enclosed sulfur tanks or sulfur pits with air sweep systems, the sealing steam should be fed into the enclosure very near the air inlets. As the sealing steam vents backward through the air inlets, the sealing steam will quickly stop air ingress to the fire. Sealing steam should be fed into the sulfur tank or sulfur pit for a minimum of 15 minutes or until the temperature has returned to near normal. For further information and good engineering practice regarding sealing steam, refer to *Molten Sulfur Fire Sealing Steam Requirements.*

C.1.2.3 Other Publications.
Mosher, A. D., McGuffie, S. M., and Martens, D.H., *Molten Sulfur Fire Sealing Steam Requirements*, Brimstone Sulfur Symposium, Vail, CO, September 2015.

In February 2015, the above information was discussed with the NFPA 655 Committee that oversees changes to the document. The committee accepted the concept that was being presented but some wording changes were made and the statement about 1.0 lb/min (0.45 kg/min) of steam per 100 ft^3 was relocated to the document annex. In April 2015 the

committee members voted to accept the revised wording. The next step in the approval process is posting of the first draft of the revised document followed by a second public comment period in the fall of 2015, with the final goal of issuing a new edition of NFPA 655 in 2017.

1.0 Introduction

National Fire Protection Association (NFPA) 655, *Standard for Prevention of Sulfur Fires and Explosions*,(1) contains information about snuffing steam requirements for extinguishing fires in sulfur tanks and sulfur pits. The rate that is listed in Chapter 5, Handling of Liquid Sulfur at Normal Handling Temperatures, is excessive and causes problems with the venting systems of these enclosures and can cause built-up back pressure within these enclosures that exceeds the original design pressure.

Sulfur produced in oil and gas facilities contains quantities of hydrogen sulfide (H_2S). This H_2S is slowly released from the molten sulfur during storage. To eliminate the flammable mixture, sulfur tanks and sulfur pits in these facilities are typically designed with air sweep systems to prevent the accumulation of H_2S in the vapor space. Continuous sweeping with air also prevents accumulation of pyrophoric iron sulfide (FeS) by oxidizing the material. The FeS is generated by corrosion of carbon steel components in contact with H_2S. The air intake and exhaust systems for sulfur tanks and sulfur pits must be carefully designed with consideration for very low pressure drops during normal operation, must account for the buoyancy effect of the heated air intakes, and must account for the effect of wind blowing across the vents. Developing a vent design that accounts for all the normal operating parameters can be quite difficult and can become impractical when the vents must also be capable of venting the snuffing steam fed at the NFPA 655 rate of 2.5 pounds per minute (lb/min) per 100 cubic feet (ft^3) of volume.

This paper focuses on the potential problems caused by the current NFPA 655 snuffing steam rate and recommendations for a revised rate by:

- Presenting analysis of available actual field data for extinguishing fires in sulfur tanks and sulfur pits provided by owners of oil and gas facilities.

- Providing the basis for a recommendation to the NFPA 655 committee to consider defining a steam rate to suitably seal the sulfur tanks and sulfur pits to exclude oxygen and, thereby, safely extinguish sulfur fires.

- Recommending a sealing steam rate based on documented industry practice for extinguishing fires in sulfur tanks and sulfur pits and computational fluid dynamics (CFD) studies.

Comments on good engineering practice resulting from the analysis of the information gathered and from CFD modeling that was completed are included.

NFPA 655 is currently being updated and will be reissued in 2017. The original revision of this paper was prepared to document issues with the current NFPA 655 snuffing steam rate for molten sulfur fires and recommend incorporating a sealing steam rate to NFPA during the first public comment period for NFPA 655 that ended on January 5, 2015.

Note: No part of this document addresses fire fighting for solid dust sulfur fires. This document only addresses steam requirements for molten sulfur fires.

2.0 Brief History of NFPA 655 Snuffing Steam Requirements

The fire fighting techniques listed by NFPA for molten sulfur have evolved since the initial adoption of NFPA 655 in 1940. The following information was taken from documents such as revision history, Technical Committee Reports, etc., available on NFPA's website.[1]

2.1 1968 Edition

The Technical Committee Report for Amendments to be included in the 1968 edition of NFPA 655 included the following text:

> 45. Fire Fighting.
>
> 4501. Covered liquid sulfur storage tanks should be provided with some inert gas system for extinguishing fires that may occur in the tank. The inert gas may consist of carbon dioxide, nitrogen, flue gas or steam. Since the inert must be supplied rapidly enough to displace the ventilation air from the vents, steam is usually the most effective and economical choice.
>
> 4502. Where liquid sulfur containers are of sufficiently small size to permit such action, it is recommended that they be so arranged so that they can be sealed rapidly to exclude air in case of fire; formation of sulfur dioxide will exhaust the oxygen in the enclosure and smother the fire. The system should be allowed to cool below 154C (310F) before reopening it to the atmosphere.
>
> 4503. Liquid sulfur stored in open containers can best be extinguished with a fine water spray. Avoid the use of pressure hose streams which may scatter the burning liquid sulfur. The quantity of water used should be kept to a minimum.

2.2 1982 Edition

The Technical Committee Report for Amendments to be included in the 1982 edition of NFPA 655 included the following text:

> 4-4 Fire Fighting.

[1] NFPA's website is www.nfpa.org

4-4.1 Covered liquid sulfur tanks shall be provided with a gaseous fire extinguishing system. (See Appendix E of NFPA 86A, Standard Ovens and Furnaces, Appendix E, and NFPA 69, Standard on Explosion Prevention Systems.)

4-4.1.1* Where a fixed inerting system is used, thin Teflon ® rupture discs shall be placed over the inerting nozzles so that sulfur cannot condense within the nozzle.

4-4.2* Where liquid sulfur containers are small enough, they may be arranged so that they can be rapidly sealed to exclude air in case of fire. The sulfur dioxide produced by the fire will smother the fire. In such cases, the system shall be allowed to cool below 154C before reopening.

4-4.3 Liquid sulfur stored in open containers may be extinguished with a fine water spray. Use of high pressure hose streams shall be avoided. Quantity of water used shall be kept to a minimum.

2.3 1993 Edition

The Report of the Committee included the following recommendation, which was accepted and became part of the 1993 edition:

1. Revise 4-4.1" and add an Exception to read:

4-4.1* Covered liquid sulfur tanks shall be provided with a steam extinguishing system or an inert gas system in accordance with NFPA 86, Standard for Ovens and Furnaces and NFPA 69, Standard on Explosion Protection Systems.

Exception: Where liquid sulfur containers can be rapidly sealed to exclude air, the SO_2 produced will smother the fire. In such cases, steam extinguishing systems or inert gas systems shall not be required. The system shall be allowed to cool below 154C (309F) before reopening.

2. Delete existing text of 4-4.2.

2.4 2001 Edition

The Report of the Committee included the following recommendation, which was accepted and became part of the 2001 edition:

RECOMMENDATION : Revise 4-4.1 as follows:

4-4.1 Protection for covered liquid sulfur storage tanks, pits and trenches shall be by one of the following means:

(a) Inert gas system in accordance with NFPA 69, Standard for Explosion Prevention Systems.

(b)* **Steam extinguishing system capable of delivering 8 lbs/min of steam per 100 cu ft of volume.** – *Bold added by current authors*

(c) Rapidly seal the enclosure to exclude air.

A-4-4.1(b) The steam should preferably be introduced near the surface of the molten sulfur. See NFPA 86, Standard for Ovens and Furnaces, Appendix E-3.

SUBSTANTIATION: This recommendation brings the steam flooding requirement in line with NFPA 86. The recommendation is based on 1934 FMRC fire test of a gasoline fire where the steam was applied above the gasoline fire and combustion air was introduced below the steam injection point. It in essence requires supplying 200 cu ft/min steam for every 100 cu ft of enclosure volume. For hot enclosures (above 220F) where the steam is injected at the surface of the liquid sulfur, a supply capable of 4 cu ft/min per 100 cu ft of enclosure volume would be satisfactory. This requirement ensures that the available steam supply is adequate to furnish enough steam at a rate sufficient to extinguish the fire.

2.5 2007 Edition

The Report of the Committee shows a recommendation and acceptance of a complete revision of the 2001 edition of NFPA 655 to become the 2007 edition. The 2007 edition showed the following text:

5.5 Fire Fighting.

5.5.1 Protection for covered liquid sulfur storage tanks, pits, and trenches shall be by one of the following means:

(1) Inert gas system in accordance with NFPA 69, *Standard on Explosion Prevention Systems*

(2)* **Steam extinguishing system capable of delivering a minimum of 2.5 lb/min (1.13 kg/min) of steam per 100 ft^3 (2.83 m^3) of volume** – *Bold added by current authors*

(3) Rapid sealing of the enclosure to exclude air

5.5.2* Where a fixed inerting system is used, thin corrosion-resistant rupture discs shall be placed over the inerting nozzles so that sulfur cannot condense within the nozzle.

5.5.3 Water Extinguishing Precautions.

5.5.3.1 Liquid sulfur stored in open containers shall be permitted to be extinguished with a fine water spray.

5.5.3.2 Use of high-pressure hose streams shall be avoided.

5.5.3.3 The quantity of water used shall be kept to a minimum.

5.5.4 Dry Chemical Extinguishers. Where sulfur is being heated by a combustible heat transfer fluid, dry chemical extinguishers complying with NFPA 17, *Standard for Dry Chemical Extinguishing Systems* shall be provided.

2.6 2012 Edition

The Report of the Committee shows a recommendation and acceptance of a revised wording of the 2007 edition of NFPA 655 to become the 2012 edition as follows:

5.5 Fire Fighting.

5.5.1 Protection for covered liquid sulfur storage tanks, pits, and trenches shall be by one of the following means:

(1) Inert gas system in accordance with NFPA 69, *Standard on Explosion Prevention Systems*

(2)* Steam extinguishing system capable of delivering a minimum of 2.5 lb/min (1.13 kg/min) of steam per 100 ft^3 (2.83 m^3) of volume

(3) Rapid sealing of the enclosure to exclude air

~~5.5.2* Where a fixed inerting system is used, thin corrosion-resistant rupture discs shall be placed over the inerting nozzles so that sulfur cannot condense within the nozzle.~~

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5.5.2.3 The quantity of water used shall be kept to a minimum.

5.5.3 Dry Chemical Extinguishers. Where sulfur is being heated by a combustible heat transfer fluid, dry chemical extinguishers complying with NFPA17, *Standard for Dry Chemical Extinguishing Systems*, shall be provided.

2.7 2017 Edition

The next edition of NFPA 655 is due to be published in 2017. The public input closing date was January 5, 2015.

2.8 Equivalency of Various Required Snuffing Steam Rates

Table 1 provides a comparison of different snuffing steam rates for molten sulfur that have been listed in different editions of NFPA 655.

Table 1. Snuffing Steam Rates for Molten Sulfur Listed in NFPA 655

	lb/min per 100 ft^3	ft^3/min per 100 ft^3	Comment
2001 Edition	8	214	Based on 1934 Factory Mutual Research Corporation (FMRC) fire test of a gasoline fire.
2001 discussion prior to issue of official edition	0.14	3.8	Comment made as part of substantiation of item above. When steam is injected at the surface of the liquid sulfur, this rate would be satisfactory.
2007 Edition	2.5	67	

3.0 Issues with Current NFPA 655 Snuffing Steam Requirement

Most existing and new sulfur recovery units (SRUs) within oil refineries and gas processing facilities have enclosed below grade sulfur pits and/or above grade sulfur tanks for storage of produced molten sulfur. Many of these sulfur pits and sulfur tanks have been designed with air sweep systems in the vapor space to maintain the concentration of H_2S below 25 percent of the lower flammable limit (LFL) in accordance with NFPA 69, *Standard on Explosion Prevention Systems*[2], Chapter 8, Deflagration Prevention by Combustible Concentration Reduction. Because of safety concerns regarding possible venting of H_2S to the environment through leaks in the sulfur pit, many of the sulfur pits and sulfur tanks are operated with a slight vacuum. The vacuum is often created by mechanical blowers or ejectors that pull the required amount of sweep air through the vapor space of the enclosure and then discharge that air/vapor to an appropriate disposal location/device at a slightly elevated pressure. Because of the buoyancy effect, the vacuum can also be created by the height difference between a heated vent stack and the heated air intake. The typical design internal and external pressures of sulfur tanks are low (approximately -3 to +10 inch water column [inch WC] or less), and therefore, the vent systems must be carefully designed to prevent excessive vacuum from causing damage to the sulfur tank. Unlike tanks or vessels, sulfur pits may or may not be designed with the intention of having a specific internal design pressure. However, sulfur pits are typically designed with a concrete roof thickness of 12 to 15 inches. Based solely on the weight of the roof slab, the sulfur pit should be able to contain a pressure of 1-1.3 pounds per square inch (psi) (28-36 inch WC). However, sulfur pit roofs frequently contain access hatches. Precast concrete hatches typically range from 4 to 6 inches thick and can therefore withstand an internal pressure of only approximately 0.35 to 0.51 psi (10-14 inch WC) before lifting. Roof hatches or deflagration hatches can also be made from thin aluminum sheet material that is much lighter than the concrete and therefore able to withstand an internal pressure of only approximately 0.25-0.50 inch WC before lifting. The air inlets to the sulfur pit or sulfur tank are typically heated with steam (steam jacketed) to prevent sulfur solidification and the resulting plugging within the air inlet. The heating of the air intakes causes a buoyancy effect to occur, and the sulfur pit or sulfur tank must be operated under a slight vacuum to overcome this buoyancy effect and ensure that air is flowing into the sulfur pit or sulfur tank. Wind blowing across the roof of a sulfur tank also causes uplift on the leeward side that can cause a reversal of air flow from the air intakes and vent the vapor space out through the air intakes rather than out through the exhaust. The typical operating pressure of the vapor space of a sulfur pit or sulfur tank is in the range of 0.01-1 inch WC vacuum. The number and size of the air inlets must be carefully selected so that the air inlets will provide enough air flow to achieve the required air sweep but also induce enough pressure drop so that the vapor space remains at or below the required vacuum needed to offset the buoyancy effect and uplift caused by wind. If there is too much air inlet area, the air intakes can draft backward and allow the air intakes to exhaust H_2S to the atmosphere. Therefore, the air inlet area is set on the basis of the required air rate for a proper sweep of the vapor space but, at the same time, making sure that the vapor space stays at a vacuum level greater than the buoyancy effect caused by the heated air intakes.

After the air intake area is set for normal operation (and in the absence of a relief valve, which most sulfur pits and sulfur tanks do not have), then that is the only area available to vent snuffing steam when steam is used to extinguish an internal fire. The current snuffing steam extinguishing system requirements in NFPA 655 of 2.5 lb/min per 100 ft^3 of volume become a very high steam flow rate for most sulfur tanks and some sulfur pits so that this rate can easily overpressure the sulfur tank and sulfur pit, causing the sulfur tank or sulfur pit to rupture. It is not practical to design a sulfur tank air sweep system to provide the necessary vacuum to prevent flow reversals in the air inlets during normal operation and provide the necessary air intake area to vent the required snuffing steam rate during a fire scenario.

To illustrate the issues with overpressure of sulfur tanks, the authors evaluated six existing sulfur tanks that were designed for air sweep of the vapor space to reduce the H_2S concentration and the resulting back pressure if steam is fed to snuff a fire according to NFPA 655's rate of 2.5 lb/min per 100 ft^3 (refer to Table 2).

As shown in Table 2, the NFPA 655 snuffing steam rate ranges from approximately 30 to 200 times the original sweep air rate. This snuffing steam rate results in a built-up back pressure within the sulfur tank of 0.23-59.3 inch WC. This built-up back pressure would exceed the design pressure of 4 out of 6 of the sulfur tanks, as shown by the red text in Table 2. Tanks C and D have lower built-up back pressure, and they have a total volume less than 6,000 ft^3. All the tanks with a volume of approximately 50,000 ft^3 and larger would have built-up back pressure far higher than their design pressure. A general statement can likely be made that the vents on smaller tanks may be able to vent the current NFPA 655 snuffing steam rate, but it is likely that the vents on larger tanks cannot vent the current NFPA 655 snuffing steam rate without the built-up back pressure exceeding the tank design pressure.

Figure 1 is a scaled comparison of the size of the six existing sulfur tanks that were evaluated.

Table 2. Existing Sulfur Tanks with Steam at 2.5 lb/min per 100 ft^3

	Tank A	Tank B	Tank C	Tank D	Tank E	Tank F
Dimensions	66-6" Dia x 35'-0" H	59-6" Dia x 48'-0" H	19'-8" Dia x 17'-9" H	14'-5" Dia x 16'-4" H	42'-8" Dia x 32'-10" H	47'-6" Dia x 24'-10" H
Volume, ft^3	138,500	148,635	5,800	2,833	48,885	49,435
Design Pressure, inch WC	-3 / +10	-1.5 / +2.5	-3 / +10	-3 / +10	-1.1 / +3.2	-0.9 / +3.5
Air Inlets	Six - 10"	Two - 16"	Three - 6"	Three - 6"	Six - 6"	Six - 6"
Air Outlet	One - 10"	One - 16"	One - 8"	One - 8"	One - 18"	One - 8"
Air Movement Method	Blower sucks air through tank and pushes through caustic scrubber	Natural draft 2 inlets, 1 outlet	Natural draft 3 inlets, 1 outlet	Natural draft 3 inlets, 1 outlet	Natural draft 6 inlets, 1 outlet	Natural draft 6 inlets, 1 outlet
Normal Op Pressure, inch WC	-0.05	-0.0031	-0.00005	-0.00008	-0.029	Unknown
Air Sweep Objective	<16% H_2S lower flammability limit (LFL), with 150 parts per million (weight) (ppm[wt]) H_2S in sulfur feed	<21% H_2S LFL, with 150 ppm(wt) H_2S in sulfur feed	<50% H_2S LFL, with 150 ppm(wt) H_2S in sulfur feed	<50% H_2S LFL, with 150 ppm(wt) H_2S in sulfur feed	<25% H_2S LFL, with 300 ppm(wt) H_2S in sulfur feed	Unknown
Pressure inch WC with steam at 2.5 lb/min/ 100 ft^3	59.3	50.8	1.05	0.23	8.1	29
Steam volumetric rate (@ 2.5 lb/min/100 ft^3) compared to sweep air rate	29 x	190 x	198 x	79 x	53 x	Unknown

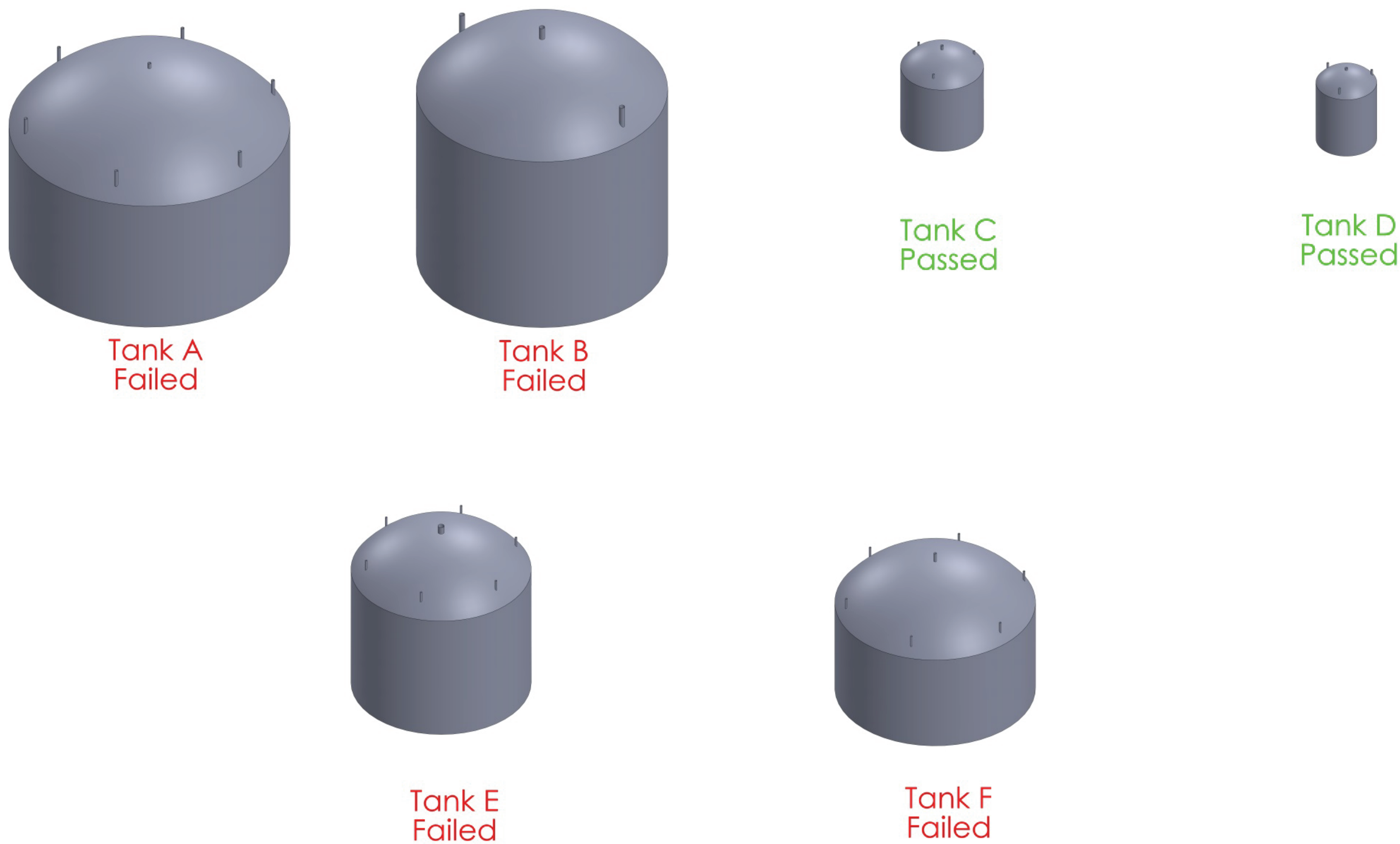

Figure 1. Sulfur Tank Size Comparison

To illustrate the issues with overpressure of sulfur pits, the authors evaluated five existing sulfur pits that were designed for air sweep of the vapor space to reduce the H_2S concentration and the resulting back pressure if steam is fed to snuff a fire according to NFPA 655's rate of 2.5 lb/min per 100 ft^3 (refer to Table 3).

As shown in Table 3, the NFPA 655 snuffing steam rate ranges from approximately 10 to 31 times the original sweep air rate. This snuffing steam rate results in a built-up back pressure within the sulfur pits of 17.6 inch WC to 1,585 inch WC (50 pounds per square inch gauge [psig]). This built-up back pressure would exceed the pressure rating of the hatch covers on all five sulfur pits, as shown by the red text in Table 3. For all five sulfur pits analyzed, the hatch covers would lift if steam was fed at the current NFPA 655 rate of 2.5 lb/min per 100 ft^3. No calculations were performed to determine the resulting built-up back pressure that would remain in the sulfur pit after the hatch covers lifted, because that would require extensive and difficult calculations. The one sulfur pit that would theoretically achieve 50 psig pressure in the pit (if the hatch covers did not lift) is large, with a total capacity of 60,665 ft3. This sulfur pit is associated with an SRU with a capacity of approximately 675 long tons per day (LTPD), which is a big plant, but certainly there are other existing plants that are much larger. This particular sulfur pit has a large reduction in inlet line size--8 inches down to 4 inches to feed into a flow meter. The flow reaches sonic velocity in this 4 inch diameter section, resulting in very high built-up back pressures. A general statement can likely be made that the vents on most sulfur pits associated with an SRU cannot vent the current NFPA 655 snuffing steam rate without the built-up back pressure exceeding the pressure that can be contained by the hatch covers. When these hatch covers lift, steam containing H_2S and sulfur dioxide (SO_2) will vent to the atmosphere at ground level and cause a serious safety concern.

Figure 2 is a scaled comparison of the size of the five existing sulfur pits that were evaluated.

Table 3. Existing Sulfur Pits with Steam at 2.5 lb/min per 100 ft^3

	Pit A	Pit B	Pit C	Pit D	Pit E
Dimensions	24'-0"W x 35'-0"L x 10'-6"D	47'-7"W x 72'-2"L x 17'-8"D	14'-0"W x 34'-0"L x 11'-0"D	13'-2"W x 49'-10"L x 9'-2"D	21'-0"W x 30'-0"L x 8'-0"D
Volume, ft^3	8,820	60,665	5,236	6,015	5,040
Design Pressure, inch WC	-unknown / +9.5 set by precast concrete access hatch covers	-unknown / +0.54 set by aluminum hatch covers	-unknown / +9.6 set by precast concrete access hatch covers	-unknown / +14.2 set by precast concrete access hatch covers	-unknown / +0.42 set by aluminum hatch covers
Air Inlets	One - 6"	Two - 8"	One - 4"	One - 4"	One - 6"
Air Outlet	One - 6"	Two - 8"	One - 4"	Two - 3"	One - 6"
Air Movement Method	Ejector sucks air through air inlet and pushes to thermal reactor	Ejector sucks air through air inlets and pushes to thermal reactor	Ejector sucks air through air inlet and pushes to thermal reactor	Ejector sucks air through air inlet and pushes to incinerator	Ejector sucks air through air inlet and pushes to incinerator
Normal Op Pressure, inch WC	-0.22	-6.9	-1.2	-0.30	-0.22
Air Sweep Objective	<15% H_2S LFL, with 300 ppm(wt) H_2S in sulfur feed	<25% H_2S LFL, with 300 ppm(wt) H_2S in sulfur feed	<25% H_2S LFL, with 300 ppm(wt) H_2S in sulfur feed	Unknown	Unknown
Pressure inch WC with steam at 2.5 lb/min/ 100 ft^3	57.8	50 psig if hatch covers do not lift, sonic velocity back through air inlets	266	230	21.4/17.6 (Note 1)
Steam volumetric rate (@ 2.5 lb/min/100 ft^3) compared to sweep air rate	16 X	31 x	17 x	30 x	9.7 x

Notes:

1. The second value listed is the built-up back pressure for this sulfur pit based on the ejector staying in operation. All other sulfur pits analyzed have a safety instrumented system (SIS) that will trip ejectors when fire is detected.

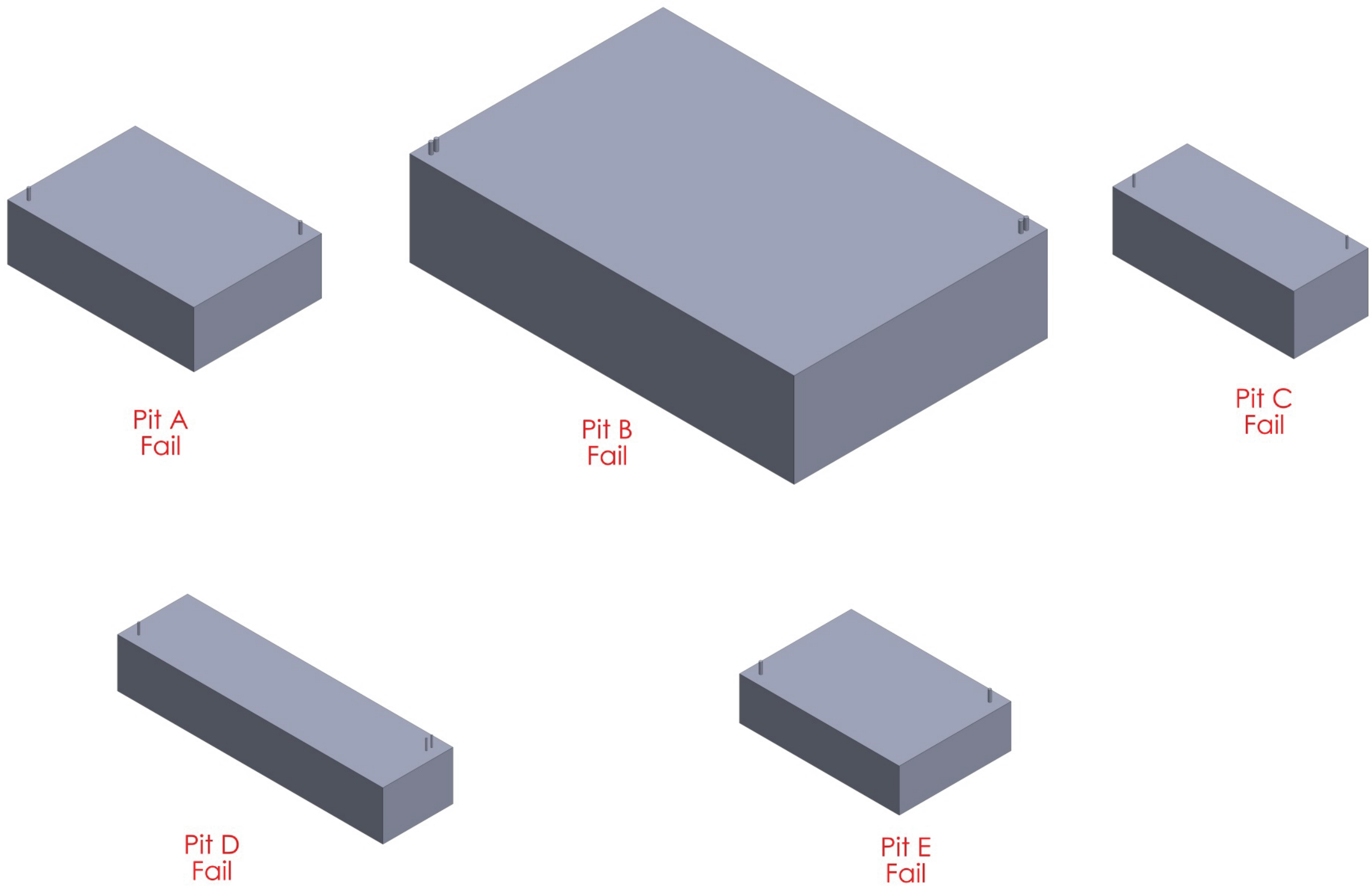

Figure 2. Sulfur Pit Size Comparison

4.0 Attempted Oxygen Concentration Dilution Calculation

When considering a new approach to determining an adequate steam rate to extinguish a sulfur fire, the authors first considered a dilution calculation for oxidant concentration reduction or combustible concentration reduction as described in NFPA 69, *Standard on Explosion Protection Systems*. To be able to complete the dilution calculation, the limiting oxygen concentration (LOC) or LFL of the vapor mixture must be known. Surprisingly, the LOC and LFL for molten sulfur could not be found. Several searches were conducted: an internet search, a search of common reference books, and a search of sulfur specific books. Several research organizations and numerous engineering/operating/simulation companies that specialize in SRUs were contacted. The LOC and LFL of molten sulfur are not readily available at any of these sources. Some material safety data sheet (MSDS) were located that showed an LFL of molten sulfur, but further investigation showed that the LFL listed was actually for H_2S. Some MSDS actually added a footnote indicating the value listed is for H_2S, and others did not include the detail. At the normal temperature that molten sulfur is typically stored, it could be argued that the sulfur vapor pressure is so low that the real danger for fire is based on the concentration of H_2S that has evolved from the sulfur and not the sulfur itself. The LOC and LFL for H_2S are available.

It has been shown experimentally that the LFL of a substance typically decreases with increasing temperature. Zabetakis[3] developed some correlations for predicting the temperature effect on the LFL for paraffin hydrocarbons. The LFL of a paraffin hydrocarbon approaches zero at temperatures above approximately 2,192F (1,200C). The LOC of a substance also typically decreases with increasing temperature. The LFL and LOC of a substance also vary with the specific inert that is present. Without experimental data for H_2S and molten sulfur with steam as the inert, it can only be speculated on what happens to the LFL and LOC in gas mixtures near an existing fire. However, it could reasonably be speculated that the LFL and LOC of H_2S and molten sulfur will fall to near zero, if the fire raises localized temperatures to where they approach 2,192F (1,200C). Even at lower localized temperatures, the LFL and LOC concentration will be very low. Therefore, once a fire has started, considering LFL and LOC as parameters to target for snuffing steam dilution calculations is not productive.

5.0 Actual Operating Data for Molten Sulfur Fire Extinguishing Steam

The authors were unable to find any published data on testing completed on molten sulfur fires or data collected from actual fires in industrial molten sulfur applications. Through various molten sulfur production forums (technical conferences, sulfur production specialist user groups, etc.) and personal contacts in the industry, the authors contacted a broad spectrum of sulfur production specialists at the major refining and gas plant companies in North America that operate SRUs to request data on any sulfur fires that have occurred in sulfur pits and sulfur tanks at the owner's facilities. The sulfur production specialists contacted should have had access to data from approximately 75 locations in North America that operate SRUs. Some locations operate more than one SRU and some locations have as many as 10 sulfur pits or sulfur tanks. On the conservatively low side, the request should have been able to gather data from 100 to 200 sulfur pits and sulfur tanks.

The request was made with the promise that the sources of all data would remain anonymous.

The request elicited some useful information about actual molten sulfur fires that have occurred in sulfur pits and sulfur tanks. Many owner responses indicated they had been fortunate enough to never have experienced a fire. Several owner responses indicated that they have had fires, but they occurred more than 10 years ago and therefore cannot remember much about them. Some owner responses indicated that they had experienced fires, but their corporate practice is such that they could not get corporate legal approval to allow data released outside of the organization. Some owner responses indicated that they had experienced sulfur fires, but they were unable to find sufficient documentation to indicate how the fires had been extinguished, or they knew that steam had been used, but they had no way to determine how much steam was used and the duration of the steam flow. One owner indicated that fires had occurred in three separate sulfur pits at one location and the fires were extinguished with a combination of steam and nitrogen, but no rate information was available.

The authors analyzed the sulfur fire data that were made available by four owners. The rest of this section describes the data that were collected and the analysis of that data.

5.1 Detection of Sulfur Pit and Tank Fires

As a side note, one outcome of the data collection was to discover how some owners detected and responded to sulfur pit fires.

For newer unit designs, it is relatively common to have a Safety Instrumented System (SIS) that receives inputs from instrumentation around the sulfur pit. If unsafe conditions are detected, the SIS will isolate certain systems around the sulfur pit in an attempt to prevent damage to equipment, environmental releases and exposure of operators to toxic or dangerous environments. It is not uncommon for the SIS to monitor the vapor space temperature of a sulfur pit, and if the temperature increases above a high set point, the SIS will trip the ejector system and stop drawing air through the sulfur pit. This trip system is in place to prevent air from being drawn through the sulfur pit and intensifying the fire.

One owner responded that it specifically did not want its ejector system to shut down on high sulfur pit vapor space temperature. That owner wanted the ejector system to stay online during a fire so that the majority of the SO_2 generated could be routed by the ejector to the SRU incinerator, allowing the emissions to be tracked and recorded. If the ejector system was shut down, the owner would need to estimate the emissions to be able to report them to the regulator agency. This particular owner experienced a number of sulfur pit fires in two sulfur pits over a 5 year period before the systems could be analyzed and modified to eliminate the sources of the fires. During this 5 year period, the owner's operations staff determined that whenever they experienced a rapid increase in the incinerator stack SO_2 emissions (the concentration would increase from a normal value of 75-90 parts per million by volume [ppmv], through the alarm point at 125 ppmv, to 1,000-1,200 ppmv), it was typically a sulfur pit fire. This causal relationship was so strong that procedures were modified to train the operators to immediately start steam to the sulfur pit whenever they saw the incinerator stack SO_2 emissions climb rapidly. The operators would start steam to the sulfur pit and allow the steam to flow for 15 minutes before shutting it off. After the steam was shut off, the operators would monitor the incinerator stack SO_2 emissions, and in most cases, the emissions levels returned to normal. If the emissions limits did not return to normal, the operators would then look at other causes, such as an upset in the tail gas treating unit (TGTU). This owner stated that when a fire occurred in the sulfur pits, the results could be seen in the incinerator stack first, then, about 30 seconds later, the sulfur pit vapor space temperature would begin to rise. The sulfur pit vapor space temperature would only increase by approximately 50 to 60F (28 to 33C) during a fire. The operators considered the sulfur pit vapor space temperature increase as confirmation of a fire but used the incinerator stack emissions increase as their indication to immediately start steam to the sulfur pit.

Figure 3 is a plot of the distributed control system (DCS) data showing the incinerator stack SO_2 emissions and the sulfur pit vapor space temperature during a typical sulfur pit fire for this owner. The data on Figure 3 show a 30 to 40 second difference in the time between when the incinerator stack SO_2 emissions start to increase and when the sulfur pit vapor space temperature starts to increase. Figure 3 is a re-plot of the raw data and not the actual plot the operators would see. When operators look at a plot trend generated by the DCS, it will have different scales associated with each parameter. In fact, the incinerator stack SO_2 emissions are reported by both a low range analyzer 0 to 500 ppmv and a high range analyzer, greater than 500 ppmv. Therefore, it makes sense that the operators would notice the initial rapid increase in the incinerator stack SO_2 emissions more easily than the slower increase in the sulfur pit vapor temperature. Because of the quick action by the operators, the incinerator stack SO_2 emissions decreased below the alarm setting of 125 ppmv within 25 minutes of the initial alarm.

It should be considered that, for the example described above, the thermocouple that was in the sulfur pit vapor space never indicated a significant temperature increase during fire events. This is likely due to the location of the thermocouple compared to the location of the fire within the vapor space. It could be concluded that, during the fires experienced in the sulfur pit examples described above, the fires were somewhat localized and did not consume the entire vapor space. For configurations that intend to leave the ejectors operating through a fire event, locating the temperature indicator in the ejector suction line is likely better than locating it in the sulfur pit vapor space. At least with the temperature indicator in the ejector suction line, the thermocouple will see an "average" temperature of the gas passing through the sulfur pit vapor space rather than seeing a point temperature at a single location within the vapor space.

Sulfur tanks typically do not include an SIS with high temperature input, and therefore, the typical method for sulfur fire detection is a visual indication of a yellow plume being vented from the tank. Some tanks do have a temperature indicator that operators can use to indicate that a fire is occurring.

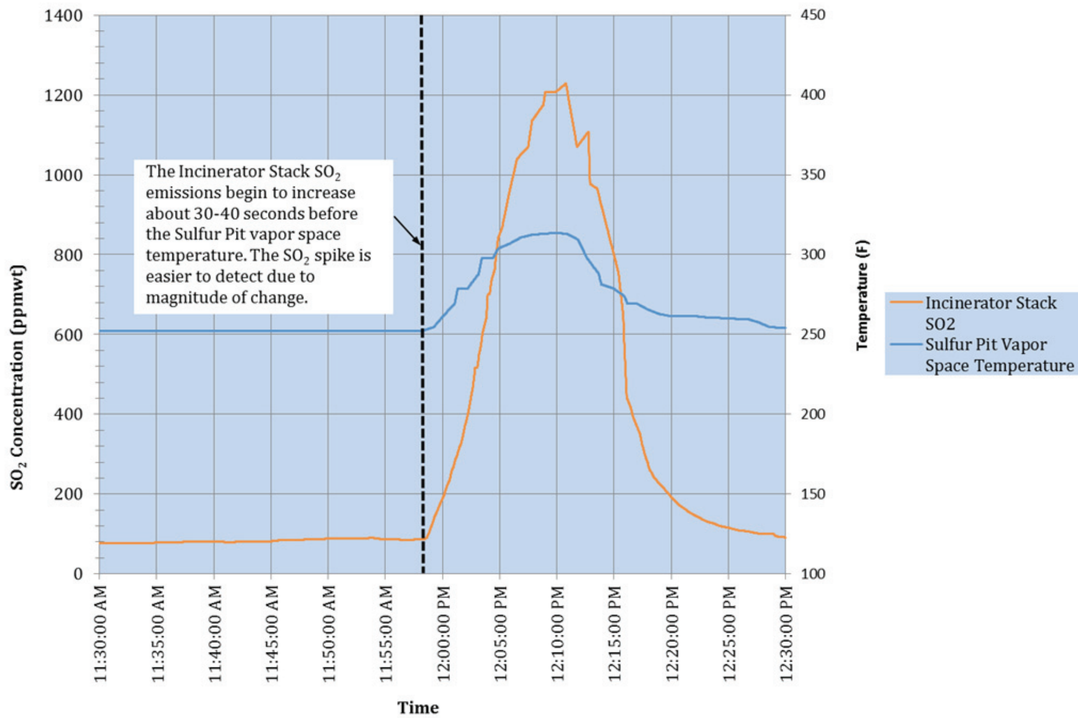

Figure 3. Incinerator Stack SO_2 and Sulfur Pit Vapor Space Temperature During a Sulfur Fire

5.2 Sulfur Pit Fires

Owner No. 1 experienced a number of sulfur pit fires in two sulfur pits over a 5 year period before the systems could be analyzed and modified to eliminate the sources of the fires. This owner provided data on how sulfur pit fires are extinguished. The sulfur pits in question are 21'-0" W x 30'-0" L x 8'-0" D, and each has a single 2 inch steam line from the header that reduces to 1 ½ inches near the connection on the roof of each sulfur pit. The sulfur pits are typical concrete pits that are completely enclosed, with one air inlet line and one air exit line that feeds an ejector for each sulfur pit. The ejector sweeps air through the vapor space of the sulfur pit and discharges to an incinerator. When a sulfur fire is suspected, the operators immediately open the 2 inch gate valve in the steam line to start steam flow to the sulfur pit. The owner reported that the operators will open the gate valve to a point where they see steam flowing out of the single 6 inch air intake line on the sulfur pit, which indicates they have put in enough steam to overcome the capacity of the sulfur pit ejector and sealed the enclosure/sulfur pit. The owner reported that the 2 inch gate valve is approximately one-third open when the operators see steam exiting from the air intake line. The steam is left flowing for a period of 15 minutes, then the flow is stopped, and the operators look at the incinerator stack SO_2 emissions to see if they have returned to normal. In almost all cases that this owner experienced, after 15 minutes of steam flow, the fire had been extinguished. The owner could only recall one incident when the fire returned after the steam was stopped. The owner speculated that for this one case, a re-ignition event may have occurred, rather than lack of suppression of the first fire.

Owner No. 1 provided the piping isometric for the steam line. Hydraulic calculations were completed for the steam based on the steam header pressure, the one-third open gate valve, and information from the piping isometric. The analysis showed that the steam flow achieves sonic velocity in the 1 ½ inch section of pipe near the steam line exit into the sulfur pit. The flow of the steam was calculated to be 2,644 pounds per hour (lb/hr). The total volume of the sulfur pit is 5,040 cubic feet (ft^3). Calculating the steam rate to sulfur pit volume ratio shows that the steam rate this owner has been using is 0.87 lb/min per 100 ft^3 of total sulfur pit volume. The owner reported that multiple sulfur fires have been successfully extinguished in the sulfur pits with this rate when the steam has flowed for 15 minutes. This rate is 2.87 times less than (or about 35 percent of) the current NFPA 655 specified value of 2.5 lb/min per 100 ft^3 for snuffing steam methodology. The owner reported that no damage has been experienced in these sulfur pits by the numerous fires because of the fact that the fire can be extinguished in 15 minutes.

It is difficult to accurately determine the resistance coefficient (K) for a partially opened gate valve without having true flow test data from the manufacturer of the actual gate valve. The authors determined that with a completely open full port gate valve (K values are available) the flow of steam would only increase to 2,900 lb/hr because the steam flow hits sonic velocity in the 1 ½ inch section near the sulfur pit roof. Therefore, the maximum flow of steam possible with the existing piping configuration is 2,900 lb/hr. Calculating the steam rate to sulfur pit volume ratio shows the maximum steam rate this owner could possibly feed, assuming a completely open gate valve, would be 0.96 lb/min per 100 ft^3 of total sulfur pit volume. This number is not substantially different from the estimated rate with the gate valve only one-third open.

It should be considered that for the sulfur pit evaluated above, the operators specifically adjust the steam flow until they see steam coming out of the air intake piping. The flow of steam effectively seals the air intake and prevents air from entering the sulfur pit. The steam is also diluting the air that is in the vapor space and pushing some of it out of the air intake piping. In the Computational Fluid Dynamics Modeling of a Sulfur Pit section, CFD is used to determine the oxygen concentration during the 15 minute period when steam is fed.

As the fire consumes sulfur and oxygen from the air, SO_2 is produced. This SO_2 is heavy and could possibly sit on the surface of the molten sulfur, helping to limit the fire access to oxygen in the vapor space. Alberta Sulphur Research Ltd (ASRL) has completed some preliminary evaluations of fires in rail cars. According to Clark [Clark, P.D. personal communication October 8, 2014], ASRL completed experiments that simulated what happens if a rail car of solid sulfur ignited. What they observed was that the sulfur started to burn only after it became liquid. In addition, they saw that the flame temperature never reached the maximum value in air (ca. 1,200F [650C] but stalled around 840F (450C), after all of the solid had liquefied. They preliminarily concluded that the SO_2 produced at the sulfur surface prevented mass transfer of air to the sulfur, limiting the rate of combustion. These experiments were done in an open box without a lid. Clark also speculated that since the surface of the liquid sulfur was adjacent to the hot vapor at 840F (450C), evaporation of liquid sulfur to the gas phase may be impeded by a viscous sulfur layer at or near the surface. Thus, the equilibrium vapor pressure at the bulk liquid sulfur temperature (ca. 356F [180C]) might not be obtained during a fire in a pit due to the kinetic effects of evaporation.

Even if the SO_2 is well dispersed within the vapor space, by effectively sealing all air entrances to the sulfur pit with steam, the fire becomes self-limiting and is quickly extinguished.

Owner No. 2 experienced a sulfur pit fire in one sulfur pit recently. This owner provided the authors with data on how the sulfur pit fire was extinguished. The sulfur pit in question is 19'-6" W x 57'-0" L x 10'-0" D and has a single 2 inch steam line from the header that branches into three separate 2 inch lines, which each feed a 3 inch connection with a rupture disk on 3 inch connections on the roof of each sulfur pit. The three connections on the sulfur pit roof are roughly 20 feet apart and feed the common vapor space above different sections within the sulfur pit. The sulfur pit is a typical concrete pit that is completely enclosed with one air inlet line and one air exit line that feeds two ejectors (one ejector can be used to feed the sulfur pit sweep air to the incinerator, and the other can be used to feed the sulfur pit sweep air back to the front end of the SRU at the thermal reactor). The owner reported that when an increase in temperature of the sulfur pit vapor space was noticed (120F [66.7C] in just a few minutes), the steam 2 inch ball valve was opened about one quarter. The steam was left flowing for a period of approximately 2 minutes, the sulfur pit vapor space temperature began to decrease, and the steam flow was stopped. The operators then monitored the sulfur pit vapor space temperature and noticed that, approximately 30 minutes after stopping the steam flow, the temperature started to increase again. At that point, the operator cracked open the 2 inch ball valve in the steam line and let the steam flow for an additional minute until they saw the sulfur pit vapor space temperature start to decrease. The steam valve was then closed, and the fire did not return.

Figure 4 is DCS data showing the temperature of the sulfur pit vapor space and the liquid sulfur temperature during the fire in Owner No. 2's sulfur pit. As can been seen, the sulfur pit vapor temperature increased 120F (66.7C) approximately 8 minutes after a sulfur pump tripped due to high viscosity (molten sulfur viscosity increases as temperature increases). Steam was started for 2 minutes and, when the operators saw the temperature begin to decrease, the steam was stopped. The sulfur pit vapor space and liquid sulfur temperature continued to decrease to normal values over an approximate 30 minute period. Then a second temperature spike occurred in the sulfur pit vapor and liquid sulfur. A small amount of steam was added for about 1 minute, and the temperatures again started to decrease toward normal values.

When the steam flow was initially started, only one of the three rupture disks actually burst. The rupture disk that was closest to the steam supply valve was the disk that burst. The other two rupture disks remained intact through both steam events. Although not perhaps apparent during the original design, but obvious in hindsight, having multiple rupture disks on a single steam supply line will likely result in only one disk bursting. The rupture disks are located directly on the sulfur pit nozzles to prevent sulfur pit vapors from backing into the steam line, condensing, and then solidifying and plugging the line during normal operation. The rupture disks are located at practically the lowest pressure in the piping system. Therefore, with slight differences in the actual bursting pressure of the rupture disks and slightly different pressures in each section of piping feeding the rupture disks, it is logical that only one of the rupture disks would burst, and all the flow would enter the sulfur pit at that location.

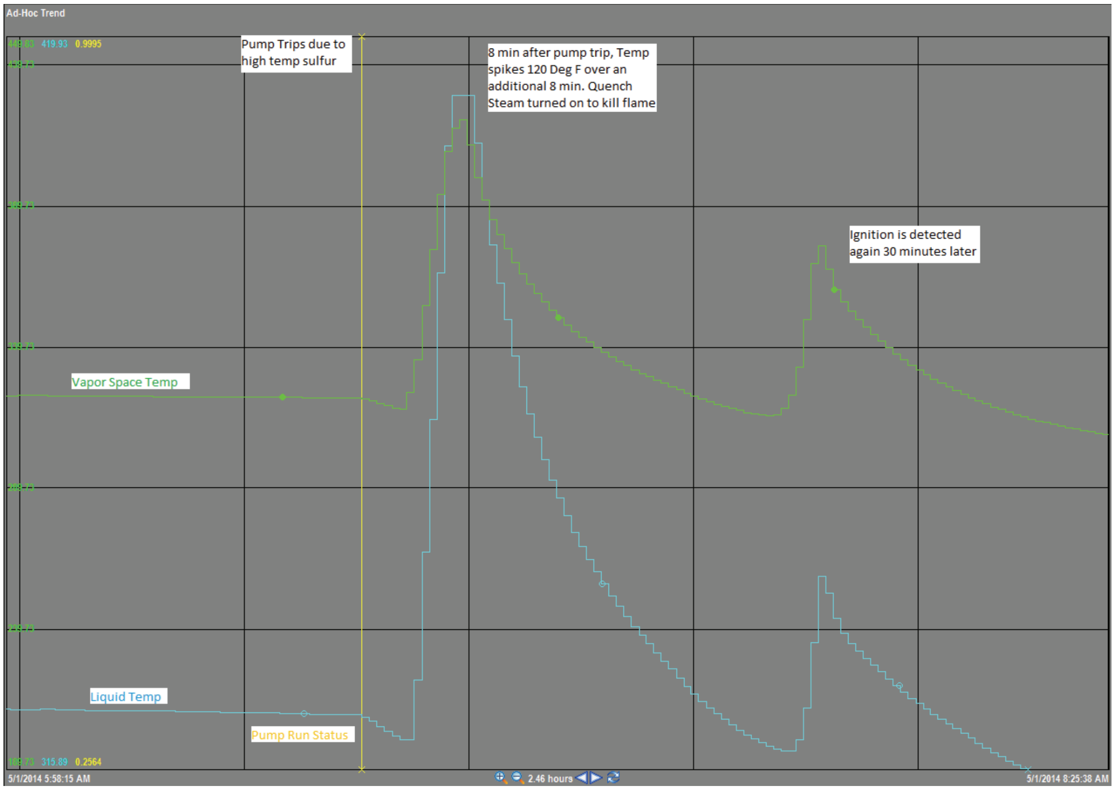

Figure 4. Sulfur Pit Fire DCS Temperature Data

Owner No. 2 provided the piping isometric for the steam line. Hydraulic calculations were completed for the steam based on the steam header pressure, the one-quarter open ball valve, and information from the piping isometric. The flow of the steam was calculated to be 891 lb/hr. The analysis shows that the steam flow only achieves about 10 percent of sonic velocity in the upsized 3 inch section of pipe near the steam line exit into the sulfur pit. The total volume of the sulfur pit is 11,115 ft^3. Calculating the steam rate to sulfur pit volume ratio shows the steam rate this owner used was 0.13 lb/min per 100 ft^3 of total sulfur pit volume. This rate likely was successful in extinguishing the initial sulfur fire in the sulfur pit when this rate was used for only about 2 minutes. The owner did experience a second fire 30 minutes later, but it was likely a re-ignition event. The authors did not calculate a steam rate for the second event because the operators said they only cracked the valve open slightly for 1 minute. Therefore, the steam rate fed the second time was less than the first rate shown above. The steam rate above is 19 times less than (or about 5 percent of) the current NFPA 655-specified value of 2.5 lb/min per 100 ft^3.

The rate discussed above of 0.13 lb/min per 100 ft^3 is practically the same value as listed in Table 1 of Section 2.8 regarding a statement made in substantiation of changes to the 2001 edition of NFPA 655, namely, that, if steam is injected at the surface of the sulfur, 4 ft^3/min per 100 ft^3 of enclosure volume would be satisfactory (4 ft^3/min per 100 ft^3 is equal to 0.14 lb/min per 100 ft^3).

It is difficult to accurately determine the resistance coefficient (K) for a partially opened ball valve without having true flow test data from the manufacturer of the actual ball valve. The authors determined that with a completely open full port ball valve (K values are available), the flow of steam would only increase to 2,779 lb/hr. The velocity at this rate was still only 29 percent of sonic velocity in the 3 inch section near the sulfur pit roof. The maximum flow of steam possible with the existing piping configuration is 2,779 lb/hr. Calculating the steam rate to sulfur pit volume ratio shows the maximum steam rate this owner could possibly feed, assuming a completely open ball valve, would be 0.41 lb/min per 100 ft^3 of total sulfur pit volume. This number is more than 3 times the estimated rate with the ball valve only one-quarter open. However, this steam rate is still 6 times less than (or about 16 percent of) the current NFPA-655 specified value of 2.5 lb/min per 100 ft^3.

Owner No. 3 experienced a sulfur pit fire in one sulfur pit in December 2013. That fire was the first known sulfur pit fire in the 21 years of operation of that unit. This owner provided data on how the sulfur pit fire was extinguished. The sulfur pit in question is 12'-0" W x 36'-6" L x 8'-0" D and has a single 2 inch steam line from the header that branches into three separate 2 inch lines, each of which feeds a 3 inch connection on the roof of the sulfur pit. The three connections on the sulfur pit roof feed the vapor space in the sulfur pit. The sulfur pit is a typical concrete pit that is completely enclosed, with one air inlet line and one air exit line that feeds an ejector. The steam driven ejector sweeps air through the vapor space of the sulfur pit and discharges to an incinerator. The owner stated that their written procedure for a sulfur pit fire is to open the 2 inch valve in the steam line 100 percent and keep the steam on for at least 15 minutes. The owner reported that, when troubleshooting high incinerator stack SO_2 emissions, they reduced the motive steam flow to the ejector, and almost immediately (less than 5 minutes) the incinerator stack SO_2 emissions returned to normal. By temporarily reducing the motive steam flow to the ejector, the ejector pulled less air through the sulfur pit, and the fire extinguished itself. No steam flow was required for this particular sulfur fire.

5.3 Sulfur Tank Fires

Owner No. 4 experienced a few sulfur tank fires. This owner provided data on how the sulfur tank fires were extinguished. The sulfur tank in question is 20'-0" Dia x 32'-0" H and has a 4 inch steam line from the header that feeds four 2 inch connections on the roof of the sulfur tank. The sulfur tanks are typical carbon steel tanks with a fixed roof and with multiple air inlet lines around the periphery of the roof and one center air exit line that vents to the atmosphere. The owner reported that, when they noticed a fire in the sulfur tank, they opened the steam 4 inch ball valve about one-quarter. The steam was left flowing for a period of 30 minutes and then the flow was stopped. The owner stated that they noticed the temperature in the tank decreased after 5 to 10 minutes, but they kept the steam on for 30 minutes to be sure the fire was completely extinguished.

The authors completed hydraulic calculations for the steam based on the steam header pressure, the one-quarter open valve, and information regarding the piping routing. The flow of the steam was calculated to be 10,840 lb/hr. The analysis showed that the steam flow achieves only about 60 percent of sonic velocity in the downsized 2 inch sections of pipe at the nozzles on the sulfur tank. The total volume of the sulfur tank is 123,150 ft^3. Calculating the steam rate to sulfur tank volume ratio showed the steam rate this owner has been using is 0.15 lb/min per 100 ft^3 of total sulfur pit volume. The owner reported successfully extinguishing the sulfur fire in the sulfur tank with this rate when the steam flowed for 30 minutes (fire was likely out in 5 to 10 minutes). This rate is 17 times less than (or about 6 percent of) the current NFPA 655-specified value of 2.5 lb/min per 100 ft^3. The owner reported that no damage was experienced in the sulfur tank by this fire, because it was likely extinguished in 5 to 10 minutes.

It is difficult to accurately determine the resistance coefficient (K) for a partially opened valve without having true flow test data from the manufacturer of the actual valve. The authors determined that with a completely open full port valve (K values are available), the flow of steam would only increase to 14,836 lb/hr. The velocity at this rate was still only 80 percent of sonic velocity in the 2 inch section of pipe at the nozzles on the sulfur tank roof. The maximum flow of steam possible with the existing piping configuration is 14,836 lb/hr. Calculating the steam rate to sulfur pit volume ratio shows the maximum steam rate this owner could possibly feed, assuming a completely open valve, would be 0.20 lb/min per 100 ft^3 of total sulfur pit volume. This number is not substantially different from the estimated rate with the valve only one-quarter open.

Owner No. 4 reported that fires had occurred in sulfur tanks at another location, but it had been 10 years or more since the last one. For this site, when a fire occurred steam valve(s) would be opened for a period of 20 to 30 minutes.

6.0 Computational Fluid Dynamics Modeling of a Sulfur Pit

A CFD model of the first sulfur pit described in Section 5.2 was created. The CFD model was set up to determine concentrations of oxygen and steam as well as the velocities throughout the model. The model did not include the effects of actual combustion of oxygen with sulfur. Therefore, all changes in oxygen concentration are a direct result of dilution of the oxygen with steam and exhausting the oxygen-containing air from the sulfur pit through the ejector suction line and backward through the air intake line. All reported oxygen concentrations are, therefore, conservative, and the actual values would be lower because of the consumption of oxygen by combustion of sulfur. Two flow conditions were considered with the model: a current configuration model and a model that considered a relocation of the steam inlet. It should be noted that the disturbance of the sulfur's surface by possible high-speed jets, which would result in more sulfur available for a pit fire, was not considered in these analyses.

As has been shown in a previous publication by one of this paper's authors(4), the following steps are involved in all CFD analyses:

- Selection and construction of computational domains.
- Development of computational grid.
- Selection of domain physics.
- Application of boundary conditions.
- Solution.

The following subsections detail how each of these steps was implemented for the CFD analyses, the results and general discussion from the analyses.

6.1 Selection and Construction of Computational Domains

The model was based on the overall internal dimensions of the sulfur pit, along with the dimensions of the air inlet and ejector suction lines. The overall domain for both models included the pit vapor space at a 45 percent fill level. Figure 5 shows the three geometric domains created for the analyses, the main pit space (steel blue light, 40 percent transparent) and the two abandoned sparger boxes (turquoise green).

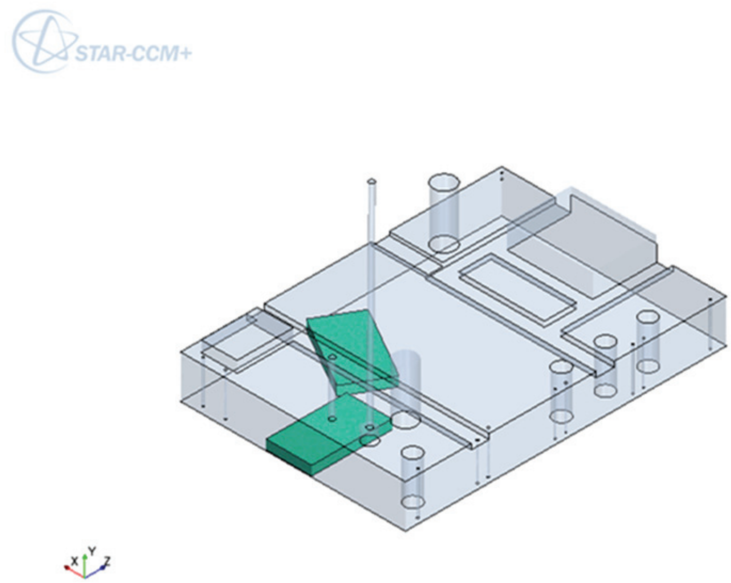

Figure 5. Domains Used for CFD Analyses

6.2 Development of Computational Grid

The computational grid was constructed using Star-CCM+'s automatic polyhedral mesher with wall prism layers enabled. The final computational grid contained 1,001,116 cells and is shown on Figure 6.

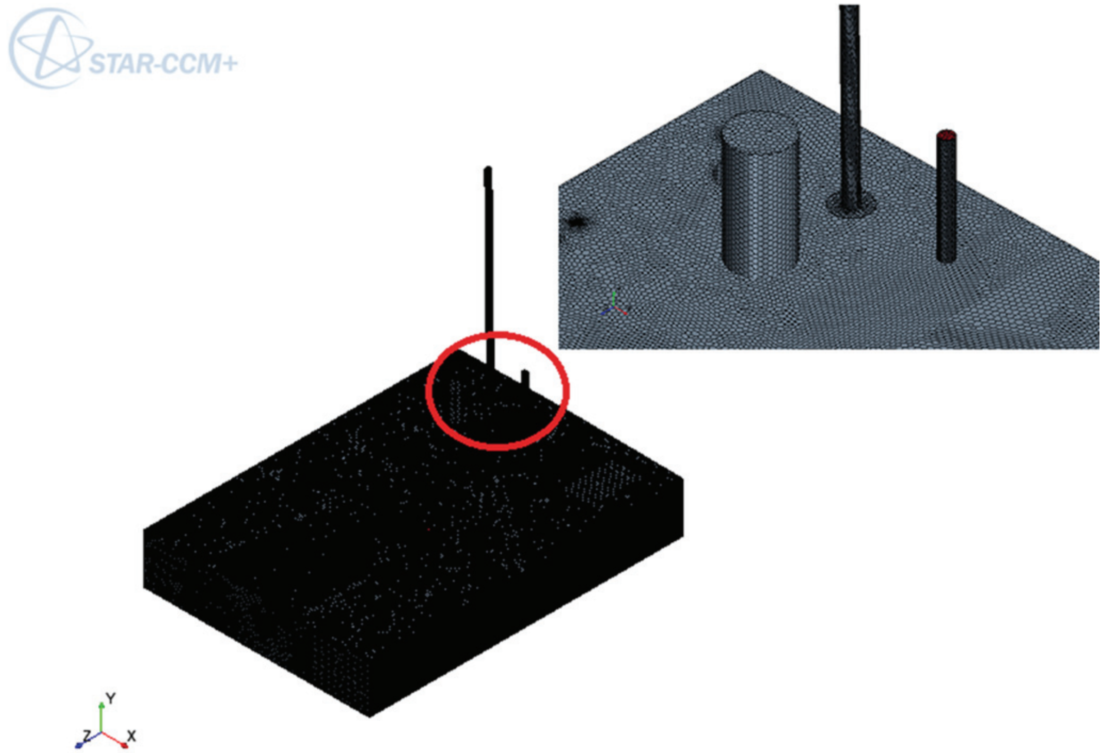

Figure 6. Computational Grid Developed for CFD Analyses

6.3 Selection of Domain Physics

The following physics models were enabled for the analyses:

- Space – 3-dimensional.
- Time – Implicit unsteady.
- Material – Multispecies, gas (H_2S, H_2O, O_2 and N_2).
- Equation of state – Ideal gas.
- Turbulence - RANS, Realizable k-ω, All y+ Wall Law.
- Segregated fluid temperature.
- Gravity (-9.81 m/s in y-direction).

6.4 Selection of Boundary Conditions

Figure 7 shows the boundary conditions applied for the current configuration analysis. The steam inlet is denoted by the dot in the red circle, and the air inlet is denoted by the top of the pipe in the blue circle. The ejector outlet is shown in yellow. The steam inlet was defined as a mass flow inlet, with an inlet flow rate of 2,456 lb/hr. The steam inlet was sized to have an inlet velocity of 0.7 Mach, as sonic flow would require considerably more computational resources to solve. The air inlet was defined as a stagnation inlet at atmospheric pressure. The ejector was defined as a velocity outlet with a flow rate based on the design data sheet value of 350 actual cubic feet per minute (acfm).

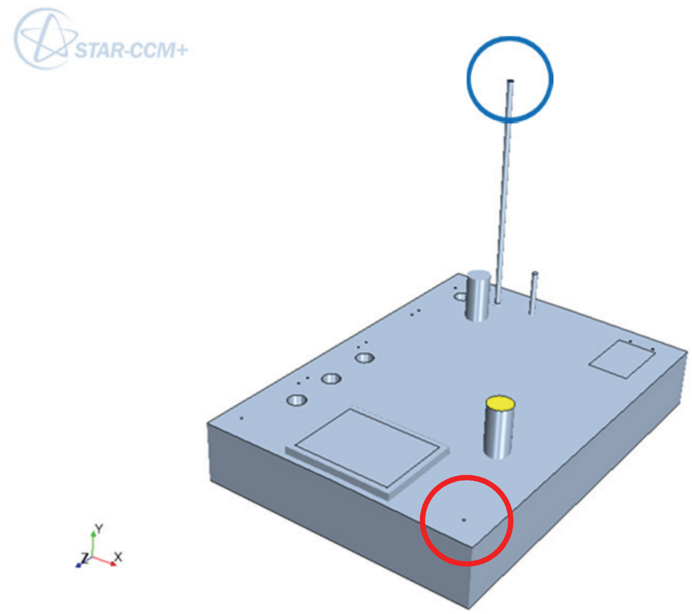

Figure 7. Boundary Conditions Applied for Current Configuration Analysis

Figure 8 shows the boundary conditions applied to the steam inlet moved model. The air inlet is circled in blue, the steam inlet is circled in red and the ejector outlet is circled in yellow. Since this model was originally run with a pressure boundary at the ejector outlet, there is a contraction to prevent backflow. The same values listed above were applied to this model.

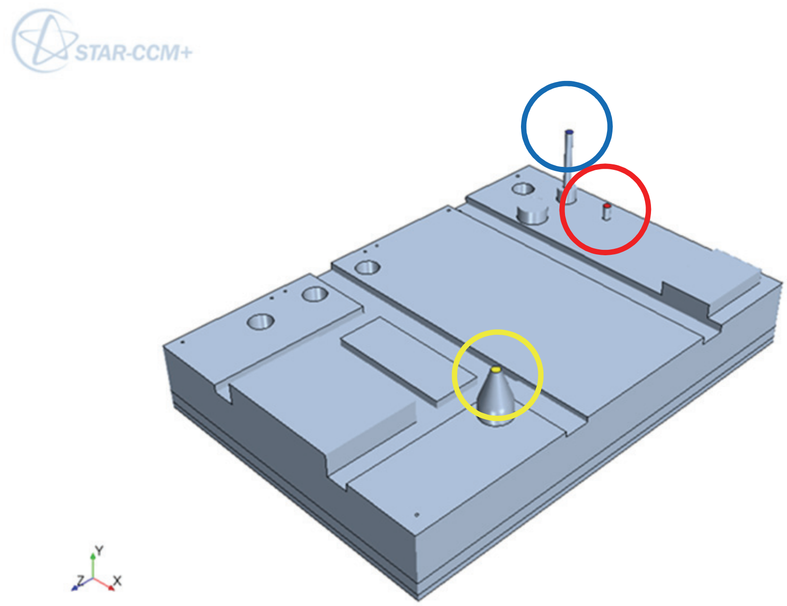

Figure 8. Boundary Conditions Applied to Steam Inlet Moved Model

Figure 9 shows the common boundary conditions applied to the models. The unheated sparger walls are shown in magenta. The heated sulfur level is shown in yellow, and the sulfur rundowns are shown in white. Both the sulfur level and rundowns were set to a defined temperature of 315.5F (157.5C).

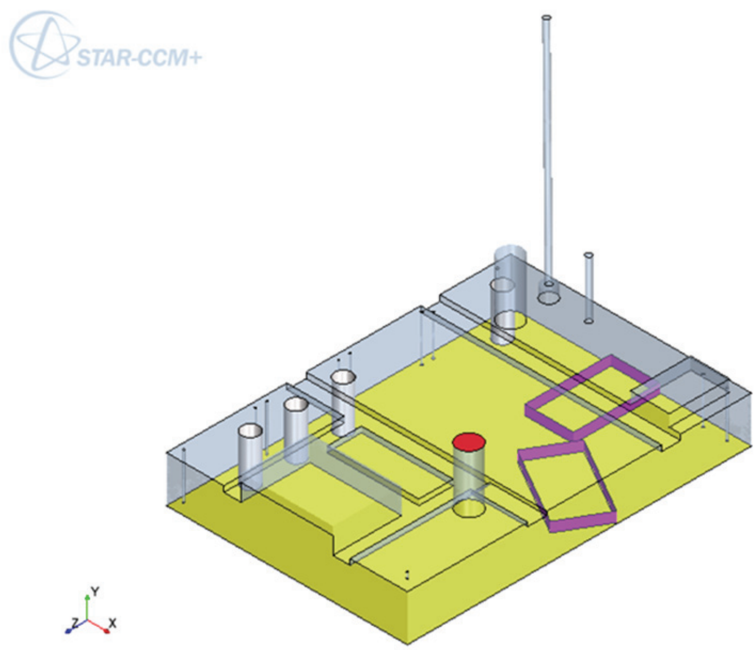

Figure 9. Common Boundary Conditions Applied to Models

6.5 Solution

The transient solutions were conducted on a high-performance computing cluster (HPCC) using 120 processors. An adaptive time-step was used so that the maximum convective Courant number was below 1 for each time-step.

6.6 Results

The following subsections detail the results for the two configurations that were analyzed.

6.6.1 Current Configuration Results

The maximum and the average oxygen concentration in the sulfur pit vapor space versus time, for the current configuration case, are plotted on Figure 10. As can be seen on the figure, at the end of the 15 minute steam period, the maximum oxygen concentration in the sulfur pit vapor space is about 0.24 mole%. However, the average oxygen concentration is only about 0.015 mole%. The average oxygen concentration is 16 times lower than the maximum value, indicating that there are very few locations within the vapor space of the sulfur pit with oxygen concentrations near the maximum. The very low average oxygen concentration supports the field data that the sulfur pit fire is extinguished before the steam is stopped after 15 minutes. The actual oxygen concentration in the sulfur pit vapor space will be even lower than indicated on the figure because the CFD model does not account for the oxygen consumed by the sulfur fire.

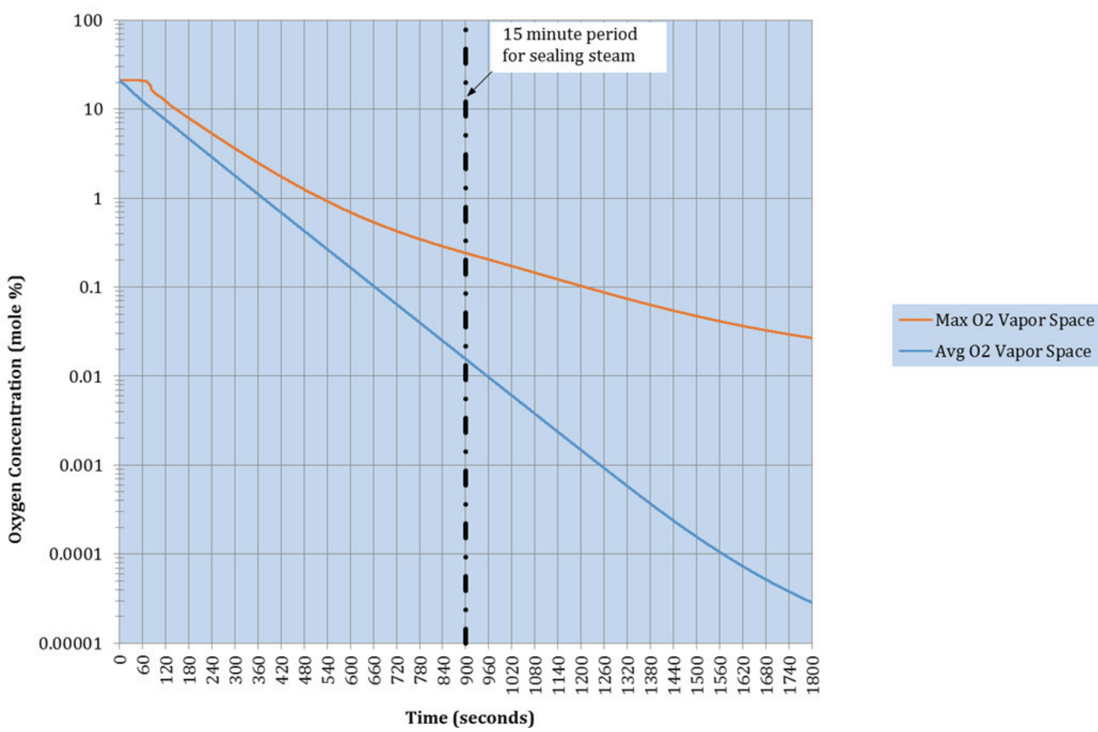

Figure 10. Oxygen Concentrations in Sulfur Pit Vapor Space

Data were also extracted from the CFD model to show the maximum oxygen concentration in the sulfur pit air inlet line and in the suction line to the ejector. These data, along with the maximum oxygen and the average oxygen concentration in the sulfur pit vapor space, are plotted on Figure 11. The figure shows that the maximum oxygen concentration in the ejector suction line immediately starts to decrease after the steam is started. This is as expected since the steam is fed into the sulfur pit near the nozzle on the sulfur pit that feeds the ejector suction. The figure shows that the maximum oxygen concentration in the air inlet line remains at the ambient value of 21 mole% for about 15 seconds as the steam passes through the vapor space of the sulfur pit to reach the air inlet on the far side of the sulfur pit. After about 15 seconds, the maximum oxygen concentration in the air inlet line begins to decrease (as steam begins flowing backward through the air inlet line) and basically matches the maximum oxygen concentration in the ejector suction line after 90 seconds. The maximum oxygen concentration in the ejector suction and the maximum oxygen concentration in the air inlet line practically lie on top of the line for the average oxygen concentration in the sulfur pit vapor space, making it difficult to distinguish the three lines in the figure. Although not shown on the figure, the average oxygen concentration and the maximum oxygen concentration in the ejector suction line do not differ by more than 1 percent after about 25 seconds of elapsed purge time. The fact that the maximum oxygen concentration in the ejector suction line, air inlet line and the vapor space are basically the same value indicates that the sulfur pit vapor space is fairly well mixed and venting the same concentration from both ends of the sulfur pit.

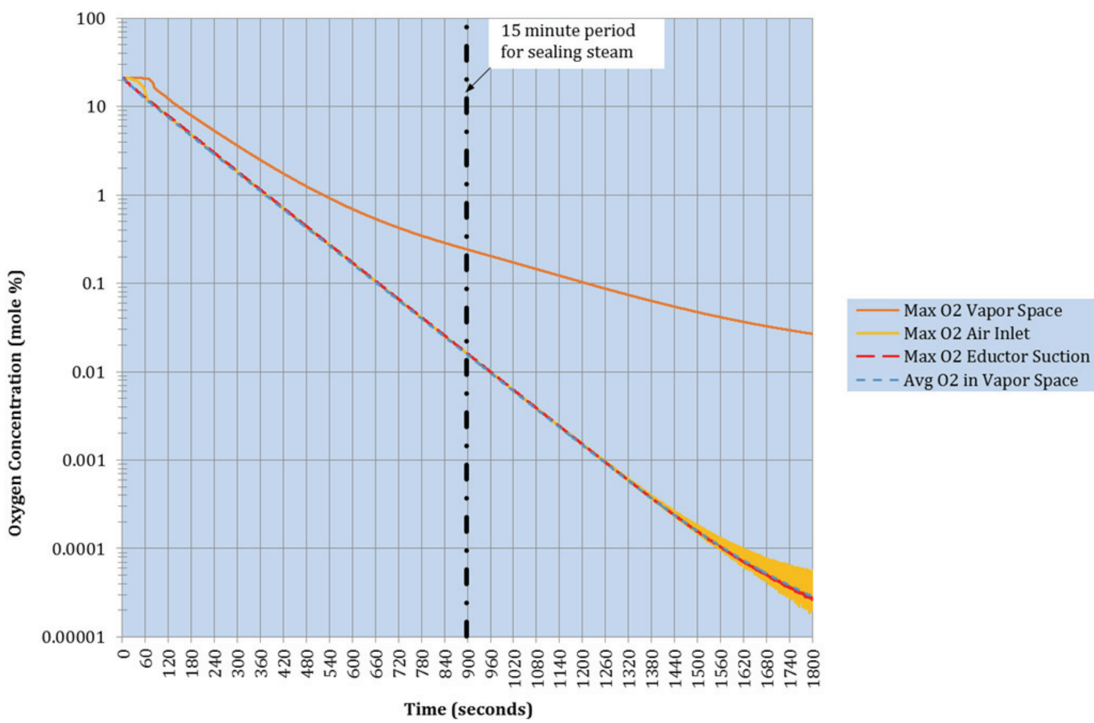

Figure 11. Oxygen Concentrations in Sulfur Pit Vapor Space, Air Inlet and Ejector Suction

6.6.2 Relocated Configuration Results

The maximum and the average oxygen concentration in the sulfur pit vapor space versus time for the current steam location, and with the steam relocated near the air inlet line are plotted on Figure 12. As can be seen on the figure, relocating the steam inlet near the air inlet line significantly lowers the average and maximum oxygen concentration in the sulfur pit vapor space compared to those same parameters with the steam at its existing location. The model was stopped after about 12 minutes (720 seconds) because the oxygen concentrations were so low. At the end of 12 minutes, the maximum oxygen concentration in the sulfur pit vapor space was less than 0.0005 mole%, and the average oxygen concentration in the sulfur pit vapor space was less than 0.00003 mole%. Again, the actual oxygen concentration in the sulfur pit vapor space will be even lower than indicated on the figure because the CFD model does not account for the oxygen consumed by the sulfur fire. It is obvious from the data that introducing the steam near the air inlet line will seal the air inlet line quicker and thereby drive the oxygen concentration in the vapor space to low levels much faster than locating the steam on the far side of the sulfur pit near the ejector suction line. The data indicate that by relocating the steam feed to near the air inlet line, after about 5 minutes the maximum and average oxygen concentrations in the sulfur pit vapor space can be decreased to values similar to the values achieved in 15 minutes with the existing steam location.

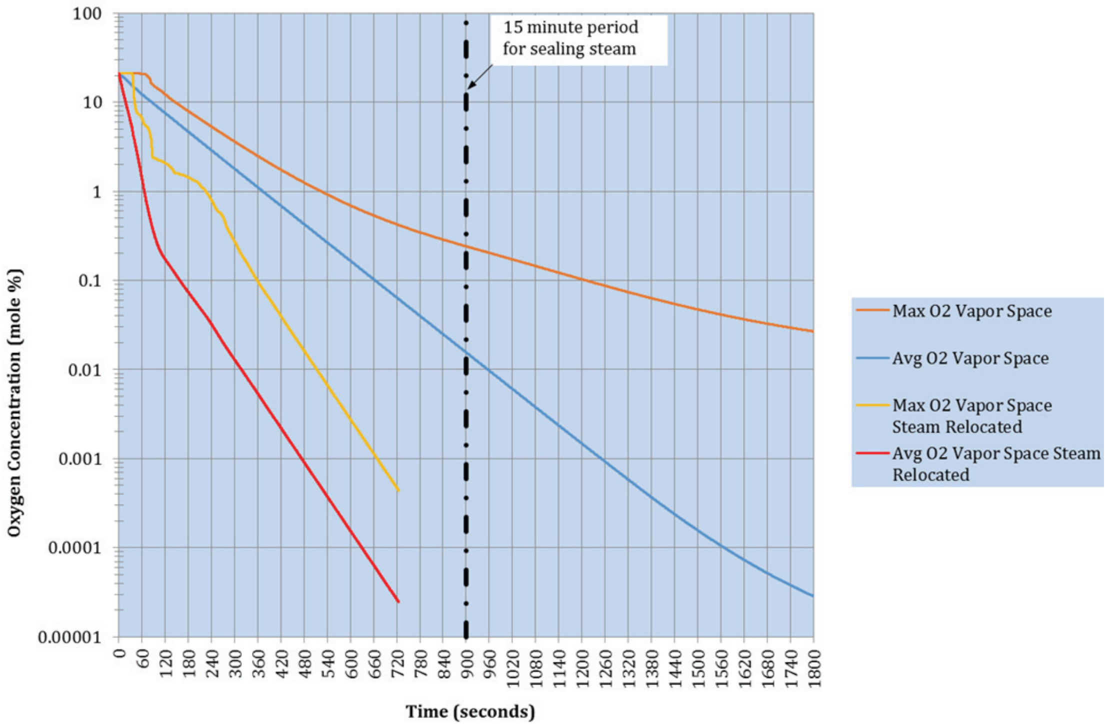

Figure 12. Oxygen Concentrations in Sulfur Pit Vapor Space with Steam Relocated Near Air Inlet

6.6.3 Velocity Streamline Comparisons

Figure 13 shows the velocity streamlines for the current configuration analysis. As can be seen, the high-speed jet impinges on the liquid sulfur surface and then travels around the perimeter. In this flow condition, little purging is occurring in the center of the pit, which results in the longer purge times shown on Figure 10 through Figure 12.

Figure 14 shows the velocity streamlines for the steam inlet relocated configuration. As can be seen in this case, a large portion of the steam enters the pit and is immediately exhausted through the air inlet. This will result in rapidly stopping all O_2 flow into the pit.

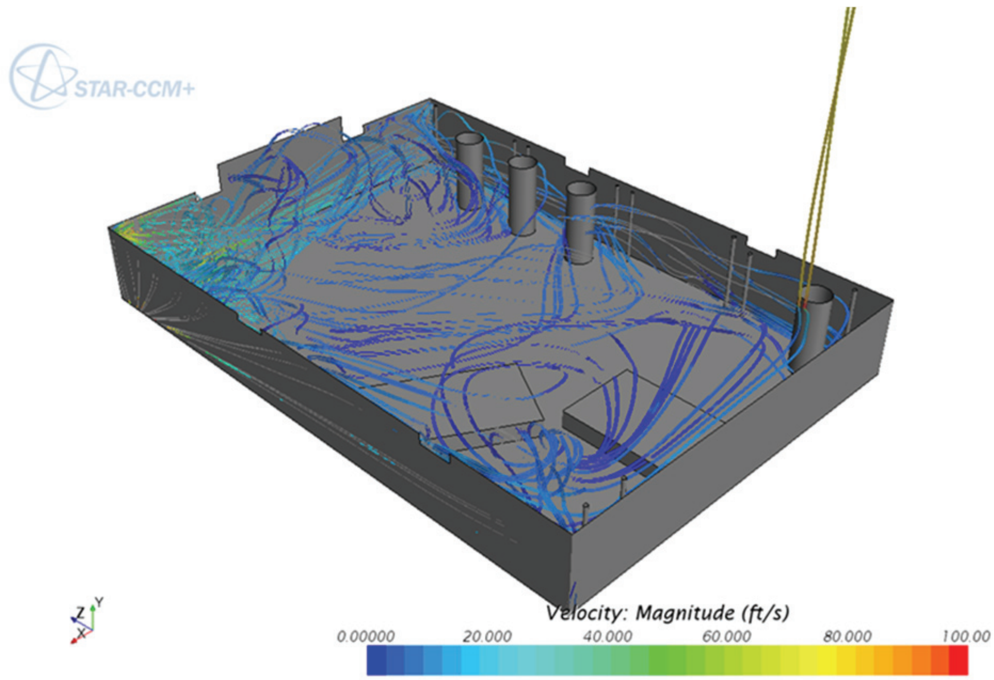

Figure 13. Velocity Streamlines for Current Configuration Analysis

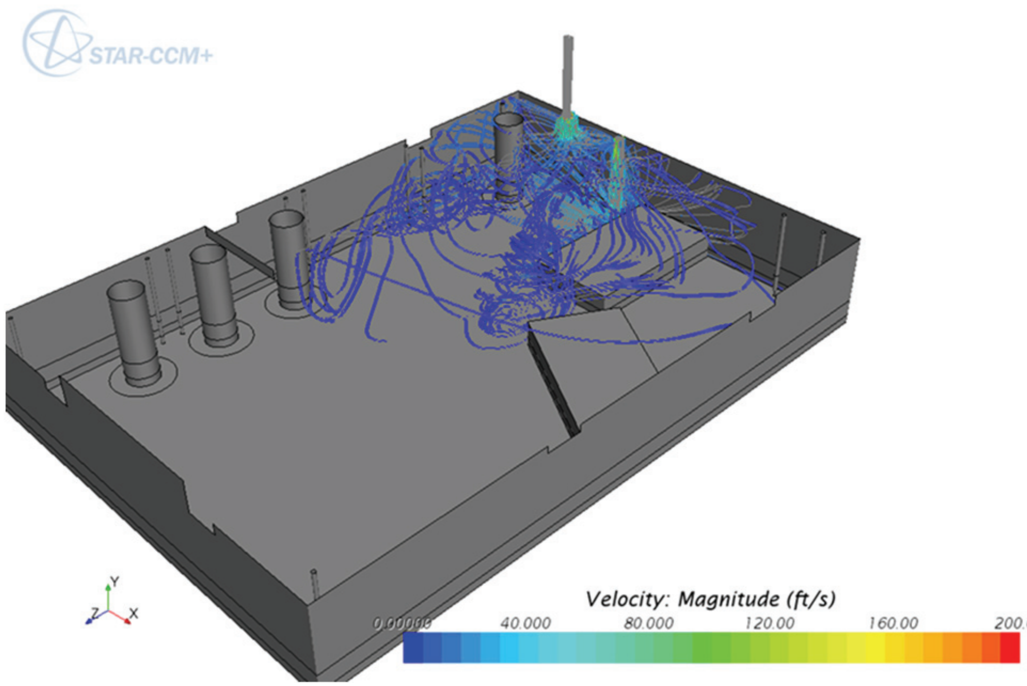

Figure 14. Velocity Streamlines for Moved Steam Inlet Case

6.7 General Discussion

Additional CFD studies are needed to verify the impacts of locating the steam connection near the air inlet lines for other sulfur pit configurations. However, it is logical to conclude that by locating the steam near the air inlets, the steam will quickly seal the air inlets and thereby stop ingress of oxygen that would maintain the sulfur fire. It is also logical to assume that locating the steam near the air inlets rather than near the ejector suction allows more time for the ejector to remove the existing sulfur pit vapor space gas mixture (air, sulfur vapor, H_2S, SO_2) before the mixture begins to be diluted with steam. Therefore, the oxygen is removed from the sulfur pit vapor space more quickly.

Additional CFD studies are also needed to confirm how the oxygen concentration is reduced for designs where the sulfur pit ejector is tripped off on the basis of the sulfur pit vapor space temperature.

Porter McGuffie Inc. estimates that it would take approximately 3 man-days to set up a new sulfur pit model and execute one set of conditions. Each additional set of conditions would require about 1.5 man-days to execute.

7.0 Potential Rapid Sealing Steam Rate

On the basis of the data collected and the analysis completed in Sections 5.0 and 6.0, it appears that a steam rate of 1.0 lb/min per 100 ft^3 would be sufficient to extinguish sulfur fires in enclosed sulfur tank and sulfur pits. This value is still higher (more conservative) than the rates collected from any of the owners that provided data. It is possible that an even lower steam rate could be used successfully, but not enough data could be collected to justify a lower rate.

It is apparent that industry has successfully extinguished fires in sulfur tanks and sulfur pits without using the NFPA 655 snuffing steam rate recommendation but by using a lower steam rate that effectively seals the enclosures, prevents air ingress and extinguishes fires safely.

The authors completed evaluations of the sulfur tank vent systems for six existing sulfur tanks when steam was fed at a rate of 1.0 lb/min per 100 ft^3 of volume. The sulfur tanks evaluated were the same sulfur tanks that were evaluated in Section 3.0. Table 4 shows the same data presented in Table 2 in Section 3.0, except that two additional rows (shown in yellow) have been added to the bottom to show the built-up back pressure with steam flowing at a rate of 1.0 lb/min per 100 ft^3 and how the volume of steam compares to the original air sweep rate.

As can be seen in Table 4, the steam rate of 1.0 lb/min per 100 ft^3 ranges from about 12 to 80 times the original sweep air rate. This steam rate results in a built-up back pressure within the sulfur tank of 0.04-9.1 inch WC. This built-up back pressure would exceed the actual design pressure of two out of six of the sulfur tanks, as shown by the red text in Table 4. However, if the sulfur tanks had been specified with a consistent design pressure of -3 / +10 inch WC, then the steam rate of 1.0 lb/min per 100 ft^3 could be vented from the sulfur tanks without exceeding the design pressure and without needing to modify the venting systems on the sulfur tanks.

Table 4. Existing Sulfur Tanks with Steam at 1.0 lb/min per 100 ft³ Compared to 2.5 lb/min per 100 ft³

	Tank A	Tank B	Tank C	Tank D	Tank E	Tank F
Dimensions	66-6" Dia x 35'-0" H	59-6" Dia x 48'-0" H	19'-8" Dia x 17'-9" H	14'-5" Dia x 16'-4" H	42'-8" Dia x 32'-10" H	47'-6" Dia x 24'-10" H
Volume, ft^3	138,500	148,635	5,800	2,833	48,885	49,435
Design Pressure, inch WC	-3 / +10	-1.5 / +2.5	-3 / +10	-3 / +10	-1.1 / +3.2	-0.9 / +3.5
Air Inlets	Six - 10"	Two - 16"	Three - 6"	Three - 6"	Six - 6"	Six - 6"
Air Outlet	One - 10"	One - 16"	One - 8"	One - 8"	One - 18"	One - 8"
Air Movement Method	Blower sucks air through tank and pushes through caustic scrubber	Natural draft 2 inlets, 1 outlet	Natural draft 3 inlets, 1 outlet	Natural draft 3 inlets, 1 outlet	Natural draft 6 inlets, 1 outlet	Natural draft 6 inlets, 1 outlet
Normal Op Pressure, inch WC	-0.05	-0.0031	-0.00005	-0.00008	-0.029	Unknown
Air Sweep Objective	<16% H_2S LFL, with 150 ppm(wt) H_2S in sulfur feed	<21% H_2S LFL, with 150 ppm(wt) H_2S in sulfur feed	<50% H_2S LFL, with 150 ppm(wt) H_2S in sulfur feed	<50% H_2S LFL, with 150 ppm(wt) H_2S in sulfur feed	<25% H_2S LFL, with 300 ppm(wt) H_2S in sulfur feed	Unknown
Pressure inch WC with steam at 2.5 lb/min/ 100 ft^3	59.3	50.8	1.05	0.23	8.1	29
Steam volumetric rate (@ 2.5 lb/min/100 ft^3) compared to sweep air rate	29 x	190 x	198 x	79 x	53 x	Unknown
Pressure inch WC with steam at 1.0 lb/min/ 100 ft^3	9.1	7.9	0.17	0.04	1.3	5.0
Steam volumetric rate (@ 1.0 lb/min/100 ft^3) compared to sweep air rate	11.7 x	76 x	79 x	32 x	21 x	Unknown

The authors evaluated the sulfur pit vent systems for five existing sulfur pits when steam was fed at a rate of 1.0 lb/min per 100 ft^3 of volume. The sulfur pits evaluated were the same sulfur pits that were evaluated in Section 3.0. Table 5 shows the same data presented in Table 3 in Section 3.0, except that two additional rows (shown in yellow) have been added to the bottom to show the built-up back pressure with steam flowing at a rate of 1.0 lb/min per 100 ft^3 and how the volume of steam compares to the original air sweep rate.

As can be seen in Table 5, the steam rate of 1.0 lb/min per 100 ft^3 ranges from approximately 4 to 12 times the original sweep air rate. This steam rate results in a built-up back pressure within the sulfur pit of 2.1 to 49 inch WC. The largest sulfur pit (total capacity of 60,665 ft^3) could reach a pressure of 366 inch WC (13.2 psig) if the covers did not lift. This particular sulfur pit has a large reduction in inlet line size, 8 inches down to 4 inches to feed into a flow meter. The flow reaches sonic velocity in this 4 inch diameter section, resulting in very high built-up back pressures. The built-up back pressure would exceed the pressure rating of the hatch covers on four out of five sulfur pits, as shown by the red text in Table 5. However, if the sulfur pits had been specified with precast concrete hatch covers instead of aluminum and a slight adjustment made in the air inlet line size, the steam rate of 1.0 lb/min per 100 ft^3 could likely be vented from the sulfur pits without exceeding the design pressure. It appears that to be able to vent a steam rate of 1.0 lb/min per 100 ft^3, the typical sulfur pit design pressure and sulfur pit vent system would require more modifications than those that would be required for typical sulfur tanks. However, it does appear possible to design a sulfur pit system to accommodate the lower steam rate of 1.0 lb/min per 100 ft^3. Additional engineering studies, including the use of CFD, may be appropriate to establish an even lower sealing steam rate for an existing sulfur pit.

Table 5. Existing Sulfur Pits with Steam at 1.0 lb/min per 100 ft³ Compared to 2.5 lb/min per 100 ft³

	Pit A	Pit B	Pit C	Pit D	Pit E
Dimensions	24'-0"W x 35'-0"L x 10'-6"D	47'-7"W x 72'-2"L x 17'-8"D	14'-0"W x 34'-0"L x 11'-0"D	13'-2"W x 49'-10"L x 9'-2"D	21'-0"W x 30'-0"L x 8'-0"D
Volume, ft³	8,820	60,665	5,236	6,015	5,040
Design Pressure, inch WC	-unknown / +9.5 set by precast concrete access hatch covers	-unknown / +0.54 set by aluminum hatch covers	-unknown / +9.6 set by precast concrete access hatch covers	-unknown / +14.2 set by precast concrete access hatch covers	-unknown / +0.42 set by aluminum hatch covers
Air Inlets	One - 6"	Two - 8"	One - 4"	One - 4"	One - 6"
Air Outlet	One - 6"	Two - 8"	One - 4"	Two - 3"	One - 6"
Air Movement Method	Ejector sucks air through air inlet and pushes to thermal reactor	Ejector sucks air through air inlets and pushes to thermal reactor	Ejector sucks air through air inlet and pushes to thermal reactor	Ejector sucks air through air inlet and pushes to incinerator	Ejector sucks air through air inlet and pushes to incinerator
Normal Op Pressure, inch WC	-0.22	-6.9	-1.2	-0.30	-0.22
Air Sweep Objective	<15% H_2S LFL, with 300 ppm(wt) H_2S in sulfur feed	<25% H_2S LFL, with 300 ppm(wt) H_2S in sulfur feed	<25% H_2S LFL, with 300 ppm(wt) H_2S in sulfur feed	Unknown	Unknown
Pressure inch WC with steam at 2.5 lb/min/100 ft³	57.8	50 psig if hatch covers do not lift, sonic velocity back through air inlets	266	230	21.4/17.6 (Note 1)
Steam volumetric rate (@ 2.5 lb/min/100 ft³) compared to sweep air rate	16 X	31 x	17 x	30 x	9.7 x
Pressure inch WC with steam at 1.0 lb/min/100 ft³	8.9	13.2 psig if hatch covers do not lift, sonic velocity back through air inlets	49	39	3.5/2.1 (Note 1)
Steam volumetric rate (@ 1.0 lb/min/100 ft³) compared to sweep air rate	6.4 x	12 x	6.9 x	12 x	3.9 x

Notes:

1. The second value listed is the built-up back pressure for this sulfur pit based on the ejector staying in operation. All other sulfur pits analyzed have an SIS that will trip ejectors when fire is detected.

8.0 Good Engineering Practice for Use of Sealing Steam

On the basis of the data collected for this paper and the analysis completed, the following points (not listed in any particular order) could be considered good engineering practice for sulfur tanks and sulfur pits to address extinguishing fires:

- Sulfur tanks should be designed with design pressure of at least -3 / +10 inch WC.

- Sulfur pits need to be carefully evaluated and designed to allow the chosen sealing steam rate to vent from the air inlets without lifting the hatch covers.

- The valve that is used to supply sealing steam to the sulfur tank or sulfur pit should be located at a safe location (typically at least 50 feet away) away from the sulfur tank or sulfur pit. The valve should be located near grade elevations, easily accessible and clearly marked.

- Sealing steam lines should contain a drip leg and steam trap ahead of the valve used by operators so that the line will remain warm and not collect condensate ahead of the valve. Feeding built-up condensate through the sealing steam line to the sulfur tank or sulfur pit when the steam valve is opened will result in a very large increase in pressure in the enclosure and possibly result in overpressuring the enclosure.

- Sealing steam should be fed near the air inlet lines to sulfur tanks or sulfur pits so that steam will quickly backflow out of the air intakes and prevent further oxygen ingress during a fire.

- Preliminary CFD results show that slowing the steam down (oversized inlet nozzle) prior to the entrance to the sulfur tank and sulfur pit may help limit agitation of the liquid sulfur surface and, thereby, reduce the amount of fuel that is available to burn in the vapor space. Additional CFD work is still needed to clarify the effect of the steam entrance velocity.

- Sealing steam systems that use rupture disks to prevent sulfur vapor from backing into the line, condensing and solidifying should have a separate steam supply valve for each rupture disk instead of multiple rupture disks fed from one steam supply valve. An alternative to having separate steam supply piping/valve for each rupture disk would be to oversize the supply pipe so that the vast majority of the pressure drop is across the section that contains the rupture disks. A careful hydraulic study would need to be performed to ensure that even if one rupture disk burst, there would still be enough pressure in the steam supply line to burst all remaining rupture disks.

- If rupture disks are not used to help prevent plugging in the steam supply system near the connections to the sulfur tank or sulfur pit, the open sealing steam line should be tested on a routine basis (at least monthly) by passing steam through the system to ensure the steam supply lines and nozzle are free of solidified sulfur.

- The location of the thermocouple that is used to detect a fire in a sulfur pit needs to be evaluated carefully. For configurations that intend to leave the ejectors operating through a fire event, locating the temperature indicator in the ejector suction line is likely better than locating it in the sulfur pit vapor space. At least with the temperature indicator in the ejector suction line, the thermocouple will sense an "average" temperature of the gas passing through the sulfur pit vapor space rather than a point temperature at a single location within the vapor space. For systems that will trip the ejectors during a fire event, it is suggested that more than one thermocouple be used as input to the SIS. One thermocouple should be close to the ejector suction line to sense the temperature of the vapor mixture as it exits the sulfur pit, and other thermocouples should be located in suspected low velocity areas where temperature increases may be noticeable. A CFD model could be used to help place the thermocouples in optimum locations.

- A CFD model can be used to evaluate flow patterns in the sulfur tank or sulfur pit vapor space both during normal operation and during sealing steam injection. The results of the CFD model can help the designer to determine proper placement of air inlet nozzles, vent nozzles, thermocouples and sealing steam injection locations.

9.0 Conclusions

The following conclusions can be drawn from the results of this paper and the authors' experiences while preparing this paper:

1. The vent systems on typical sulfur pits and sulfur tanks (for storage of molten sulfur) must be carefully designed to ensure that the proper environment is maintained within the vapor space to prevent flammable mixtures from forming.

2. For sulfur pits and sulfur tanks that use an air sweep system to prevent flammable mixtures from forming, the enclosures are typically operated under a slight vacuum to prevent stray emissions of H_2S and sulfur vapor. This vacuum level is set according to the required air sweep rate and air inlet line sizes. The vacuum level needs to be set so that the buoyancy effects of the heated air intake lines are accounted for, and for sulfur tanks, the vacuum level should consider the effects of wind blowing across the outer surface of the tank.

3. It is extremely difficult and impractical to design the air sweep systems for sulfur tanks and sulfur pits without exceeding the design pressure of the enclosure if they also must be able to vent the current NFPA 655 snuffing steam requirement of 2.5 lb/min per 100 ft^3 of total volume.

4. It appears that a sealing steam rate of less than 1.0 lb/min per 100 ft^3 of total volume has been successful in extinguishing numerous fires in sulfur tanks and sulfur pits.

5. New sulfur tanks and sulfur pits can be designed to vent a sealing steam rate of 1.0 lb/min per 100 ft^3 of total volume without major changes to the typical design parameters already being followed by a number of companies. Typical sulfur pits may need more changes than typical sulfur tanks; however, the changes required are not onerous.

6. Sealing steam should be fed into the sulfur tank or sulfur pit for a minimum of 15 minutes or until the temperature has returned to near normal. If the sulfur does not cool down before the sealing steam is stopped and the air sweep system reestablished, reignition can occur.

7. The sealing steam will almost immediately seal the air intake(s) to prevent further oxygen ingress and will begin to purge oxygen out of the enclosure. The actual operating vapor space volume in the sulfur tank or sulfur pit will only affect the time it will take for the fire to be fully extinguished.

10.0 Recommendations

The following recommendations can be drawn from the results of this paper and from the authors' experiences while preparing this paper:

1. The authors recommend that NFPA modify the sealing method in NFPA 655, *Standard for Prevention of Sulfur Fires and Explosions* (current edition: 2012), Chapter 5, Handling of Liquid Sulfur at Normal Handling Temperatures, Section 5.5, Fire Fighting, to recommend a sealing steam rate of 1.0 lb/min of steam per 100 ft^3 of volume.

2. The authors also recommend that the good engineering practice points defined in Section 8.0 be considered and implemented on sulfur tanks and sulfur pits as applicable.

11.0 Acknowledgements

The authors wish to thank the efforts of all the sulfur production specialists that were contacted for data for this paper. The authors also thank Lon Stern (Stern Treating & Sulfur Recovery Consulting, Inc - lhstern@earthlink.net) for posting their request for data on the Amine Best Practices Group Data Exchange Network.

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