AM-17-60   # Characteristics of Sour Flare Gas Streams that Impact H_2S Treatment Technologies

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CHARACTERISTICS OF SOUR FLARE GAS STREAMS
THAT IMPACT H₂S TREATMENT TECHNOLOGIES

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Abstract

Many refineries have flare gas streams that contain sulfur compounds, especially H_2S, which need to be removed from the gas so that it can be flared or used as fuel gas elsewhere in the plant. Different technologies can be used to remove the H_2S from flare gas streams including amine treating, caustic scrubbing, solid scavengers, and liquid scavengers. In this paper, a brief overview of these technologies is presented first followed by in-depth discussions on how the characteristics of the flare gas stream impact the design and performance of the different H_2S treating technologies. For example, it is critical that a good design basis is established since the H_2S treating equipment usually must be sized to handle the maximum flare gas flow rates, H_2S concentrations, and H_2S loadings as well as typical operating conditions. Examples of the variation of these parameters observed in the field and some of the criteria used to define an appropriate design basis are provided. The effect of operating temperature and pressure on the various H_2S treatment processes is also discussed. The effects of key species in the flare gas stream (carbon dioxide, ammonia, hydrogen, oxygen, water, hydrocarbons, and H_2S) are also described. Descriptive examples and illustrations of how each of these parameters impacts the H_2S removal technologies are provided. This will help refiners better understand when certain H_2S removal processes are more applicable so that the most appropriate technology can be selected.

1.0   Introduction

At the 2016 annual AFPM meeting, Trimeric Corporation presented a paper on alternatives to flare gas recovery for sour gas (McIntush, et al., 2016). The previous paper compared the performance and relative economics of using different H_2S treating processes instead of flare gas recovery for an example refinery flare gas. This paper is a follow-on to that 2016 paper and focuses on the important flare gas characteristics and design basis requirements that refiners should consider when evaluating H_2S treating processes.

In the treatment of sour gas streams different technologies are often considered depending upon the amount of H_2S that needs to be removed, and H_2S removal applications are generally characterized by the amount of H_2S that is removed from the gas stream. H_2S removal technologies that can be used over the range of possible industrial applications include but are not limited to: non-regenerable solid and liquid H_2S scavengers, caustic scrubbing, liquid redox and other regenerable liquid chemical processes, amine treating, and numerous others. Depending on the situation at the refinery, other site-specific alternative H_2S removal processes could also be considered, such as ammonia scrubbing.

Sulfur load is not the only gas characteristic that affects the selection of H_2S treatment technology. For instance, the use of caustic scrubbing can be affected by the CO_2 content of the sour gas because CO_2 also reacts with the caustic and can significantly increase caustic consumption and costs. The presence or lack of water in the flare gas stream can also impact the longevity of some solid scavengers. Oxygen in the flare gas stream increases degradation of many amine treating systems. These are just a few examples of the need to understand the important characteristics of the sour flare gas stream when selecting an H_2S removal technology. It is also critical to develop a sound design basis upon which to evaluate the performance of the technologies; flow rate, temperature, pressure, and composition of flare gas streams can vary widely over time. Thus, the characteristics of the flare gas stream and design basis have a significant impact on the economics (capital and operating costs) and performance of the H_2S treating technology.

This paper first discusses the importance of developing a representative design basis to be used for evaluating the H_2S treatment technologies for a hypothetical refinery case. Then, some of the significant flare gas characteristics that impact performance of four different H_2S treating technologies are reviewed: amine treating, caustic scrubbing, solid scavengers, and liquid triazine scavengers. Although there are other technologies that could be used to remove H_2S from sour flare gas, these technologies are considered to be representative of those used in the refining industry. Background information is provided for these technologies so that the impact of important flare gas characteristics can be understood. The flare gas characteristics that are reviewed for each technology include typical sulfur loads, the effect of temperature and operating pressure, impacts of various flare gas components, and other important refinery site considerations.

2.0   Design Basis Selection

It is important to understand the regulatory drivers when establishing the design basis for the flare gas. The main driver is typically the need to meet the NSPS Ja limit that sets the treated gas H_2S concentration at 162 ppmv H_2S. The design basis should include a safety factor to this limit to ensure that the regulatory requirement can be met over most conditions. A target design value sometimes used is 100 ppmv H_2S. It is also necessary to understand if the permit for the refinery allows for any excursions in H_2S concentration or other factors that need to be taken into account when establishing the design basis.

Historical data for the flare gas stream should be reviewed carefully to establish a representative design basis for the flare gas application since the stream characteristics can change widely over time. It may be possible to delete some data from consideration that might narrow the design range. Data from extremely unusual occurrences or any occurrence that exempts the refinery from the regulation limit may be ignored. The remaining data set can then be used to establish the design basis for the work.

Some of the important flare gas characteristics to track are the gas flow rate, temperature, pressure, and composition. Figure 1 shows a hypothetical example of the variability in the flare gas flow rate and H_2S concentration for a refinery flare gas stream. In this case, the average flare gas flow rate was on the order of 5.5 Mscfh but there were times when the gas rate increased to as high as 20 Mscfh. For this case, it was determined that it would be necessary to design the H_2S treating technology to cover the entire range in gas flows since the H_2S concentrations were also high at some of the high gas flow rates (worst case or limiting design). In other cases, high gas flow rates may be attributed to

bringing a hydrogen unit or other piece of refinery equipment off line where the corresponding H_2S concentration is low (10 ppmv for example) and H_2S treatment is not required; it may be possible to deal with the high-flow, low-H_2S stream without it having to pass through the flare gas treatment unit.
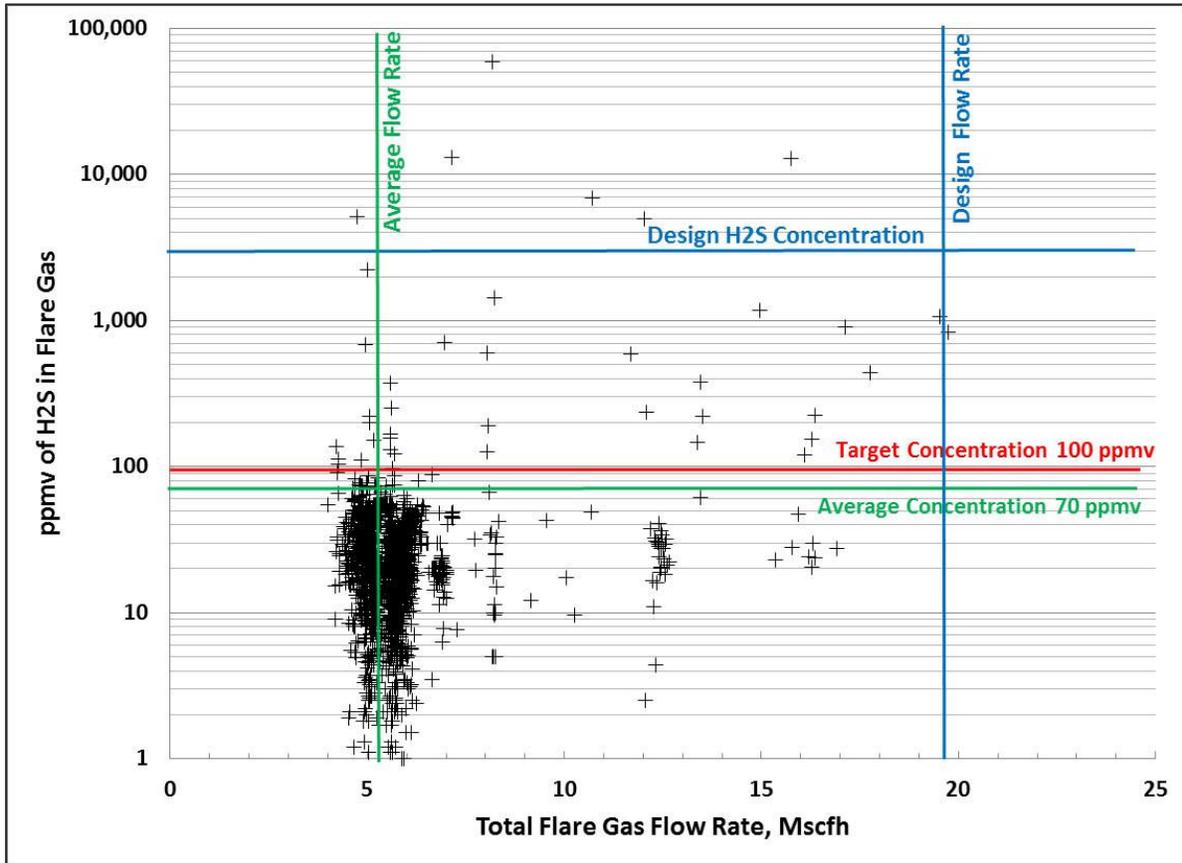

Figure 1. Hypothetical Example of the Variability in H_2S Concentration and Flare Gas Flow Rate

In Figure 1, the average H_2S concentration was slightly less than the target concentration of 100 ppmv. However, in this case, the sour flare gas stream would still flow to the treating unit where even lower concentrations could be achieved. This approach was taken because it was thought to be simpler than trying to bypass flow through the treating unit during times when the H_2S is below the target value. The H_2S concentration varied from very low levels (< 1 ppmv) to as high as 60,000 ppmv. It was determined that designing the H_2S treating system to handle 3,000 ppmv H_2S would suffice for the permit limits of the refinery; operational practices that resulted in the H_2S excursions above 3,000 ppmv could be changed to avoid these occurrences.

It is also important to review the H_2S mass flow rate (lb/hr) as well as the concentration since these parameters may have differing levels of importance in the equipment design for various H_2S treating technology. The H_2S mass flow rate data provide an indication of the physical amount of sulfur that needs to be removed from the flare gas stream, which can impact utility and chemical usage as well as operating expenses for the H_2S treating technology.

The temperature of the flare gas stream can vary greatly as well as shown in Figure 2. The flare gas temperatures typically follow ambient temperatures since the flare gas flows through long pipe runs that may be uninsulated and/or heat-traced. This variability in operating temperature can impact some of the H_2S treating technologies as discussed later in the paper and needs to be accounted for in the design of the equipment for these processes.
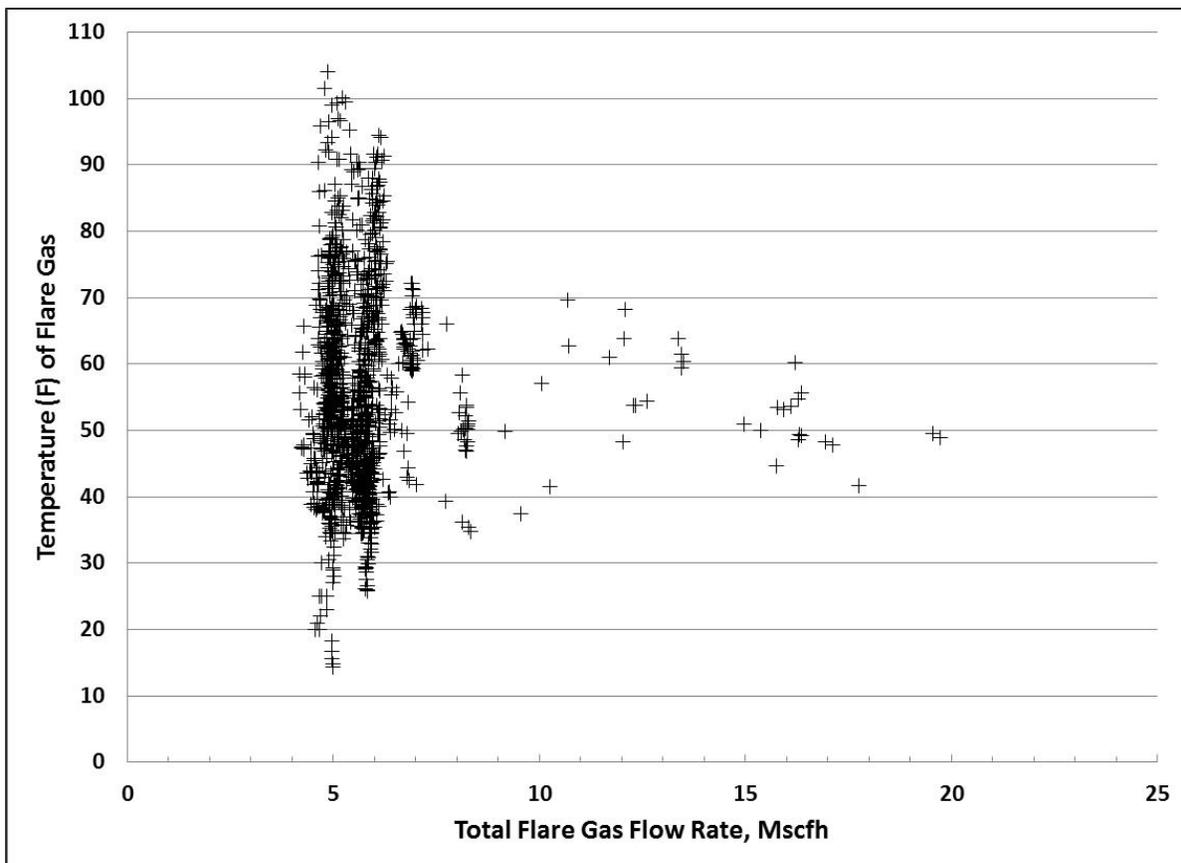

Figure 2. Hypothetical Example of the Variability in Temperature of Flare Gas Streams

The pressure of the flare gas streams is generally low, from a few inches of water column to a few psig. Operating at low pressures can make reaching low H_2S levels in the treated gas difficult for some H_2S treating technologies, for example, amine systems. The low operating pressure also needs to be taken into account to ensure that the pressure drop through the H_2S treating equipment is low enough so that the treated flare gas stream can flow to the downstream flare without the need for pressure-boosting equipment.

The composition and variability of other components in the gas should also be examined if analytical data are available. Different species present in refinery flare gas streams can impact and influence H_2S removal technology selection as discussed later in this paper.

The extent of the data that is considered in the design basis strongly depends on the permit requirements for a specific refinery. In the hypothetical example refinery case, the design maximum flare gas flow rates, H_2S concentrations and H_2S mass rates used in the design basis generally

represented at least the 98 percentile of the data and in many instances over the 99.5+ percentile. When evaluating the economics of potential H_2S treating technologies, the design maximum conditions are often used to size the equipment in the process, while the average conditions more accurately represent the approximate annual operating costs (i.e., chemical usage and replacement, power consumption, etc.) expected for the system.

The remainder of this paper discusses several of the H_2S treating technologies used on flare gas streams, including descriptions of the processes and important flare gas characteristics that impact their performance.

3.0   Amine Treating of Refinery Flare Gas

Amine treating to remove H_2S from sour gas streams is commonly used in refinery settings. This process typically involves contacting a lean amine (MDEA, DEA, etc.) with the sour gas counter currently in a packed or trayed tower. The H_2S in the gas reacts reversibly with the amine. The sweet gas leaves the top of the tower. The rich amine solution leaves the contactor and flows to a flash drum (depending on the operating pressure), a rich/lean exchanger where heat is absorbed from the lean solution, and a stripper. As the solution flows down the column to the reboiler, it is stripped of H_2S. The amine solution leaves the bottom of the stripper as a lean solution and is recycled back to the contactor.

Flare gas streams typically have low sulfur loads such that installing a dedicated, continuous operating amine unit may not be economically justified. However, it may be reasonable to install a new standalone amine contactor tied into an existing amine circuit as shown in Figure 3.
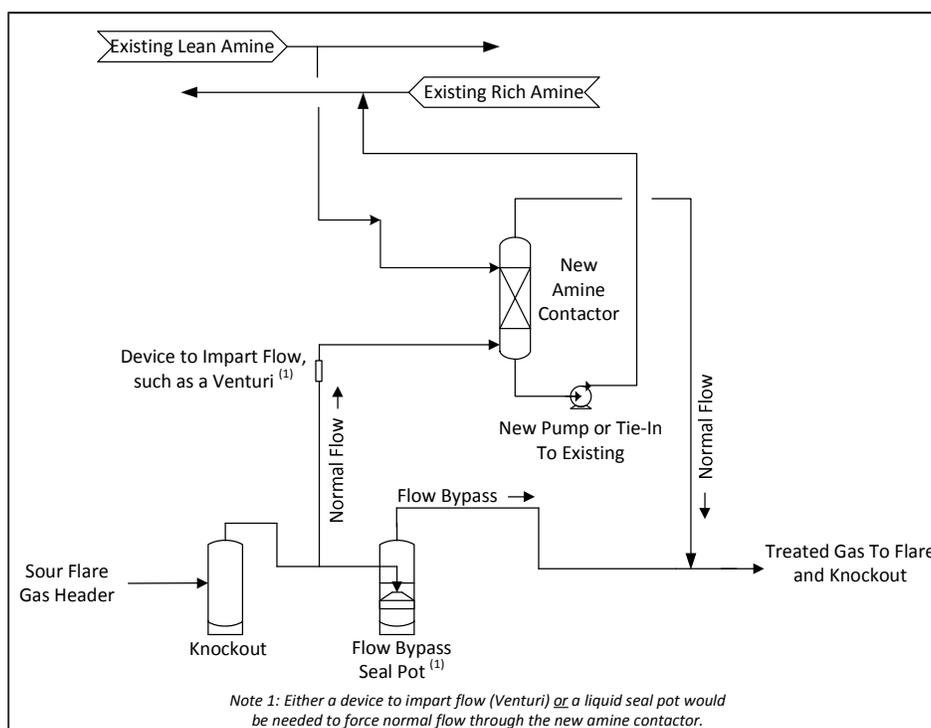

Figure 3. Example Amine Treating with New Contactor

In this scenario, lean amine from the existing amine unit could be removed and routed to the new contactor that would treat the flare gas stream for H_2S removal at low pressure. The rich amine from the flare gas contactor would be returned to the rich amine line in the amine unit. This H_2S treating concept offers several advantages including a simple process with no need to purchase or dispose of chemicals. Plus, the operators would already be familiar with the technology. It would be important to determine whether the existing amine unit has enough capacity to handle the extra rich amine load.

The next sections discuss how the characteristics of sour flare gas streams might impact an amine contactor used for H_2S removal from the flare gas.

Impact of Refinery Flare Gas Sulfur Load on Amine Treating

Amine treating is used for essentially all ranges of sulfur loads. The key consideration is what to do with the H_2S once it is captured by the amine solution. If the H_2S load in the flare gas is high, and if an amine contactor can be tied into an existing amine regenerator system and sulfur recovery unit (SRU) that has sufficient capacity, then amine treating may be an economically favored option. Installing an amine contactor for flare gas use can require more capital than some other options, e.g., scavengers, caustic treating. But, when the sulfur load is high, those other options tend to have high operating costs, whereas an amine contactor tied into an existing amine/SRU system should have a relatively low operating cost.

Effect of Refinery Flare Gas Operating Temperature and Pressure on Amine Treating

One concern with using amine technology on flare gas streams is that the operating pressure is low, and relatively deep H_2S removal (to 100 ppmv) is required. High operating temperature and low pressure can hinder the absorption capacity of the amine. The viability of the lean amine from the existing amine plant for treating the flare gas should be considered carefully.

Vapor/liquid equilibrium calculations should be used to determine the lean loading required to reach the desired H_2S treat at the flare gas operating temperature and pressure, and the required lean loading should be compared to the lean loading typically achieved by the existing amine plant. Literature data or simulation software can be used. Equilibrium calculations represent the "best case" removal possible. A reasonable approach to equilibrium (for example, 70%) should be used to establish a more realistic estimate of the H_2S removal achievable with the available lean amine. An example of the lean amine loading requirement for a 30 wt% DEA system is shown in Figure 4. As shown in the figure, at a temperature of 150°F, a lean amine loading of 0.0051 mol acid gas/mol amine would be required to achieve 100 ppmv H_2S at 1 psig, while at 110°F the lean amine loading would only need to be 0.0092 mol acid gas/mol amine.
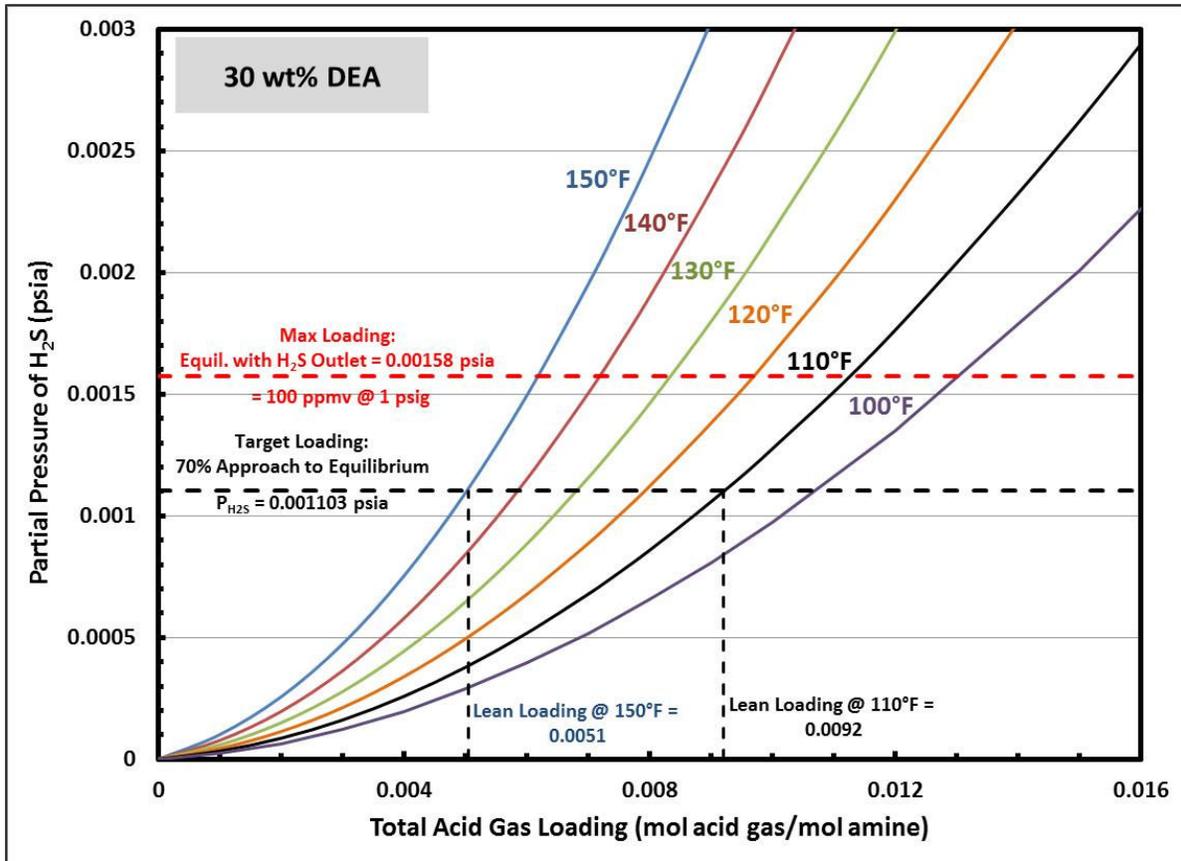
Figure 4. Example Vapor Liquid Equilibrium for H₂S Treat (Curves generated in Aspen Plus®)

If the lean amine available from the existing amine plant is not lean enough to treat the flare gas stream to the desired H$_2$S concentration, some other options can be considered. For example, a small steam (or other) stripper could be installed to strip the lean amine to achieve lower lean loadings before going to the flare gas contactor. Another option is to install an H$_2$S scavenger to further reduce the H$_2$S concentration of the amine-treated flare gas. If the temperature of the lean amine from the main unit is too high, then it may be an option to cool the lean amine using a chiller; a potential complication to this is that the lean amine that is too cool may condense and knock out hydrocarbons from the flare gas such that a liquid-liquid phase separator may be required on the rich amine. Finally, changes to the existing amine plant operations (such as operating the main stripper to produce extra-lean and /or cooler amine) could be considered, or combinations of the above.

Impacts of Refinery Flare Gas Components on Amine Treating

Oxygen - The presence of O$_2$ in gas feeds to amine units is usually considered to be detrimental in that it is known to react with amines, forming heat stable salts and resulting in corrosion and/or increased need for purge and makeup of fresh solution or solution reclaiming (Jones et al., 2010 and Sexton et al., 2016). However, some refinery amine units operate on gas streams with some O$_2$ already present so the addition of a flare gas stream with O$_2$ may not result in any significant changes. The O$_2$ content of the flare gas stream should be evaluated carefully; consultation with the amine chemical supplier should be considered.

Carbon dioxide - The amine used at the refinery and the amine contactor design can be selective to H_2S removal or it can remove both H_2S and CO_2. For this reason, when performing the vapor-liquid equilibrium calculations to evaluate the lean amine loading as described above, both H_2S and CO_2 (total acid gas loading) may need to be considered.

Impact of Refinery Flare Gas Site Considerations on Amine Treating

The location of the main amine unit and the standalone flare gas contactor would need to be taken into account when considering amine treating of flare gas. If a new, standalone, low-pressure contactor is used for the flare gas stream, then the pipe runs for the feed lean amine and return rich amine will need to be considered, and an additional feed lean amine pump will also likely be needed. The cost of the pipe runs may be a substantial cost factor.

It may also be that the flare gas stream could be treated in the existing refinery amine unit if a compressor is used to boost the pressure to the necessary operating pressure of the amine system. This is the typical flare gas recovery (FGR) scheme. Special liquid-ring compressors are often used with a downstream separator that removes the compressed flare gas from the seal water and condensed hydrocarbon liquids (if any). A water-cooled or air-cooled exchanger on the seal water loop is used to remove the heat of compression generated in the system and one or two small blowdown streams are usually generated from the liquid-ring system. However, the cost of compression, liquids treatment, and long recovered-product pipelines should be considered, all of which can be expensive (McIntush et al., 2016).

4.0   Caustic Scrubbing of Refinery Flare Gas

The use of NaOH solutions to scrub H_2S from gases is well known. Packed or trayed towers can be used to ensure deep H_2S removal, or bulk removal can be obtained in a sparged tank. An example of a typical packed tower arrangement is shown in Figure 5.

In this arrangement, the sour flare gas is contacted counter currently with a recirculating caustic solution over a single packed bed. The caustic solution may need to be cooled to maintain temperature due to the heat of reaction of H_2S with caustic, and a blowdown stream is required since the process is not regenerative. Many other flow schemes can be used with caustic depending on the characteristics of the sour gas as discussed later in the paper. One of the strongest advantages of caustic is that it is relatively inexpensive and often readily available at the refinery. It is a relatively simple process and the addition of the chemicals to the scrubber can be automated.

The main concerns with caustic scrubbing are the waste of caustic due to CO_2 pickup in solution and/or operation at higher than necessary pH, the risk of salts precipitation, and the blowdown/waste volume and characteristics. Disposal options (e.g., for shipping off site, injecting into disposal well, diluting into a waste water treatment system, on-site treatment) vary greatly. Thus, the final disposition of the spent caustic material and the associated requirements of that destination need to be considered carefully for flare gas applications.
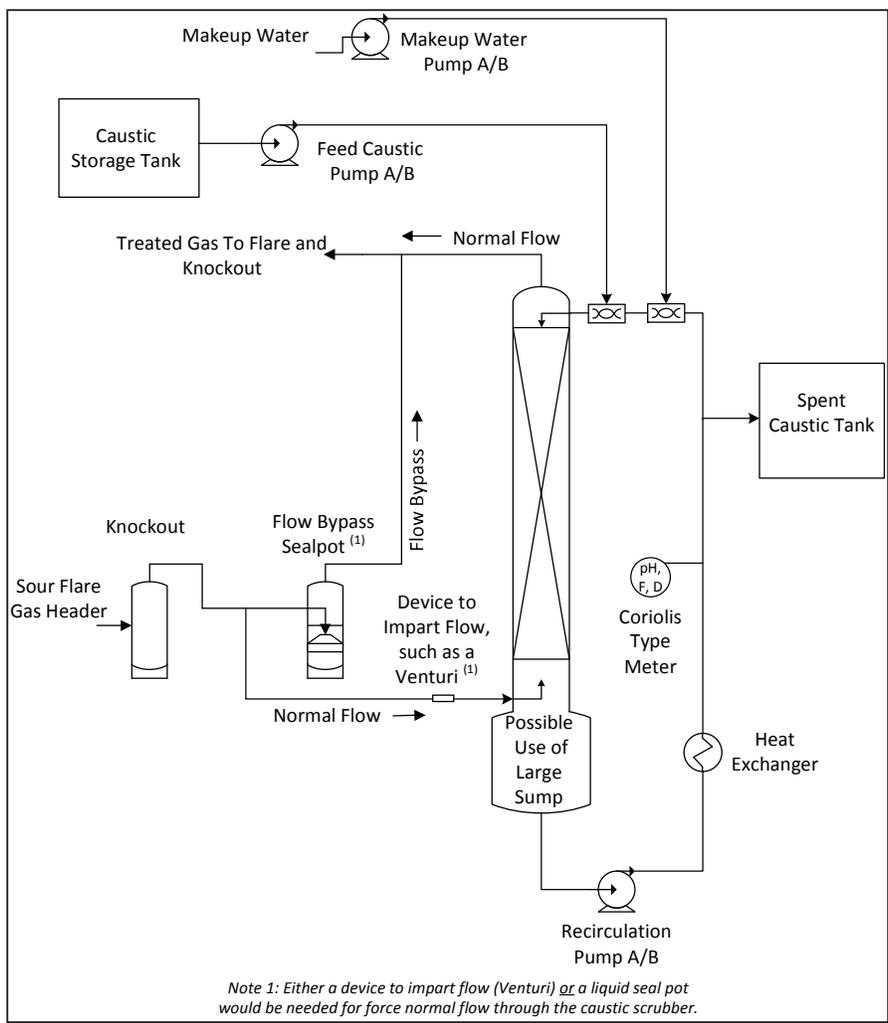
Figure 5. Example Single-Loop Caustic Scrubber System

Impact of Refinery Flare Gas Sulfur Load on Caustic Scrubbing

Caustic scrubbing is often used when the sulfur load is less than 0.1 LTPD to as high as 10 LTPD or more; the high end of the range tends to occur when the caustic scrubber is designed to make a NaHS product of good quality for sale. However, with flare gas H_2S scrubbing, the emphasis is usually on simplicity and reliability, and a salable product is not made. In these cases, assuming that the caustic is not regenerated, the caustic is considered to be a scavenger.

Effect of Refinery Flare gas Operating Temperature and Pressure on Caustic Scrubbing

The operating temperature and pressure can have a large impact on the performance of a caustic system. Operating at especially high temperatures can potentially limit the maximum H_2S removal efficiency. The equilibrium partial pressure of H_2S in the gas increases with temperature, limiting H_2S removal. High operating temperatures can also result in the need to build the scrubber system from more robust and expensive materials (stainless steel, AL-6XN, Alloy 20, etc.) depending on the caustic

strength. Carbon steel (without stress relief) can generally be used below 120ºF at caustic strengths up to 50 wt% (NACE, 1971).

With caustic scrubbers, the pH can usually be kept high enough to achieve almost any desired treat level at the usual operating pressures seen in flare gas systems.

Impacts of Refinery Flare Gas Components on Caustic Scrubbing

The presence of CO_2 in the gas feed is an important consideration in the application of caustic scrubbers. If little or no CO_2 is present relative to the amount of H_2S, then caustic scrubbing can be done in a similar arrangement as shown in Figure 5. A more complicated, dual-loop design can also be used in which distinct high strength and partially spent (low strength) caustic recirculation loops are maintained in a two-section column to allow for the removal of H_2S to low levels while minimizing caustic use (or producing a high quality NaSH product) (Mamrosh et al., 2013; Mamrosh et al., 2014).

Caustic scrubbing of gases with high CO_2 levels is particularly problematic because the CO_2 in the gas because will also be scrubbed, which could result in excessive use of caustic and potential problems with carbonate salt precipitation. Special designs have been developed that allow the H_2S to be scrubbed preferentially while slipping the majority of the CO_2 in the gas; these designs take advantage of the fact that (similar to alkanolamines) the absorption of CO_2 in caustic is significantly slower than H_2S (Mamrosh et al., 2008; Mamrosh et al., 2009). However, the H_2S-selective caustic scrubbing designs are generally more complex and operationally difficult than simpler designs, and thus are not common on refinery flare gas applications.

Caustic reacts with hydrogen sulfide and carbon dioxide as shown in the following simplified reaction:

1) $NaOH + H_2S \rightarrow NaHS + H_2O$
2) $NaHS + NaOH \rightarrow Na_2S + H_2O$
3) $NaOH + CO_2 \rightarrow NaHCO_3$
4) $NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O$

At moderately basic pH's, bicarbonate and bisulfide products dominate (reactions 1 and 3 only), while at very high pH's sulfide and carbonate products dominate (reaction continues to 2 and 4). Since CO_2 removal is not required, CO_2 removal wastes caustic. Further, since reaction to Na_2S and Na_2CO_3 requires twice as much caustic as for NaHS and $NaHCO_3$, it is desirable to operate in moderate pH ranges to minimize additional wasted caustic.

Another component frequently present in refinery gas streams that may need to be considered is ammonia. If ammonia is present in the feed gas, some will be absorbed into the liquid phase in the caustic scrubber (although the high pH of caustic scrubbers limits its solubility). Ammonia can cause odor issues that make the spent caustic product difficult to sell and may pose issues with disposal options depending on the requirements. A stripped caustic scrubber design can be utilized where the H_2S is contacted with caustic in a scrubber, and then steam is used to remove the NH_3 absorbed in the spent caustic product in a stripper. However, the design is more complex and not commonly used on flare gas systems.

Other contaminants, such as organic sulfur compounds and aromatic compounds, could also be absorbed into the caustic solution. Caustic solution will generally remove some portion of any acidic species (e.g., mercaptans) or species that have some solubility in water (e.g., aromatics) and may need to be taken into account depending on the disposal option at the refinery.

Impact of Refinery Flare Gas Site Considerations on Caustic Scrubbing

As with amine treating, any significant pipe lengths from a flare gas caustic scrubber to and from existing caustic storage tanks, and spent caustic tanks, needs to be considered in the economics of this process. The distances can be significant in a refinery setting, since the flare gas H_2S treatment system is often located near the flare and at a substantial distance from caustic sources.

The allowable pressure drop through the H_2S treating unit is a refinery specific parameter. Some refineries have had up to 15 psig to work with while at other refineries the pressure drop requirement is very low (less than 1 psig) depending on the source of the flare gas stream and the downstream flare equipment and requirements. The pressure drop requirement can dictate the type of caustic scrubbing equipment used; for example, a sparged tower arrangement where the sour gas is dispersed at the bottom of a tank through a pipe with holes may not be suitable for a flare gas application with a low pressure drop requirement. Some contacting devices such as Venturis and eductors can yield a lower pressure drop than conventional contactors like packed tower.

5.0   Solid H_2S Scavengers for Refinery Flare Gas

Solid H_2S scavengers are solids that react with H_2S, are not regenerated, and must be periodically replaced. There are several different solid materials that can be used as H_2S scavenger materials (Fisher et al., 1999). Many currently used solid H_2S scavengers are based on the use of iron oxide. Other solid materials containing potassium permanganate and other metal oxides can be used for H_2S removal but these are not considered in this paper. The desired reaction of iron oxide solid scavengers with H_2S can be summarized as:

$$3\ H_2S + H_2O + Fe_xO_y \rightarrow Fe_xS_y + 4\ H_2O$$

The iron oxide can be obtained as a pure granular solid, or supported on an inert substrate that is not flammable, such as clay. An arrangement for a fixed bed solid scavenger system is shown in Figure 6, where two vessels are used such that while one vessel is operating the spent media from the other off-line vessel can be removed and replaced.

The iron-oxide scavenger systems are relatively simple and typically require little operator attention while running. However, changing the media can take significant effort, since the vessel has to be opened and the media removed manually. Although usually not pyrophoric, the spent media can get hot when removed from service and exposed to air. The spent media itself is generally considered to be non-hazardous unless it is contaminated with a hazardous species in the gas that absorbs on the media, although this should be verified with the specific supplier of the iron oxide media.
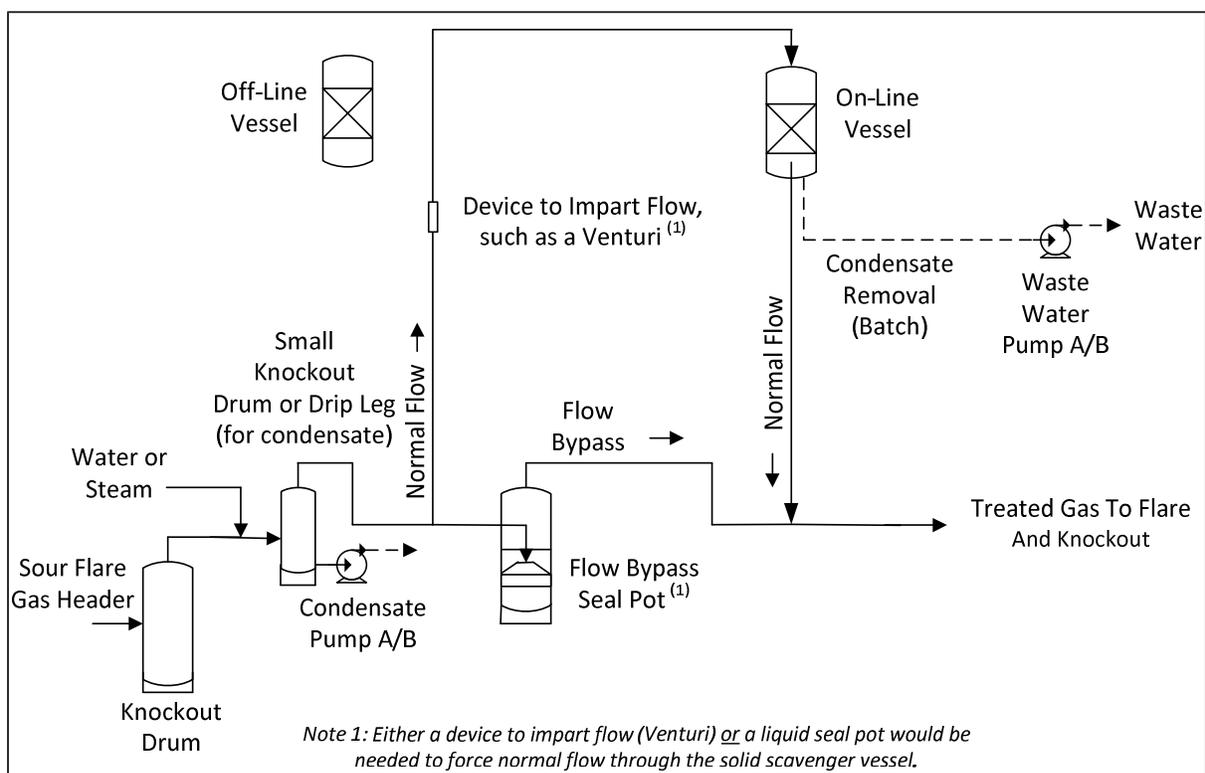
Figure 6. Example Solid H₂S Scavenger System

Impact of Refinery Flare Gas Sulfur Load on Solid H₂S Scavengers

Solid scavengers are usually used with sulfur loads below roughly 0.4 LTPD. The chemical costs associated with the use of the scavenger are high relative to the other technologies considered, but the capital cost and operating complexity are lower. Because of this, the overall treating cost of this technology can be attractive when the sulfur load in the flare gas is very low.

Effect of Refinery Flare Gas Operating Temperature and Pressure on Solid H₂S Scavengers

The performance of iron-oxide solid scavenging technology may be impacted by operating temperature. As shown previously in Figure 2, the temperature of flare gas streams may track ambient temperatures since the gas flows through long, uninsulated and/or heat-traced pipe runs. One vendor of solid scavenger media recommends keeping the flare gas temperature above 45-50ºF since media performance reportedly decreases below this temperature. A heat exchanger or heat trace could be used, or steam could be injected into the flare gas to increase the temperature, since water vapor improves the lifetime of the media. Also, temperatures up to about 200ºF have been reported by one vendor to extend the life of the media.

The operating pressure does not have a significant effect on the H₂S treatment efficiency of solid scavengers. The size of the reactor vessel can be varied so that the same residence time can be achieved regardless of the pressure.

Impacts of Refinery Flare Gas Components on Solid H₂S Scavengers

The performance of iron-oxide solid scavenging media can be impacted by water, hydrogen, oxygen and, at very high concentrations, H_2S itself.

It is a requirement for most products that the sour flare gas contain fully saturated water vapor because the presence of water vapor extends the life of the iron-oxide media. The media will treat the H_2S to low levels without water, but the media will need to be changed out much more frequently, leading to increased operating costs; more expensive mixed metal oxide scavengers can also be used to treat dry gas streams. If water is added to saturate the gas then a small knockout drum or drip leg may be recommended to separate any condensate prior to the bed of solid scavenger. Otherwise, free liquids can create channeling in the media, forming pathways for gas to shortcut and reduce the effective life of the media. Since the reaction of H_2S with iron oxide also produces water which could condense, a drain valve is required at the bottom of the reactor vessel.

Refinery flare gas streams can contain high levels of hydrogen. One iron-oxide solid scavenger vendor reported that their process could only be guaranteed for applications with 10% or less H_2 in the gas, although the reason for the limitation was not apparent; test data or additional data from other sites may be necessary to confirm this. Another vendor of similar iron-oxide media reported that their media is used on a high hydrogen stream with no known performance issues.

Oxygen has been reported to be beneficial to iron-oxide scavenging media since it can speed up the overall reaction and increase capacity. However, as shown in Figure 7, high oxygen levels and/or high H_2S concentrations can result in high theoretical heats of reaction since the H_2S reaction with the media is very exothermic. The data in this figure is considered to be a worst case condition for a high iron-oxide content solid scavenger with no ambient heat losses. The actual heatup will vary greatly from that shown in the figure due to ambient heat losses, and potential preheating of the gas through the spent zone of the media beds. At low H_2S concentrations the heatup of the bulk gas may carry the heat away, but at high H_2S concentrations heatup of the gas may be possible depending on the specific gas conditions. If the temperature of the gas were to rise significantly, the performance of the media could be impacted such that a means to mitigate it may need to be included in the design of the system although this is generally not common. Finally, oxygen will cause the formation of elemental sulfur in beds of iron oxide-based scavenging agents, sometimes resulting in a higher than normal pressure drop across the bed.

Impacts of Refinery Flare gas Site Considerations on Solid H₂S Scavengers

The pressure drop through the solid scavenging technology can be very low, with proper design. This may be important because many flare gas applications operate at low pressure such that low pressure drop through the H_2S treating equipment is needed so that the gas can flow to the flare without need for pressure boosting equipment.
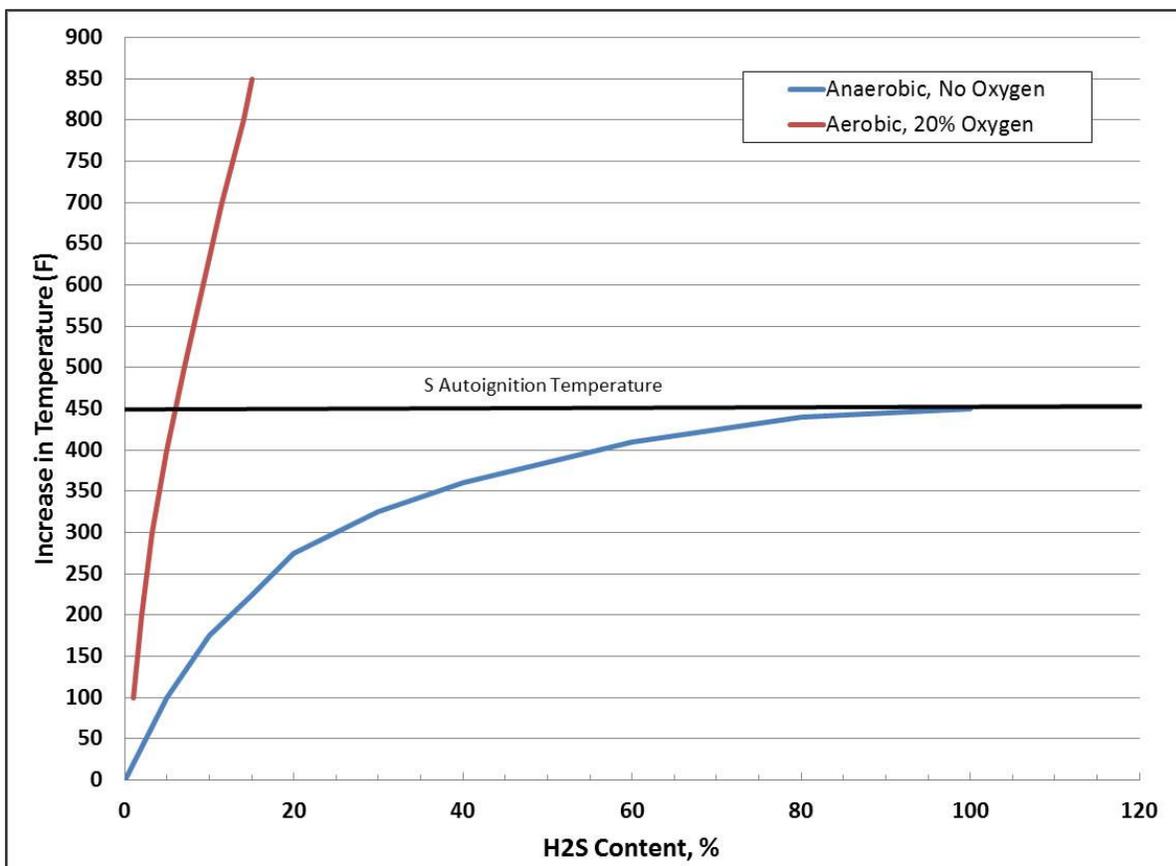
Figure 7. Example Theoretical Exotherm of an Iron-Oxide Scavenger in an Adiabatic System

6.0   Liquid H2S Scavengers for Refinery Flare Gas

While there are a number of different liquid H_2S scavengers, the most common one in refineries is triazine, and triazine is the scavenger addressed in this section. Triazine is a commercially proven liquid scavenger that has been used to remove low levels of H_2S from sour gas streams. Triazine is a reaction product of an amine (nitrogen based) and a formaldehyde typically in one of the following forms:

1,2,3-triazine   1,2,4-triazine   1,2,5-triazine
                                                  or s-triazine
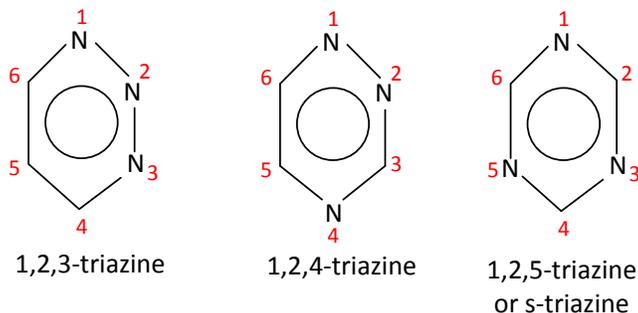
Triazines for H_2S scavenging usually have hydroxythyl side groups and are mixed with water and other chemicals (alcohols or alkanolamines) that may aid in their performance. H_2S reacts with the triazine to form water-soluble products such as diathiazine and bis-diathiazine. The spent solution is typically

100% liquid although solids can form if the solution is over spent. Loadings for liquid scavengers may range from about 0.5 lb/gal to on the order of as high as 2-3 lb/gal as reported by some vendors.

Triazine can be used in a batch vessel but it is also commonly used in direct injection in a number of refinery flare gas systems as shown in Figure 8.
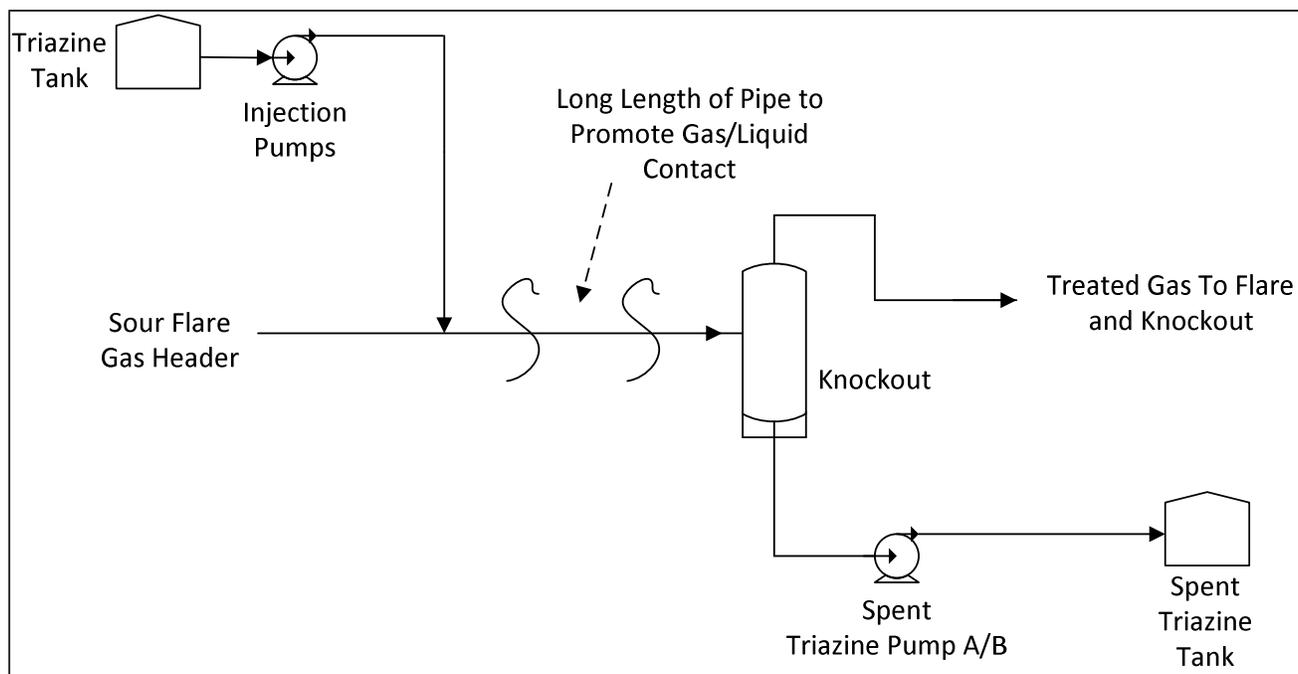

Figure 8. Example Direct Injection Liquid Triazine Scavenging System

In direct injection, the triazine is continuously added to the sour gas directly in the flare line. A separation vessel is used to recover the spent triazine. It may not be desirable to send this material to the refinery WWTP because it is a biocide and could also cause odor issues. Direct injection has low capital cost for implementation but could require significant pipe lengths and multiple injection points to achieve the desired removal.

The ability to predict the performance of direct-injection systems or achieve treatment specifications without excess chemical usage can be a challenge. For these reasons, pilot testing a direct injection system at the refinery is of substantial benefit.

Impact of Refinery Flare Gas Sulfur Load on Liquid H2S Scavengers

As with the solid scavengers, liquid scavengers are typically used with low sulfur loads (less than 0.1 LTPD average load) due to their high chemical cost and non-regenerable nature.

Effect of Refinery Flare Gas Operating Temperature and Pressure on Liquid H2S Scavengers

Low temperature gas can cause scavenger reaction kinetics to slow down and affect system performance. Operating temperatures in the 60 to 120ºF range have been used with reported success

(Fisher et al., 2005). However, operating at very high temperatures such as into relatively hot gas after compression may result in the formation of corrosive reaction products.

H_2S scavenging is generally more difficult at low pressures because the partial pressure of H_2S is lower for a given concentration and because pipes and contactor vessels are generally larger in size. The effective absorption factor or mass transfer rates (sometimes expressed as NTUs) are strongly impacted by pressures. Thus, a given length of pipe may result in much less H_2S removal at low pressures. Additional pipe length and multiple injection ports may be required for low-pressure systems, such as refinery flare gas systems.

Impacts of Refinery Flare Gas Components on Liquid H_2S Scavengers

Water addition may be required if the gas is not saturated with water at the temperature and pressure where the scavenging treatment is applied. With triazine-based liquid scavengers, the reaction products are intended to stay dissolved in the spent scavenger where they are ultimately separated from the gas from disposal. However, if the gas is sub-saturated with water and the operating temperature is relatively high, enough water may evaporate from the scavenger solution to cause unwanted precipitation of solid reaction products in the flare line. A small water injection pump can be added upstream to feed the required amount of water to saturate the gas. Use of hard water for saturation could result in the formation of scale with some scavengers (Fisher, et al., 2005).

CO_2 does not normally present a problem with triazine-based liquid scavengers because the triazine reacts selectively with H_2S. In fact, triazine scavengers can be used to scavenge H_2S from pure CO_2 at high pressures. However, in cases where H_2S scavenging is conducted at relatively high temperatures where triazines may decompose to MEA, the CO_2 will react with the MEA and adversely affect the scavenger consumption required (Fisher, et al., 2005).

Impacts of Refinery Flare Gas Site Considerations on Liquid H_2S Scavengers

Direct injection systems are vulnerable to changes in gas flow rate (Fisher et al., 2003; Fisher et al., 2005; Jamal et al., 2005; Leppin et al., 2009). The H_2S removal performance drops off severely as flow rate (and thus gas velocity) is reduced. The detailed hydrodynamics of the system and the multi-phase flow regime will vary in a fixed diameter pipe as pressure, flowrate, and possibly temperature vary and the mass transfer will change accordingly. Direct injection scavenging on an existing flare gas pipeline would likely be less efficient due to the large pipe diameters than if a newly designed direct injection system were in place to handle the flare gas.

In general, longer pipe lengths (between the injection point and the spent triazine collection point) result in improved H_2S removal and reduced chemical consumption. Finally, the importance of atomizing the scavenging agent as it is injected is very important for low-pressure, low-velocity systems, such as refinery flare gas. When gas velocities are low, pipe lengths are short, or when large pipe diameters are used (as in the case of many flare gas streams), atomization can significantly improve performance.

7.0   Conclusions

There are many significant factors that impact the selection of an H$_2$S treating technology for use with a refinery flare gas stream. As shown in Table 1, important flare gas characteristics were presented for four specific H$_2$S treating technologies: amine treating, caustic scrubbing, solid scavengers, and liquid triazine scavenger. The typical sulfur load for which the treating technologies are operated can range from <0.1 LTPD to much greater, depending on the process. The impact of operating temperature and pressure, other components in the flare gas stream, and site specific refinery factors varies greatly. The need to establish a representative design basis for the flare gas stream conditions (flow rate, operating temperature and pressure, and composition) is also important, taking into account the range and variability in these conditions. Not all of the factors and H$_2$S treating technologies could be covered in this paper, but those that were discussed should give refiners an understanding of the type of information that is necessary select an H$_2$S treating system for a flare gas stream.

Table 1. Summary of Important Flare Gas Characteristics that Impact H$_2$S Treating Technology

Parameter	Amine Treating	Caustic Scrubbing	Solid Scavenger	Direct Injection Liquid Scavenging
Typical Sulfur Load	all	0.1 to <10 LTPD	<0.4 LTPD	<0.1 LTPD
Effect of Operating Temperature	High operating temperature limits H$_2$S treat	High operating temperature may limit H$_2$S treat and special materials of construction may be required	Temperatures greater than 45ºF and less than 200ºF recommended	Temperatures from 60 to 120ºF are common; low temperatures slow kinetics; high temperatures break down scavenger
Effect of Operating Pressure	Low operating pressure limits H$_2$S treat	No significant effect	Not significant effect	H$_2$S treat is more difficult at low pressure
Other Important Flare Gas Components	O$_2$ can cause degradation	CO$_2$ reacts with NaOH and results in excess caustic use, potential carbonate precipitation, NH$_3$ absorbed and may cause odor issues in spent caustic	Water-saturated gas extends media life; high O$_2$ and/or very high H$_2$S may result in high temperature increase	Possible need for water saturation of gas if significant water evaporates from solution; selective to H$_2$S
Other Site Factors	Consider cost of amine liquid lines (with new contactor) or vapor lines (with compression)	Consider cost of caustic pipe runs and need for storage tanks; pressure drop requirements can impact scrubbing equipment	Pressure drop is typically low through reactor; significance of pipe runs is usually low	Consider scavenger tank and pipe runs; large diameter pipe and flow changes limit H$_2$S removal; atomization of chemical may be important
Additional Factors	Leanness of the available amine	Disposal of spent caustic	Disposal of spent material and laborious cleanouts	Disposal of spent scavenger

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