

USE OF CAUSTIC SCRUBBERS ON VENT STREAMS FROM MOLTEN SULFUR STORAGE AND SHIPPING EQUIPMENT

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Abstract

With increasing frequency, companies that have molten sulfur on site must put environmental controls on the vent streams from molten sulfur pits, molten sulfur storage tanks, and molten sulfur loading operations. Caustic scrubbing is a vent stream treatment technology that has been applied in a number of oil refineries, a few natural gas plants, and at numerous facilities where elemental sulfur is stored, marketed, and used. Some refineries have had significant operational difficulties with caustic scrubbers, including the formation of solids that plug the caustic scrubber and/or the piping and downstream equipment. Despite the fact that these caustic scrubbers are relatively common in refineries, and many also exist at molten-sulfur-handling/marketing facilities, there is little information on them in the literature, and so the issues that are encountered and the measures taken to overcome them are not widely known. This paper will review the types of caustic scrubbing systems employed on vent streams from molten sulfur operations, the operational issues that occur and their causes, and the key design philosophies and features that are used to alleviate the operational issues. The design concepts used to make these scrubbers work well will be compared to analogous design concepts used in other types of units where elemental sulfur solids present a plugging problem.

1.0 Introduction

The removal of H₂S from sour gas streams can be achieved with many different technologies, one of which is caustic scrubbing. Caustic solution is often used in various processing steps in refineries and its availability and familiarity make it a reasonable choice for removing H₂S from vent streams from molten sulfur operations. While caustic scrubbing is an established technology that can readily remove H₂S, its use on molten sulfur vent streams is complicated by the presence of elemental sulfur that can plug different areas of the processing equipment. The elemental sulfur in the vent gas and in the associated caustic scrubber system may be in various forms (vapor, aerosols/fog, sulfur sols, and solid particulate) so that solids plugging can occur in the piping from the source and in the scrubber itself. Minimizing sulfur plugging can be accomplished by including certain design features in the equipment and by managing the dissolution of elemental sulfur in the caustic solution. This paper first describes

the typical characteristics of molten sulfur vent gas streams as well as some of the important chemistry related to these systems in caustic scrubbers. Solids deposition issues observed in the field with caustic scrubbers operating on actual molten sulfur vent gas streams are then presented. Design and operational strategies to mitigate plugging in molten sulfur vent gas scrubbers are also summarized.

2.0 Characteristics of Molten Sulfur Vent Gas

Vent streams from molten sulfur pits, storage tanks, and loading operations are generally composed primarily of air or nitrogen, but also contain hydrogen sulfide (H_2S), sulfur dioxide (SO_2) and elemental sulfur (S_8) that must be treated to meet regulatory air emission requirements and prevent unwanted solids deposition. The amount of sulfur compounds in the vent gas varies significantly depending on the source of the molten sulfur and the handling conditions. For example, the sulfur produced in the Claus process in an oil refinery contains soluble H_2S and hydrogen polysulfides (H_2S_x). During the storage of the sulfur, the H_2S_x compounds will decompose to elemental sulfur and H_2S as the sulfur cools and is agitated. H_2S_x can take a long time to decompose to H_2S . This results in the formation of dissolved H_2S in the liquid sulfur that will desorb into the gas phase. With a stagnant head space, the H_2S then accumulates in the vapor space above the liquid sulfur. Sweep gas is often used to keep the H_2S concentration above the surface of the molten sulfur below a maximum of around 25% of the lower explosive limit for H_2S in air (McIntush et al. 2015).

Because of the significant hazards of H_2S and environmental regulations, many refineries degas the molten sulfur so that it contains less than 10-15 parts per million by weight (ppmw) total H_2S (H_2S and H_2S_x). Even with the sulfur degassed to 10-15 ppmw total H_2S , some additional H_2S will evolve during the residence time in the storage tank. This can lead to dangerous concentrations of H_2S in the storage tank vapor space and in the small vapor volume in a railcar or truck (hundreds of ppmv to low volume percent levels) (Johnson and Hatcher 2003).

Refineries that do not degas the molten sulfur have even higher levels of dissolved H_2S in the sulfur tank and at the loading area. The H_2S content in the sulfur coming from the combined SRU condensers may be on the order of 300 ppmw. If that sulfur flows first to a sulfur pit, then some of the H_2S will evolve in the pit. The sulfur after the pit will have somewhat lower levels of H_2S , even without any efforts aimed at degassing, but will still contain much dissolved H_2S . Some references use an assumption that 50% of the total H_2S evolves in the pit without degassing, but the degree of evolution of H_2S is dependent on many factors including the storage temperature, residence time, degree of agitation, whether sweep gas is used, etc. Because of the higher H_2S concentrations in un-degassed molten sulfur, the H_2S concentrations in tank headspaces or in the gas that evolves from loading operations could reach the tens of volume percent levels (Johnson and Hatcher 2003), which could potentially cause an explosion in addition to posing a very significant exposure hazard for personnel.

SO_2 is also present around molten sulfur operations. SO_2 is not flammable, but it is toxic at levels similar to H_2S (5 ppmv OSHA PEL). SO_2 is also found in the head space of sulfur storage equipment storing both un-degassed and degassed molten sulfur and, in some situations, may be present at significantly higher concentrations than the H_2S (Lagas et al. 1999). Some of the SO_2 is generally thought to originate from the elemental sulfur entering the sulfur storage equipment from the Claus SRU. SO_2 is also believed to come from reaction of the elemental sulfur with oxygen from the air in the storage tank and loading area (Johnson and Hatcher 2003).

The presence of elemental sulfur represents a unique challenge when treating vent gas in molten sulfur operations. The vent gas is commonly assumed to be saturated at its temperature and pressure

with elemental sulfur vapor. Since the stream is unlikely to be fully saturated under at least some conditions, the assumption of saturation should, in theory, give a higher elemental sulfur vapor concentration than actual. Literature sources indicate that elemental sulfur vapor may be present as S₂, S₄, S₆, and S₈ with larger molecules (through S₁₂) found in certain cases and predicted by theory (Wong, Steudel and Steudel 2003) (Meyer 1976). At the conditions expected in sulfur vent gas (250 – 300°F), the larger molecules, in particular S₈, are favored (Wong, Steudel and Steudel 2003). Higher temperatures favor the smaller sulfur molecules.

The elemental sulfur problem is further complicated by the various physical phases and forms of elemental sulfur that may be present in the vent gas and associated caustic scrubber system, including:

- Sulfur vapor
- Sulfur aerosols/fog/mist
- Sulfur sols
- Sulfur particulates/solid

The sulfur vapor can change phases as it leaves the high temperature molten sulfur tank and enters the lower temperature scrubbing system, and may be in any of the forms listed above as discussed in more detail in Section 5.0. Thus, the actual amount of elemental sulfur (as vapor, aerosols/fog, sulfur sols, or solid particulate) traveling through the vent system/caustic scrubber system is difficult to know with certainty. Further, H₂S in the gas can also react with SO₂ and/or oxygen from the sweep air to form additional elemental sulfur.

Other sulfur species such as COS and CS₂ may also be in the vent streams from molten sulfur operations. However, these species are usually thought to be at very low concentrations and are not considered further in this paper. The bulk of the remainder of the vent gas is typically water vapor, oxygen, and nitrogen from the sweep air used in the sulfur pit and sulfur storage tanks.

3.0 Industry Experience with Caustic Scrubbing of Molten Sulfur Vent Gas

Although the exact number of caustic scrubbers that treat vent gas from molten sulfur systems is not known, a knowledgeable industry contact from a company that stores, markets, ships, and uses molten sulfur (called “merchant sulfur industry” for short) guessed that there might be on the order of 50 caustic scrubbers in this service around the world. Further, Trimeric’s exposure to some data from operators of oil refineries and gas plants suggests that there are at least a dozen or more in oil refineries, in the United States. Caustic scrubbers in this service in oil refineries are often reported to have significant operating difficulties, although there are some that are said to operate acceptably.

As a result of work with clients with these systems, Trimeric contacted several parties in the merchant sulfur and the oil refining industries to gain insight into the factors associated with positive caustic scrubber operating experience. Confidential input from operating companies (primarily refining) consisting of 17 comments regarding caustic scrubbers in this application were reviewed for features that were associated with improved operation. Features mentioned that were associated with improved operation included: the use of venturi contactors prior to conventional packed scrubbers, caustic sprays at the point where the vapor line enters the scrubber, and on-line washing of the scrubber overhead equipment and lines to clean out those areas. Each of these features, and others, will be discussed further below as part of explaining how these caustic scrubbers work, describing operating problems, and reviewing features that improve operation.

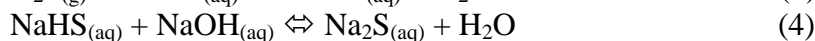
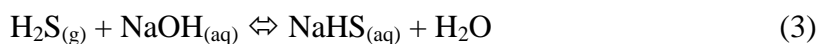
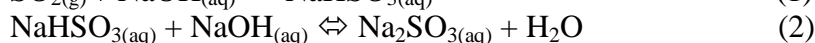
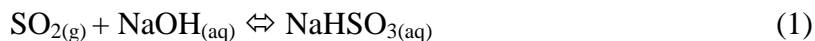
4.0 Important Chemistry for Caustic Scrubbing of Molten Sulfur Vent Gas

Because H₂S and SO₂ are hazardous gases with strong odors, emissions tend to be limited by regulations. To keep emissions of H₂S and SO₂ under the required limits, the vent streams from the molten sulfur pits, molten sulfur storage tanks, and molten sulfur loading operations commonly must be treated to remove these compounds. Caustic scrubbing of vent streams usually involves counter-current contacting of the gas phase with a recirculating caustic solution in a tower with packing or trays. The chemistry that occurs in these units is described in the subsections below.

4.1 H₂S and SO₂ Absorption and Caustic Chemistry

The overall chemistry of the caustic scrubbing system is complex, in particular because of the presence of oxygen in the sweep air of the molten sulfur. Redox reactions will produce a variety of sulfur species and intermediates which will vary based on the specific operating conditions of the system. The subsequent description focuses on the major reaction pathways only.

Caustic reacts with the SO₂ and H₂S to form several species, including sodium sulfide (Na₂S), sodium bisulfide (NaHS), sodium bisulfite (NaHSO₃), and sodium sulfite (Na₂SO₃), as shown in the chemistry below:



H₂S and SO₂ can both be readily scrubbed into aqueous solution containing caustic. SO₂ is a stronger acid than H₂S and can therefore be scrubbed into aqueous solution at a lower pH. The extent of the reactions is dependent upon the amount of NaOH that is available relative to the amount of SO₂ and H₂S in the gas feed. When greater amounts of NaOH are present relative to the amounts of sulfur species scrubbed (resulting in the solution being at a higher pH), then the products shown in reactions 2 and 4 are favored. The equilibria of the various forms of H₂S and SO₂ in water at 25°C as a function of solution pH are shown in Figure 1 (Dean 1992).

In addition, something on the order of 400 ppmv of CO₂ may be present if air is used as a sweep gas. This amount of CO₂ may be significant compared to other acid gas species in the vent gas and can be an important source of caustic consumption in the process. Therefore, consumption of caustic by CO₂ should be considered alongside the sulfur species, which are the focus of the caustic scrubber design.

Care must be taken to operate the scrubber at temperatures safely above the precipitation temperature of the salts present in the system. As shown in Figure 2, operating the scrubbing solution at high pH increases the amount of Na₂S relative to NaHS. Because sodium sulfide has a limited solubility in water, operation at higher pH and higher ionic strength can potentially result in the precipitation of sodium sulfide. Higher solution temperature can be very useful for preventing sodium sulfide precipitation. To minimize the potential for sulfide precipitation problems, feed caustic strengths of 20 wt% or less are typically employed.

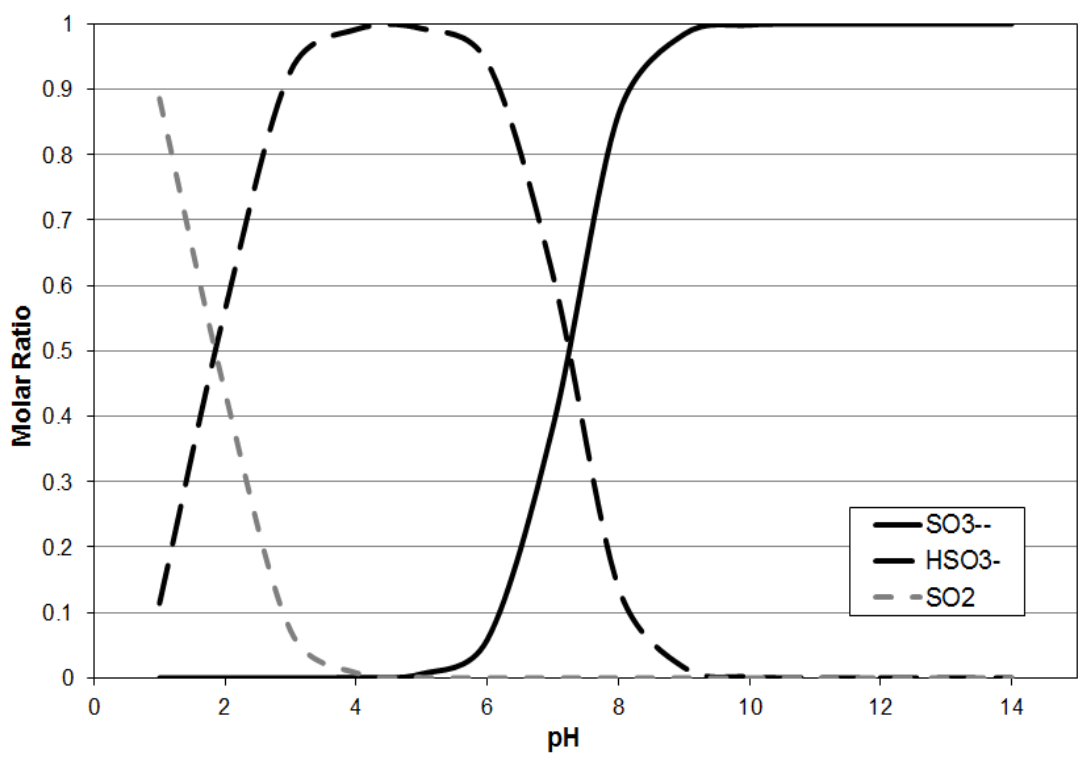
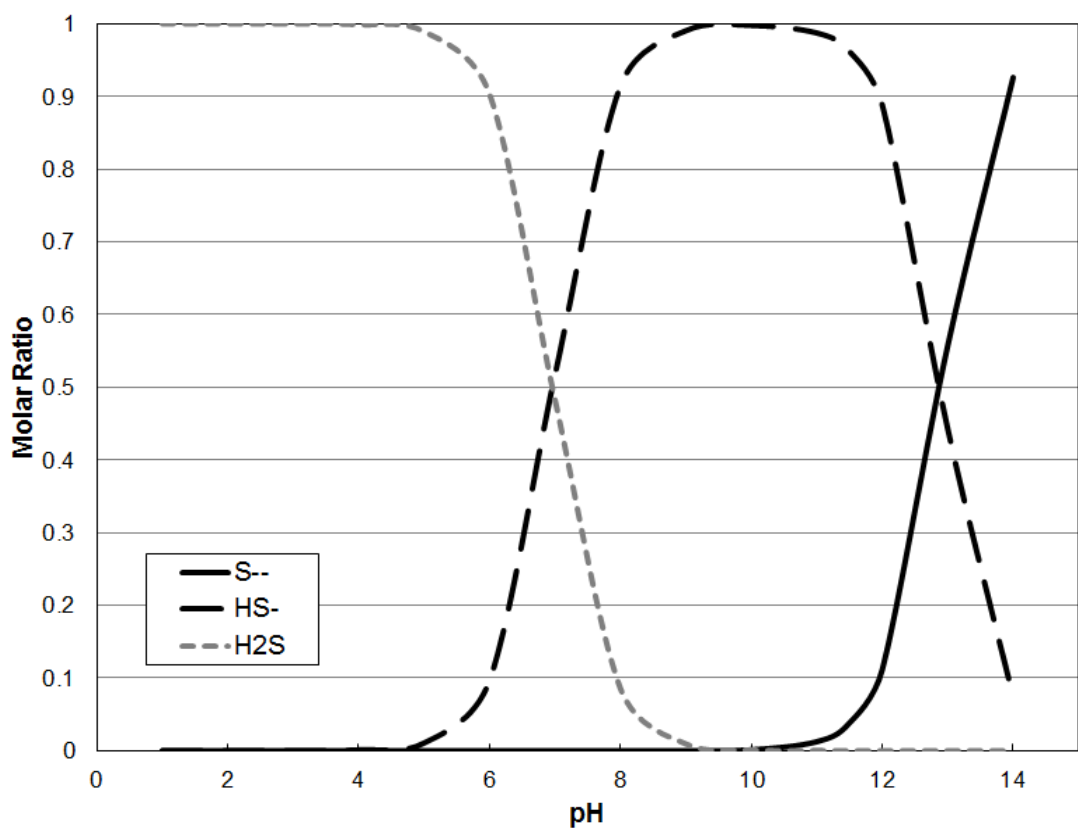


Figure 1. Solution Speciation (based on pure species in water at 25°C).

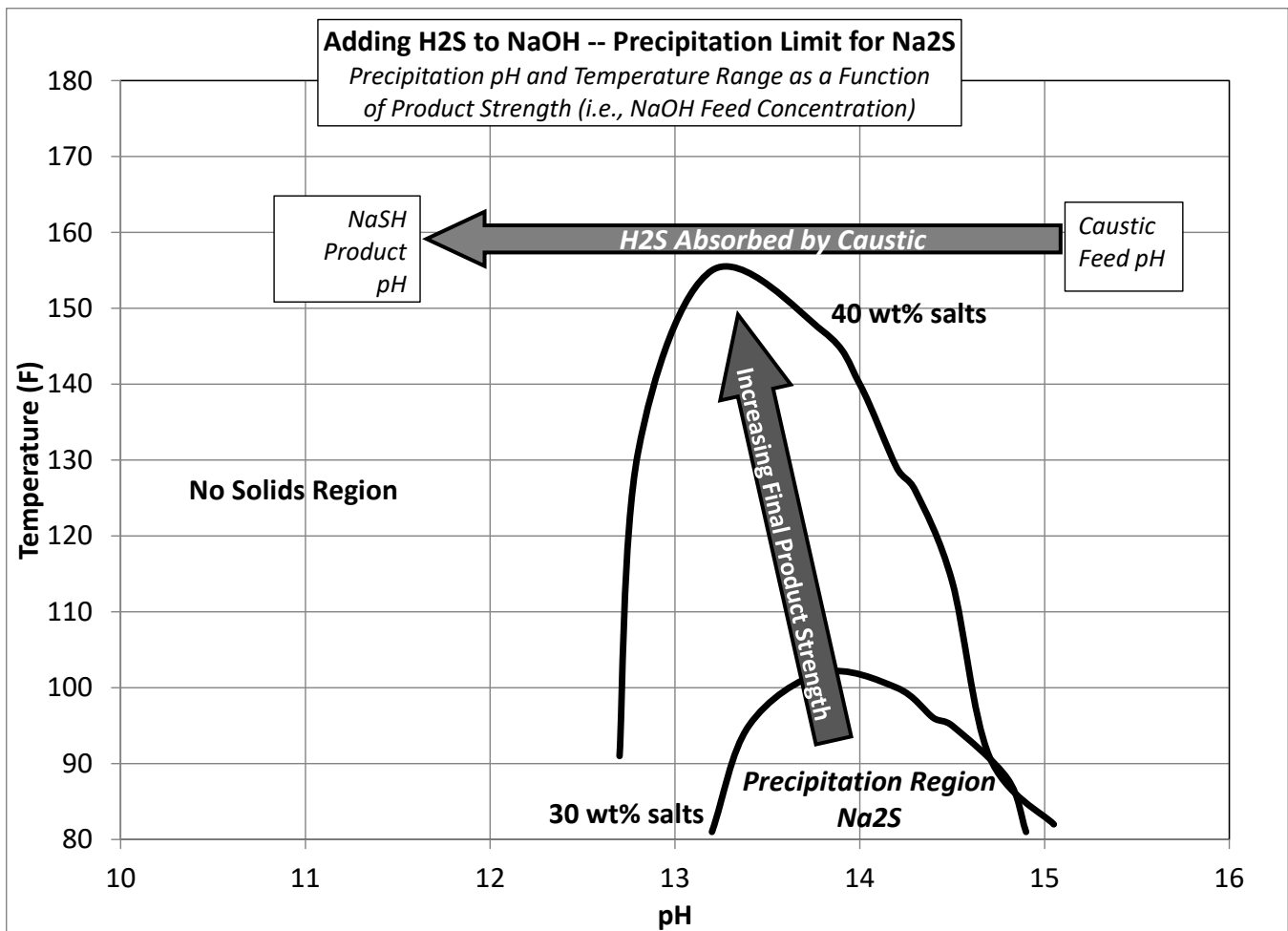


Figure 2. Example of General Trends of the Solubility Limit for a Particular Scrubbing System (30-40 wt% salt solution).

4.2 Elemental Sulfur Dissolution and Caustic Chemistry

This section will provide a brief overview of the dissolution of elemental sulfur in aqueous caustic solutions, with a focus on experimental data and information available in the literature. It is important to note that the following discussion is limited in scope in several ways compared to the complexity present in a caustic scrubbing system applied to a molten vent gas stream in the field:

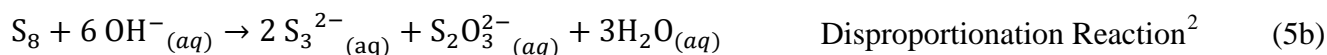
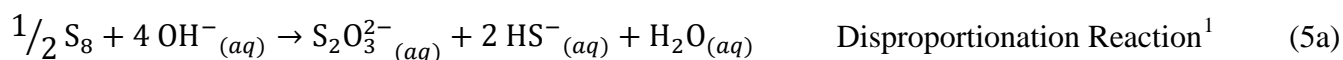
- 1) Other species present in vent gas streams from molten sulfur operations (e.g., H_2S , SO_2 , and oxygen) have potential to significantly complicate the chemistry – the following discussion focuses on caustic solution and elemental sulfur. H_2S provides an alternate source of sulfide species (HS^- , S^{2-}), and oxygen/ SO_2 introduce oxyanions and oxidized sulfur species into the solution. These species will impact the chemistry and kinetics of sulfur dissolution in practice.
- 2) Reaction pathways and mechanisms will change with specific operating conditions, particularly pH and temperature. The data in the literature may not be representative of specific conditions in the caustic scrubber.
- 3) The experimental methods used to measure dissolution (kinetic or equilibrium) may not be representative of the conditions in the caustic scrubber (particle size distribution of elemental sulfur, agitation, temperature control, etc.).

Even with the simplifying assumptions discussed above, the dissolution of elemental sulfur in caustic solutions is complex. Mechanisms that impact the dissolution of the elemental sulfur include:

- Wetting of the solid sulfur particles by aqueous solution
- Physical solubility of elemental sulfur in the aqueous solution
- Chemical reaction of caustic solution with elemental sulfur
- Diffusion of reactants and products through the solid/liquid interface boundary layer

These mechanisms, in turn, are a function of the physical properties and conditions (temperature, pH, concentrations, etc.) of the solution. In general, sulfur has a low physical solubility in aqueous solutions of caustic, but there are also a number of chemical reactions that result in significantly increasing the practical solubility of the elemental sulfur in caustic solution. In order for chemical reactions between the sulfur and caustic solution to occur, some contact between the solution and the sulfur particle must occur. The most stable and common form of elemental sulfur in the temperature range of interest is S₈ (orthorhombic sulfur), which is hydrophobic and will therefore not be readily wetted by the caustic solution. Some research has indicated that chemical reaction rates are strongly influenced by the specific surface area of elemental sulfur particles (i.e., reactions can take place on the surface of elemental sulfur particles) (Kleinjan, de Keizer and Janssen 2005) (Hartler, Libert and Teder 1967). Therefore, the wetting process of elemental sulfur (based on the specific phase/form of the sulfur) must be considered alongside any chemical/kinetic processes in the caustic solution. This section will focus on the total solubility of elemental sulfur in caustic solutions (referring to the combination of physical solubility of elemental sulfur and chemical reaction of elemental sulfur with caustic solution), but the other governing physical processes will impact overall dissolution rates.

The reactions of elemental sulfur with caustic are complex and can include multiple pathways depending on the conditions of the solution and species present in solution. However, two general routes for the reaction of elemental sulfur with caustic solution will be considered here: i) disproportionation [also called alkaline dissolution of elemental sulfur] and ii) addition reaction with sulfide/bisulfide.



The disproportionation reaction is written in two forms that are presented in literature (5a and 5b). The second reaction yields a polysulfide (S₃²⁻) species. The chemistry of polysulfides is a complicated topic beyond the scope of this paper. However, polysulfides are generally

¹ Simplified chemistry and stoichiometry represented in (Trofe, McIntush and Murff 1993)

² Alternate disproportionation chemistry proposed in (Moscardo-Levelut and Plichon 1984) that reflects formation of polysulfides.

³ Presented in (Garcia Jr. and Druschel 2014)

⁴ Generic form of reaction presented in (Moscardo-Levelut and Plichon 1984), where n = 2.

thermodynamically unstable and will decompose to form thiosulfate and sulfide species in the presence of caustic (Licht and Davis 1997). Therefore, only reaction (5a) will be considered further in this paper. Furthermore, the addition reaction for elemental sulfur can occur with bisulfide (6a) or sulfide (6b). The specific chemistry will be dictated by the conditions of the experiment or system (e.g., pH will dictate the presence and distribution of sulfide species, bisulfide vs. sulfide, as depicted in Figure 1).

This paper assumes that the sulfur dissolves via reactions (5a) and (6a) to calculate a stoichiometric limit in the following tables. The choice between addition reaction (6a) and (6b) is unimportant to the calculation of the stoichiometric limit – bisulfide or sulfide will consume the same stoichiometric amount of elemental sulfur. The approximate stoichiometric limit is calculated as follows:

- 1) Every 4 moles of caustic present (either NaOH or KOH) consumes $\frac{1}{2}$ mole of elemental sulfur (S_8) and produces 2 moles of bisulfide (HS^-) according to equation 5a.
- 2) The two moles of bisulfide can then consume $\frac{1}{2}$ mole of elemental sulfur to produce polysulfide in the form of S_3^{2-} according to equation 6a.
- 3) In total, 1 mole of elemental sulfur is consumed for every 4 moles of caustic consumed for this proposed pathway.
- 4) The stoichiometric limit of solubility can then be calculated based on the total caustic present in the initial solution (weight % of caustic).

Note that this approach is only approximate – a specific reaction pathway was selected (5a and 6a), and whatever physical solubility of elemental sulfur is possible is neglected in the calculation of this limit. However, as the data in Table 1 indicate, the estimated stoichiometric limit agrees reasonably well with the experimental data.

Table 1 includes solubility data of elemental sulfur in caustic solutions from various literature sources. Figure 3 plots the sulfur solubility from two literature sources as a function of caustic concentration in the relevant range of caustic scrubbers (≤ 20 wt% NaOH).

The available data appear to show little temperature dependence, as the sulfur solubility is effectively linear in caustic concentration despite the range of temperatures considered (77 - 255°F). These data suggest that the elemental sulfur dissolution reactions go essentially to completion; the rate of sulfur dissolution is, however, likely to be strongly influenced by temperature. Additional data over a broader range of temperatures and concentrations would be needed to confirm these findings. Moreover, it should be noted again that these experiments represent dissolution into neat caustic solutions, and are not representative of the solution encountered in a caustic scrubber.

Potassium hydroxide (KOH) may serve as an alternative base to NaOH. Table 2 includes data on the dissolution of elemental sulfur in aqueous potassium hydroxide solutions. Note that experiments 1 – 3 and 5 were conducted with excess KOH present, and therefore, do not represent sulfur-saturated conditions. However, the solubility at sulfur-saturated conditions would be at least as high as the data reported for these points, with the stoichiometric solubility limit providing some additional guidance for expected theoretical maximum solubility. Experiment 4 contained excess sulfur, and thus can be assumed to be saturated with elemental sulfur. Finally, a stoichiometric solubility limit was calculated for KOH in the same way as the limit calculated for NaOH in Table 1. As a comparison of the tables indicates, the NaOH solution has a higher theoretical capacity (stoichiometric solubility limit) for sulfur than KOH. Since both bases were assumed to behave similarly in the dissolution process (both acting as a hydroxide source for equation 5a); this is strictly a reflection of the higher molecular weight of KOH.

Table 1. Solubility of Elemental Sulfur in Caustic Solution as a Function of Temperature and NaOH Concentration (wt%).

From Data Source				Calculated	Calculated
Temperature	NaOH	Sulfur Solubility	Data Source	Stoichiometric Solubility Limit ⁵	Stoichiometric Solubility Limit ⁵
°F	wt%	g S/g soln. ⁶		g S/g soln. ⁶	g S/g NaOH
77	0.5	0.0076	(Arntson, Dickson and Tunnell 1960)	0.008	1.6
77	1.7	0.0260		0.027	1.6
77	2.2	0.0344		0.036	1.6
77	2.3	0.0354		0.037	1.6
77	3.2	0.0487		0.052	1.6
77	4.2	0.0629		0.067	1.6
231	10	0.135	(Sample Jr. 1975)	0.160	1.6
255	10	0.143		0.160	1.6
255	10	0.149		0.160	1.6
231	20	0.295		0.321	1.6
255	20	0.287		0.321	1.6
Room Temperature	66	0.215	(FREEPORT SULPHUR COMPANY 1954) ⁷	N/A	N/A

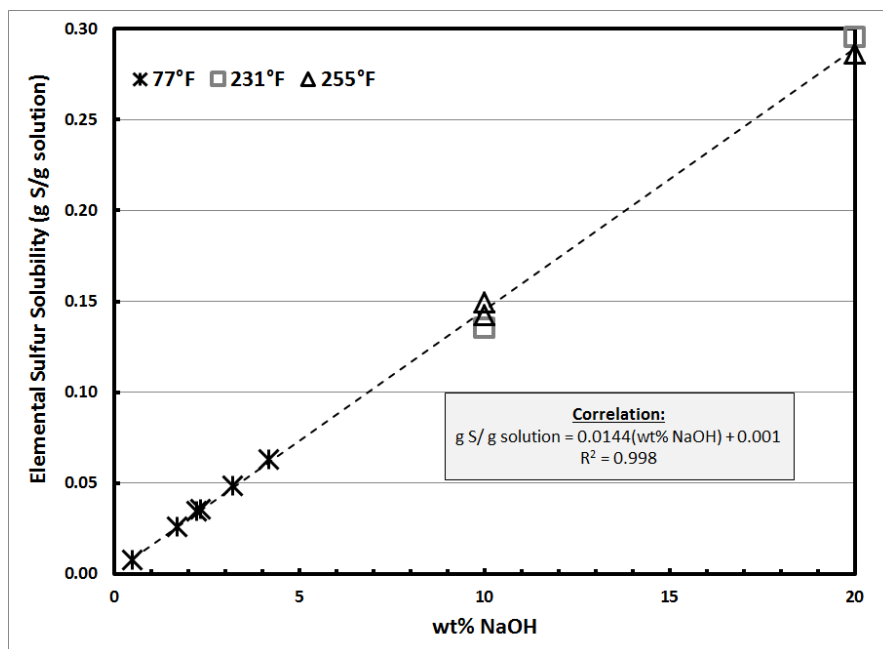


Figure 3. Solubility of Elemental Sulfur in Caustic Solution as a Function of Temperature and NaOH Concentration (wt%), Limited to 0 – 20 wt% NaOH.

⁵ Calculated by assuming that reactions 5a and 6a (see p.8) occur.

⁶ Units refer to grams of sulfur added per grams of initial or starting solution (sodium hydroxide and water).

⁷ This data point from The Sulphur Data Book (FREEPORT SULPHUR COMPANY 1954) lacks sufficient detail to be considered with the overall NaOH data set. The exact temperature is not reported, and the composition of the sodium hydroxide solution is not clear (66 wt% was given, but the basis is not explicitly provided in The Sulphur Data Book). As reported in the table, the data appears to be a significant outlier and would require further vetting or reproduction of the experiment. Therefore, this data point is reported only for general reference and completeness, because a significant portion of the audience for this paper may be familiar with it.

Table 2. Dissolution of Elemental Sulfur in Caustic Solution as a Function of Temperature and KOH Mass in Solution.

Exp	From Data Source				Data Source	Calculated
	Temperature °F	KOH g	S g	Sulfur Solubility g S /g KOH		Stoichiometric Solubility Limit ⁸ g S /g KOH
1	122	14.11	8.2	0.581	(Tartar 1913)	1.14
2	140	18.15	10	0.551		1.14
3	176	22.96	12	0.523		1.14
4	Boiling	3.678	3.93	1.069		1.14
5	203	13.122	10	0.762		1.14

As noted at the outset of this section, the discussion to this point has focused on a simplified system of elemental sulfur and neat caustic solutions (NaOH, KOH). In the case of a caustic scrubber operating on a molten sulfur vent stream, the dissolution process may vary from the simplified system. For example, caustic solutions with sulfide species present (e.g., from the absorption of H₂S) have exhibited higher rates of dissolution and capacity for sulfur uptake than comparable neat sodium hydroxide solutions. The effect of sulfide/bisulfide loading on dissolution of elemental sulfur has been documented in several places in the literature (Dickson, Arntson and Tunell 1958) (Garcia Jr. and Druschel 2014) (Moscardo-Levelut and Plichon 1984) (Trofe, McIntush and Murff 1993) (Richardson and Young 1976).

Despite the differences from dissolution behavior in caustic scrubbers, the simplified system considered thus far is valuable as a reference case – as conditions in the real system diverge from the reference case, dissolution rates and solubility of elemental sulfur can be adjusted accordingly (e.g., presence of sulfide species from H₂S absorption may enhance dissolution of elemental sulfur). At minimum, directional relationships can be developed to guide system design choices (i.e., elemental sulfur will be more/less soluble at the conditions of the real system or more/less caustic solution will be required to dissolve elemental sulfur present).

5.0 Difficulties with Caustic Scrubbers Treating Molten Sulfur Vent Gas

Some refiners have installed caustic scrubbers, sometimes called "caustic deodorizers", to treat vent gas collected from various molten sulfur operations. The operability of the scrubbers in this service can sometimes be difficult due to the formation of solids and plugging in the system. In some systems, the caustic scrubber can run for extended periods of time, while in other systems solids buildup requires frequent shutdown and cleanout of the equipment. Solids deposition in the caustic scrubbers on vents from molten sulfur operations can result from a variety of sources, as discussed below. Analytical tests could provide some insights into the source.

5.1 Salts Precipitation

Solids can form if the operating temperature drops below the precipitation point for the salt species in solution. Localized cold spots in equipment, or instrumentation that is not insulated or heat traced properly can also be a source for salts precipitation. Liquid carryover with the gas from the scrubber system may lead to solid salts buildup in downstream equipment as well.

⁸ Calculated by assuming that reactions 5a and 6a (see p.8) occur, and assume that KOH acts the same as NaOH.

The formation of solids from salts precipitation can generally be avoided or minimized by understanding the solution properties at the operating conditions of the system. There are much literature data and some simulation tools that can be used to predict the precipitation temperature for the various components in solution (as shown previously in Figure 2). Once the precipitation temperature is known, the scrubbing system only needs to be operated at temperatures safely above this (10-15°F higher). If the necessary operating temperatures cannot be maintained in the system for some reason, a more dilute caustic solution could always be used instead.

5.2 *Elemental Sulfur Deposits*

The more common and difficult to manage source of solids deposition in these types of systems is that from elemental sulfur. Vent gas from molten sulfur operations contains sulfur vapor that can deposit on solid surfaces when the gas is cooled. Elemental sulfur fog formed in the upstream molten sulfur operations may also be present. The temperature of the vent stream entering the scrubber is often below the melting point of sulfur. Also, the temperature of the caustic scrubbing system itself is often low enough that any elemental sulfur vapor entering the scrubber changes phases. Specifically, submicron aerosol or fog formation is a risk in applications dealing with elemental sulfur vapor, as documented in condensers of Claus processes (Johnstone, Kelley and McKinley n.d.). Aerosols form when the sulfur vapor is rapidly cooled below the condensation point of elemental sulfur, leading to a supersaturated vapor. If nuclei are present in the vapor and the kinetics of nucleation are sufficiently fast relative to the residence time of the supersaturated vapor, sulfur vapor will condense in the gas phase rather than forming a continuous liquid phase as in typical surface condensation processes. Researchers have developed theoretical approaches to identify the limiting conditions (partial pressure of sulfur in vapor, temperature gradient between bulk vapor and liquid, etc.) necessary for aerosol or fog formation (Johnstone, Kelley and McKinley n.d.). The aerosols are carried in the vapor and may grow or shrink depending on the conditions of the vapor surrounding the aerosol as it moves through the scrubbing process. Submicron aerosol particles are difficult to capture by traditional impaction methods (e.g., mist eliminators) as they will follow streamlines in the vapor, and these particles require special equipment for removal.

Elemental sulfur in the liquid phase that is not consumed by chemical reactions in solution (see Section 4.2) can exist as sulfur sols. “Sol” is a term that refers to a colloidal suspension of a solid or a liquid phase in a separate continuous liquid phase. Sulfur sols are emulsions of small droplets of liquid sulfur within a continuous bulk liquid phase in which the sulfur is sparingly soluble (e.g., aqueous solution). Sulfur sols can exist at temperatures far below the normal freezing point for elemental sulfur. Weimarn sols (hydrophobic sols) are expected in the conditions that would be encountered in an alkaline aqueous scrubbing process (Steudel 2003). An example of plugging attributed to sulfur sols can be found in Stretford plants that have experienced absorber plugging, “sticky” sulfur, and sulfur deposits in piping and downstream (R. Steudel 1996). In the Stretford process, a mechanism for the development of sols exists because elemental sulfur is formed in the aqueous solution via oxidation of absorbed H₂S (Trofe, McIntush and Murff 1993). However, experimental methods have also generated sulfur sols by directly contacting and rapidly cooling sulfur vapor with cold water (or aqueous solution), which would be a possible mechanism for formation of sols in the caustic scrubbing of molten sulfur vent gas (Steudel 2003). In this sense, sulfur sols in liquids are analogous to sulfur aerosols in the gas phase – both are colloidal suspensions formed by generating supersaturated conditions in different bulk / continuous phases (liquid vs. gas).

Additionally, solid sulfur particulate is also common in these vent streams. Solid sulfur can form by continued cooling of sulfur liquid in various forms (condensed vapor, sols, aerosols) in the system or be carried in sweep air (e.g., as solid particulate fog) from the molten sulfur tank. Elemental sulfur is hydrophobic and will often build a layer of floating sulfur powder in the sump of the scrubber.

The actual amount of elemental sulfur (as vapor, aerosols/fog, sulfur sols, or solid particulate) traveling through the vent system/caustic scrubber is difficult to know with certainty. However, the location of sulfur deposits in the system coupled with knowledge of the different forms of sulfur may provide insight into the source of elemental sulfur in the system. For example, collection by mist eliminators (and subsequent plugging) indicates particles captured by impaction (larger aerosols/mist or solid particulate). Sulfur that passes downstream of the scrubber (and mist eliminator, if present) in the vent gas may be indicative of small aerosols that can best be removed by high-energy (e.g., high-pressure-drop) collection devices or customized removal media. Elemental sulfur collecting or plugging in the lower portion of the column, in the sump/accumulator, or in liquid piping may be indicative of sulfur sols or sulfur that is captured by the liquid but which is not sufficiently reactive with the solution.

A possible cause of unusually high elemental sulfur (particle) load to the scrubber could be agitation due to sulfur entering the molten sulfur storage tank. Steam from leaks in heating coils in the molten sulfur storage tank has also been attributed with carrying more sulfur into the vent lines to downstream caustic scrubbers.

5.3 Solids Analytical and Characterization

Finally, analysis of the deposits that form in existing caustic scrubber systems can be used to identify whether they are salts or elemental sulfur. Usual characteristics of elemental sulfur solids include: a high sulfur analytical content, yellow color, hydrophobic, will not dissolve in pure water, powder-like material that may crumble to the touch, pH neutral with possible sulfides and thiosulfate present. In contrast, salt solids tend to form in chunks, may have a pH similar to the caustic solution, and usually readily dissolve in hot water.

6.0 Design Strategies to Mitigate Plugging of Molten Sulfur Vent Gas Scrubbers

Caustic scrubbing is typically done using a variety of equipment including packed or trayed towers, sparged tanks, in-line contactors, venturi contactors or a combination. An example of a common design for a packed tower caustic scrubber on a molten sulfur vent gas stream is shown in Figure 4. The configuration shown in Figure 4 is somewhat common in this service, but is not optimal. It is used primarily as a reference to help the reader better understand the remainder of this discussion.

In this caustic scrubber design, the vent gas leaves the molten sulfur tank and is sent to the caustic scrubbing system via a steam-jacketed blower or fan (an ejector with air or steam as the motive fluid or an eductor with caustic as the motive fluid may also be used). The vent gas may pass through a steam jacketed filter as the first place where solid sulfur could be removed. The vent gas enters the caustic scrubber below the packed bed, where it counter-currently contacts caustic solution. The vent gas leaves the packed section of the column and passes through a demister which removes entrained liquid or large particulate. The treated gas leaves the column for further treatment or, more commonly, venting to the atmosphere.

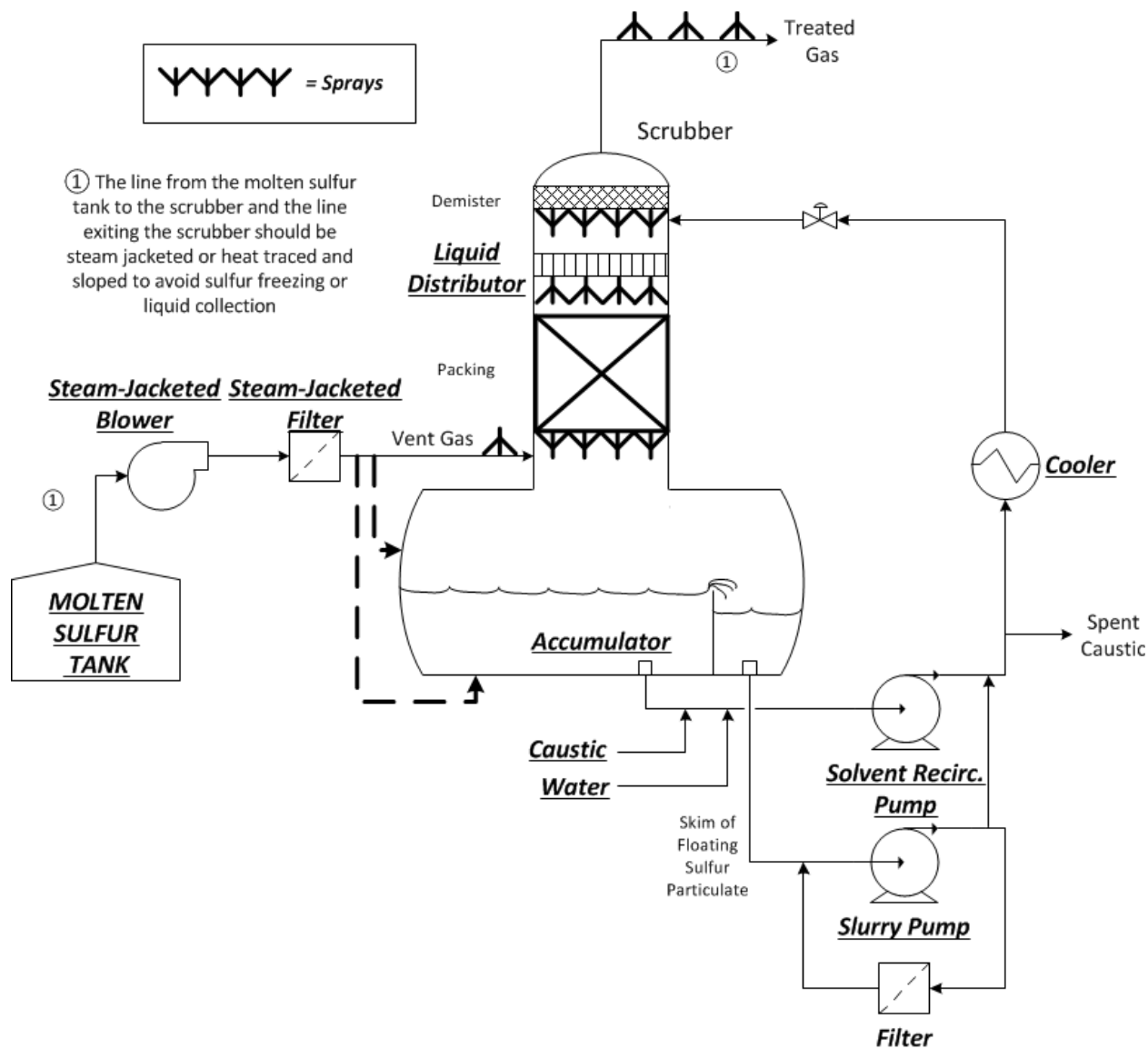


Figure 4. Generic Caustic Scrubbing Process Flow Diagram. Items highlighted in *bold, italicized, and underlined font* reflect places where equipment or process modifications can be used to manage sulfur deposition.

The caustic solution absorbs the various sulfur species discussed in Section 4.0, and passes to the sump or accumulator of the vessel. The solution is then pumped back to the top of the column, with a portion bled to remove spent caustic, and a liquid filter may be used to remove any solids carried in the solution. The solution passes through a cooler, which controls the temperature of the caustic feed, and finally, the solution is fed back to the top of the packed bed by a liquid distributor. Make up caustic and water are added to the recirculating caustic stream.

There are many design features that can be incorporated into the scrubber system to mitigate plugging of the equipment from elemental sulfur solids as described in the subsections below. Several locations for these modifications are highlighted in the diagram.

6.1 Improved Gas / Liquid Contact

The general strategy is to design the system to get elemental sulfur out of the gas and into the liquid where the sulfur can be more easily dealt with. Once in the liquid, it is important to keep any solids that form either suspended in solution or suspended as a slurry until they either dissolve or reach an appropriate point for removal from the system. The liquid load to the scrubber can be increased by using a high recirculation rate. This will help remove additional elemental sulfur from the gas (via increased gas-side pressure drop and eliminating gas bypass paths), help keep the solids swept off of the packing, and help keep the solids from settling. In addition, sulfur in all forms (aerosols, sols, vapor) will condense and crystallize on solid surfaces in the system. Higher liquid loads help eliminate dry surfaces in the packing and on column walls where sulfur might condense, solidify, and collect. In addition to a high relative circulation rate, a coarse spray distributor could be considered for uniform and more forceful liquid distribution over the packing than with other types of distributors (e.g., trough) that are sometimes used in these scrubbers. Packing is also available with a large open area that is suitable for high liquid loads; more open packing is also generally less prone to solids buildup than is packing with less open area.

Liquid spray designs could also be considered for use to remove solids from the gas at different locations in the process. Spray nozzles could be located just above the gas entry in the scrubber or even in the gas entry pipe itself. The gas entry could be submerged in (sparged into) the liquid phase in the sump of the scrubber to aid in removing some of the solids from the gas. If the elemental sulfur is prone to pass through the scrubber internals, then intermittent sprays could be used to i) wash the mist eliminator to keep it from plugging (a very frequent plugging location) and/or ii) wash the piping exiting the scrubber, if there is a downstream knockout vessel or other means to deal with the liquid. It is Trimeric's understanding from knowledgeable persons in the merchant sulfur industry that these techniques have all been tried with some success.

These methods are primarily effective via increased gas pressure drop, droplet/particle impaction, and physical washing of surfaces (with the additional benefit of reducing solid surfaces for crystallization of sulfur). Therefore, submicron particles (solid particulate "dust" or liquid aerosols) are unlikely to be effectively managed by these approaches, and in fact, plugging issues downstream of the scrubber with these features implemented may be a strong indication of submicron particles.

6.2 Removal of Elemental Sulfur Solids

The dissolution of elemental sulfur into the caustic solution is the ideal approach to manage elemental sulfur. Thus, scrubbers in this service should ideally be designed and operated so that the scrubber system dissolves any elemental sulfur that is present within them.

However, if dissolution is not possible in the specific system (sulfur content is too high; temperatures are not sufficient to allow adequate reaction rates in solution; system is already built, sulfur dissolution was not taken into account, and the system cannot be modified so as to sufficiently dissolve elemental sulfur; etc.), then it is important to manage the solids with minimal process interruption. Existing systems may be modified in order to implement some of these approaches.

Suspended elemental sulfur solids can be removed from the liquid phase in a variety of ways. The solids could be allowed to settle in a separate vessel and then be removed from the system. The liquids could also be filtered to remove solids. A weir installed in the scrubber sump to allow for overflow of a floating powder layer (if present) is a feature that has been used in some caustic scrubbers

in this service – see Figure 4 for an example of this design. Sprays can be used to periodically blast solids loose from surfaces (such as mist eliminators and piping near the outlet of the scrubber.) Finally, the piping can be designed with cleanout tees to allow solids to be removed manually.

6.3 Alternative Equipment and Process Flow Schemes

Alternative equipment such as a venturi contactor (an eductor) could be used with the caustic as the motive fluid and a high circulation rate to provide the needed contact between the gas and liquid phases. Venturi scrubbers are a known means of particulate removal from gas streams; therefore, implementing a venturi scrubber prior to the caustic scrubber should reduce the particulate load to the caustic scrubber. It may be possible to retrofit some existing systems with a venturi contactor. Another potential advantage is that a venturi scrubber, if properly designed for this purpose, may be able to replace a blower or other device to move gas through the scrubbing system.

Other commercial scrubbers have been designed to counter-currently contact the vent gas with caustic solution in a reverse jet nozzle that then separates in a wide open vessel to minimize places for sulfur solids to accumulate; chevron mist eliminators are used too as a last step to separate droplets from the gas exiting the vessel (Myer, Juno and Watts 2006).

Another approach includes use of a venturi scrubber that uses water (not caustic) to remove elemental sulfur (i.e., for particulate control) from the vapor followed by caustic scrubbing. The water circuit can be filtered as necessary. Water scrubbing towers for particulate control prior to a caustic scrubber are also used; in Trimeric's experience, some locations with water scrubbing towers for particulate control achieve successful operation and others don't. Another option is to install a filter on the vent gas stream itself to remove sulfur particles in the feed gas followed by caustic scrubbing the remaining gas; a small number of locations are known to take this approach.

Dual-loop or cascaded caustic scrubbing designs are already applied in the field to improve the quality of the caustic blowdown or waste stream (in terms of the quality of NaHS produced) (Mamrosh, McIntush and Fisher 2014). These designs may be adaptable for control of elemental sulfur in the system as well. Previous research has shown the use of a cascaded packed bed system to systematically enlarge aerosols via heterogeneous condensation of water on the aerosol by controlling the temperature of the liquid phase (Heidenreich, et al. 2000). The controlled growth of aerosols facilitates removal at desired locations (i.e., specific impaction device or filter) without the high pressure drop or customized equipment typically used for sub-micron particle removal. Furthermore, the dual-loop system allows for control over the composition of the caustic stream in the individual beds. As noted in Section 4.2, elemental sulfur reactions with sulfide and bisulfide (reactions 6a and b) are faster than reactions with caustic and are favored when sufficient sulfide/bisulfide is present. The dual-loop design may potentially create a zone where elemental sulfur absorption is enhanced by higher sulfide/bisulfide concentration.

A cross-flow (horizontal) scrubbing arrangement may offer improved operation and a longer run time before cleaning. Cross-flow scrubbers are reported to be able to withstand more than an order of magnitude more particulate than vertical counter-current scrubbers (Cheremisinoff 1993). Cross-flow scrubber use on vents from molten sulfur operations has been reported (Shields and McKee 2014).

Redundant scrubbers could be installed so that if one unit plugged, the other could be brought on line. The use of redundant scrubbing systems may be dictated by the comparison of the additional capital cost with the need for maintaining continuous gas treatment. As an alternative, specific portions of the scrubber where plugging or solids formation is likely could be duplicated or spared. For example,

the overhead vapor lines could be duplicated to allow cleaning and maintenance while re-routing the vapor to prevent shutdown of the unit.

The operation and monitoring of the molten sulfur tank may help with sulfur deposits as well. The tank can be operated with reduced levels or lower temperatures to minimize the sulfur vapor pressure and reduce fog formation potential. (It is interesting to note that those involved in the merchant sulfur and sulfur shipping industry tend to operate molten sulfur tanks at cooler temperatures [e.g., 260°F] than the refining industry [280-300°F].) The tank should also be regularly monitored for the presence of steam leaks in any internal coils, which is believed to cause additional elemental sulfur particulate to be present in the tank vapors. Piping entering and exiting the scrubber should also be steam-jacketed or heat traced to prevent elemental sulfur from condensing and plugging these lines. A specialized entry (e.g., steam heated stinger) may be useful where the vapor enters the scrubber. The lines entering and exiting the scrubber should be sloped to the scrubber so that sulfur that encounters the heated pipe wall and melts can flow downhill into the scrubber. Blowers and ejectors in the system should also be traced as well.

7.0 Operating Strategies to Mitigate Plugging of Molten Sulfur Vent Gas Scrubbers

There are also several operational changes that could be implemented to control the formation of solids or to help manage solids in the system. These strategies range from introducing surfactants to the caustic solution, monitoring the operating temperature and caustic strength, exercising the unit in order to remove solids that have begun to lay down, and using warm caustic to aid in cleanouts.

7.1 Additives

Other chemicals, such as a wetting agent (surfactant), could be added to the scrubbing liquid to help wet the sulfur particles thus allowing more rapid dissolution into the caustic solution. Research also indicates that surfactants (e.g., sodium dodecyl sulfate) can increase the amount of elemental sulfur suspended in aqueous solution by several orders of magnitude by forming micelles around the hydrophobic sulfur particles or sols and preventing growth and precipitation of solid particles (Garcia Jr. and Druschel 2014). Furthermore, the patent literature includes examples of surfactants used alongside caustic solutions to remove sulfur solids in gas production wells by increasing the solubility of sulfur in caustic with the surfactant leading to enhanced reaction in the caustic solution (Sample Jr. 1975).

Alternately, oxidizers such as bleach or peroxide could be added to the scrubbing liquid. This is normally done for H₂S and SO₂ control, but some operators have indicated that these chemicals change the properties of the solids, making them easier to remove from the liquid. Similarly, diesel oil was used in the Stretford process to enhance flotation of elemental sulfur to enhance the ability to remove sulfur from the liquid surface (Trofe, McIntush and Murff 1993). This approach can be coupled with the solids removal equipment design approaches in Section 6.2.

7.2 Temperature Control

Temperature control of the caustic scrubbing system can be used in a variety of ways to prevent or manage issues related to elemental sulfur in the system. Although it would require careful consideration of materials of construction, high-temperature scrubbing could be used to prevent condensation of sulfur vapor and enhance the reaction rate of sulfur with the caustic solution. Controlling the temperature in different parts of the scrubber could be used to prevent the formation of

aerosols and liquid sols (prevent rapid cooling of sulfur vapor in the scrubber) and control the growth of aerosols that form (cascaded scrubber design).

Although operating the scrubber solution at higher temperature may help manage sulfur plugging issues, higher temperatures increase the vapor pressure of H₂S and SO₂ in the caustic solution, thus making treatment specifications more difficult to meet. As the temperature of the caustic solution increases, it may be necessary to operating the caustic solution at a higher pH in order to achieve sufficient H₂S and SO₂ removal from the gas. However, the maintenance of a higher pH results in greater caustic usage, and operation of the system at high temperature can result in the need for more expensive materials of construction. Generally, carbon steel can be used in caustic scrubbers at low temperatures and low bisulfide concentrations. At temperatures greater than roughly 200 to 215°F, even stainless steel (304/304L and/or 316/316L) may experience significant caustic-induced corrosion rates, leading to a preference for higher allows (AL-6XN, 20, 800 or 825) depending on the weight percent of the caustic solution and the final pH. Consultation with a materials specialist is highly recommended for high temperature caustic scrubbing.

Steam sparging may also be used in specific locations of the column (e.g., mist eliminators, column vapor inlet) to maintain localized higher temperatures (prevent condensation/crystallization) with the added benefit of wetting the surfaces with the condensed steam to serve as a rinse and to limit crystallization surfaces.

7.3 *Caustic Strength*

The caustic solution should be monitored and managed with the goal of dissolution of sulfur in the bulk liquid. Higher caustic concentrations will lead to enhanced reaction rates with elemental sulfur. The caustic strength, however, has the same issue regarding column material selection as with higher temperature operations discussed in the preceding section. If the system is operated with regular feed of fresh caustic to maintain original caustic strength, this may also help with dissolution of sulfur.

7.4 *Exercising the Unit*

In other process systems where salt and solid sulfur plugging often occurs, ‘exercising’ the unit has been found useful to extend run times. An example of such a system where plugging has been experienced is a liquid redox sulfur recovery system (e.g., SulFerox, LO-CAT, Stretford). In this context, exercising the unit means varying flows, levels, and other operating conditions temporarily with the specific purpose of keeping the system clean. Control valves may be cycled, manual valves cycled, motor speeds changed, levels built and dropped with the goal of dislodging any material that is beginning to lay down so that the material can be moved through the system to a point where it can be removed (or solubilized). In Trimeric’s experience, the units that have implemented a regular system of varying flows, levels, etc. for the specific purpose of keeping the system clean have operated much longer than systems that had no such program. Trimeric has observed these exercise programs documented in operating procedures, which is likely a very good practice.

7.5 *Using Warm Caustic for Recovery and Cleaning*

If solids plug the system, then there are several different means for cleaning it. The system could be opened, cleaned, and then closed back up; however, this is labor intensive and may require significant down time. Alternately, the solid sulfur could be removed by using warm (~140 °F) caustic. As Figure 3 showed, the temperature may not affect the solubility of elemental sulfur in caustic, but temperature

does affect the rate of dissolution, with higher temperatures being associated with faster dissolution. Higher strength caustic may also be required for use on the scrubber equipment that is down. This approach has been used to dissolve / remove the sulfur deposits in other equipment (e.g., in Stretford absorbers) where elemental sulfur deposition is a problem. One patent describes a cleaning approach where caustic solution replaces the typical Stretford solution during operation to allow simultaneous cleaning of equipment and treating of the gas; the approach includes initial flooding of the column with caustic solution to allow vigorous contacting of the caustic with column internals (Herich 1999). An analogous approach for a caustic scrubbing system might be to: i) drain and clean with pure, high strength caustic at an elevated temperature or ii) temporarily increase the pH and temperature of the solution while operating with the goal of cleaning on line. The suitability of the materials of construction of the equipment should be reviewed relative to the length of time that the equipment would be exposed to the higher caustic strengths and temperatures. The patent literature also has many examples of hot caustic used to clean sulfur deposits from oil, gas, and mining production piping (Monroe Jr 1956).

8.0 Conclusions

Caustic scrubbing of molten sulfur vent gas streams has occurred with varying degrees of reliability due to the presence of elemental sulfur that can exist in several different forms (vapor, aerosol/fog, sols, and solids particulate). However, there are many design and operational modifications to enhance the performance of even the most difficult applications. Design changes can range from enhancing the gas/liquid contact with increased circulation rates, installing spray nozzles in different areas of the process, removing solids from the solution with filters or decanting floating solids, and using redundant or alternate contacting devices (dual contacting devices, piping, etc.). Operational changes can include the use of surfactants, elevated operating temperatures, and increased caustic strength. Understanding the chemistry and dissolving of the elemental sulfur into the caustic solution represents the ultimate mitigation technique, because the formation of solids is eliminated (or greatly reduced). The mechanisms for dissolving sulfur in caustic that are presented in this paper can be used to aid in the development of a more robust caustic treating system for molten sulfur vent gas streams.

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10.0 References

- Arntson, R.H., F.W. Dickson, and George Tunnell. "Systems S-Na₂O-H₂O and S-H₂O: Application to the Mode of Origin of Natural Alkaline Polysulfide and Thiosulfate Solutions." *American Journal of Science* 258 (1960): 574-582.
- Cheremisnoff, P. "Packed Wet Scrubbers." In *Air Pollution Control and Design for Industry*, p. 283. New York: Marcel Dekker, Inc., 1993.
- Dean, J. *Lange's Handbook of Chemistry Fourteenth Edition*. McGraw Hill, 1992.
- Dickson, F.W., R.H. Arntson, and G. Tunell. "Saturation Curves of Orthorhombic Sulfur in the System S-Na₂S-H₂O at 25C and 50C." *Science*, 1958: 716-718.
- FREEPORT SULPHUR COMPANY. *The Sulphur Data Book*. New York: McGraw-Hill, 1954.
- Garcia Jr., Angel A, and Gregory K. Druschel. "Elemental sulfur coarsening kinetics." *Geochemical Transactions* 15, no. 11 (2014): 1-11.

- Hartler, Nils, Jan Libert, and Ants Teder. "Rate of Sulfur Dissolution in Aqueous Sodium Sulfide." *Industrial and Engineering Chemistry Process Design and Development*, 1967: 398-406.
- Heidenreich, S., U. Vogt, H. Buttner, and F. Ebert. "A novel process to separate submicron particles from gases - a cascade of packed columns." *Chemical Engineering Science* 55, no. 15 (2000): 2895-2905.
- Herich, Charles Arnold. Method for On-Line Cleaning of Sulfur Deposits. United States of America Patent 5,979,470. November 9, 1999.
- Johnson, J., and N. Hatcher. "Hazards of Molten Sulfur Storage and Handling." *Laurance Reid Gas Conditioning Conference*. Norman, 2003.
- Johnstone, H.F., Max D. Kelley, and D.L. McKinley. "Fog Formation in Cooler-Condensers." n.d.
- Kleinjan, Wilfred E., Arie de Keizer, and Albert J.H. Janssen. "Kinetics of the Reaction between Dissolved Sodium Sulfide and Biologically Produced Sulfur." *Industrial and Engineering Chemistry Research* 44, no. 2 (2005): 309-317.
- Lagas et al., J. "Understanding the Formation of and Handling of H₂S and SO₂ Emissions from Liquid Sulphur During Storage and Transportation." *Sulphur Seminar*. Amsterdam, 1999.
- Licht, Stuart, and John Davis. "Disproportionation of Aqueous Sulfur and Sulfide: Kinetics of Polysulfide Decomposition." *The Journal of Physical Chemistry B* 101, no. 14 (1997): 2540-2545.
- Mamrosh, D.L., K.E. McIntush, and K. Fisher. "Caustic Scrubber Designs for H₂S Removal from Refinery Gas Streams." *American Fuel & Petrochemicals Manufacturers Annual Meeting*. Orlando, Fla., 2014.
- McIntush et al., K. "Molten Sulfur Storage Tank, Loading, and Vapor Ejection Systems Review." *Brimstone Sulfur Symposium*. Vail, 2015.
- Meyer, Beat. "Elemental Sulfur." *Chemical Reviews* 76, no. 3 (1976): 367-388.
- Monroe Jr, John E. Process for removal of deposits from sulfur mining pipes using hot caustic solution. United States of America Patent 2,771,284. November 20, 1956.
- Moscardo-Levelut, N.M., and V. Plichon. "Sulfur Chemistry in Equimolar NaOH-H₂O Melt: II. Chemical Reactions Between Sulfur, Sulfide, Polysulfide, and Oxyanions." *Journal of The Electrochemical Society* 131, no. 7 (1984): 1545 - 1551.
- Myer, S, e. Juno, and N Watts. "Dynawave Wet Gas Scrubbing: A New Alternative for Claus Unit Tail Gas Clean-up." *The Laurance Reid Conference*. Norman, 2006.
- Richardson, Frank Peter, and David Anthony Young. Method of Prevention and Removal of Sulfur Deposits from H₂S Absorption Equipment. United States of America Patent 3975508. August 17, 1976.
- Sample Jr., Thomas E. Method for Removing Elemental Sulfur in Sour Gas Wells. United States of America Patent 3,909,422. September 30, 1975.
- Shields, M., and S. McKee. "Vapor Emissions Scrubbing of Off-Gases from Liquid Elemental Sulfur." *Sour Oil and Gas Advanced Technology Proceedings of the 10th International Conference*. Abu Dhabi, UAE, 2014.
- Stedel. "Aqueous Sulfur Sols." In *Elemental Sulfur and Sulfur-Rich Compounds I*, by Ralf ed. Stedel, 153-166. Berlin: Springer Berlin Heidelberg, 2003.
- Stedel, R. "Mechanism for the Formation of Elemental Sulfur from Aqueous Sulfide in Chemical and Microbiological Desulfurization Processes." *Industrial Engineering and Chemistry Research* 35, no. 4 (1996): 1417-1423.
- Tartar, Herman V. "On the Reaction Between Sulfur and Potassium Hydroxide in Aqueous Solution." *Journal of the American Chemical Society* 35, no. 11 (1913): 1741-1747.
- Trofe, T.W., K.E. McIntush, and M.C. Murff. *Stretford Process Operations and Chemistry Report*. Chicago: Gas Research Institute (Prepared by Radian Corporation), 1993.
- Wong, Ming Wah, Ralf Stedel, and Yana Stedel. "Speciation and Thermodynamics of Sulfur Vapor." In *Elemental Sulfur and Sulfur Rich Compounds I*, 117-134. Berlin: Springer Berlin Heidelberg, 2003.