Caustic Scrubber Designs for H_2S Removal from Refinery Gas Streams

1 Abstract

Caustic scrubbing is a technology that has been used for the removal of H_2S and other acid species from gases in different industries for many years. Improvements in design and control strategies, favorable prices for caustic compared with other non-regenerable H_2S scavenging chemicals, and the potential for sales value for the NaHS (sodium bisulfide) product have made caustic scrubbing an economic and viable option for some refinery streams. Caustic scrubber designs are available to treat sour refinery fuel gas both with and without CO_2, sour water stripper (SWS) gas, acid gas from amine units, and other refinery gas streams. This article will review caustic scrubber designs applicable to these applications.

The presence or absence of significant CO_2 is an important consideration with caustic scrubbers. If little or no CO_2 is present, caustic scrubbing is traditionally done by contacting the gas with recirculated caustic solution in a packed tower. More complicated designs, such the dual-loop system in which distinct high strength and partially spent caustic recirculation loop are maintained in a two-section column, are available which can allow for the removal of H_2S in the gas to low levels while producing a high quality NaHS product.

Caustic scrubbing of gases containing high CO_2 levels is particularly problematic because the CO_2 can also react with caustic, causing unwanted caustic consumption and the possibility of sodium carbonate solids 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 that of H_2S. Other designs are available to treat sour water stripper off-gases containing ammonia by caustic scrubbing the H_2S followed by steam stripping the NH_3 absorbed in the spent caustic product. Caustic scrubbers have even been used as backup devices to Claus units and other processes during shutdowns.

There are many factors to consider when determining which caustic scrubber design is most appropriate for certain applications, such as the treated gas H_2S removal specification, the total quantity of H_2S to be removed, whether other components are in the gas that may be absorbed, how often the unit will be used, if the spent caustic will be sold or disposed of, and the cost of the feed caustic. This paper discusses the importance of each of these factors, and presents several caustic scrubber designs used at refineries and the rationale for implementing the different designs. Some of the important characteristics that must be considered during the detailed design of each of the scrubber systems are also presented (e.g., materials of construction, solubility, heat of reaction, and operating temperature and equilibrium limits). An important aspect in the effective design of caustic scrubber systems is the accuracy of the equilibrium data (e.g., pK_{a2} value) for H_2S removal and spent caustic composition, and the kinetic predictions for H_2S and CO_2 selectivity. Finally, the tools – simulation and other calculations – that can be used to predict that performance of caustic scrubbers are discussed, along with their limitations.

2 Background

The scrubbing of hydrogen sulfide (H_2S) using sodium hydroxide (NaOH) solution is established technology, and has been applied in a variety of industries. Since this process uses a solvent which cannot be easily regenerated, caustic scrubbers are most often applied in situations where small volumes of H_2S need to be removed. The removal of small amounts of H_2S from gas streams is typically referred to as scavenging. Caustic is often classified as an H_2S scavenger, and competes with other scavengers such as solid reactive adsorbents (e.g., iron oxides) and reactive liquid absorbents (e.g., triazine). Scavengers are most often used for the removal of H_2S in amounts of roughly 0.1 ton per day, or less. However, the product of caustic scrubbing of hydrogen sulfide at moderate pH – NaHS which is also referred to as NaSH – when produced at high quality can often be sold, and depending on the value of the product solution, caustic scrubbing may be cost effective in the United States at sulfur throughputs of as much as 10 ton/day.

In the scrubbing process, sodium hydroxide reacts with H_2S dissolved in aqueous solution to form sodium bisulfide (NaHS) and sodium sulfide (Na_2S).

$$H_2S_{(aq)} + NaOH_{(aq)} \rightarrow NaHS_{(aq)} + H_2O \qquad (1)$$

$$NaHS_{(aq)} + NaOH_{(aq)} \rightarrow Na_2S_{(aq)} + H_2O \qquad (2)$$

The extent of reactions 1 and 2 are dependent upon the amount of NaOH that is available relative to the amount of H_2S that is scrubbed into the solution. When greater amounts of NaOH are present relative to the sulfide that is present, the solution pH is higher, and continuation from reaction 1 to reaction 2 is favored. NaHS may be a valuable product; in order to maintain product quality, it may be required to control the pH of the spent caustic solution so that NaHS is the predominant sulfide species. Na_2S uses twice the amount of caustic necessary for H_2S removal and it has a limited solubility in water as well.

Carbon dioxide may also be present in many refinery gas streams. CO_2 complicates the use of caustic for H_2S scrubbing because CO_2 is also readily scrubbed into the caustic. The reactive absorption of CO_2 into caustic solution can be represented as:

$$CO_{2(aq)} + NaOH_{(aq)} \rightarrow NaHCO_{3(aq)} \qquad (3)$$

$$NaHCO_{3(aq)} + NaOH_{(aq)} \rightarrow Na_2CO_{3(aq)} + H_2O \qquad (4)$$

CO_2 absorption causes unnecessary caustic usage, contamination of the NaHS product solution with carbonate salts, and potential plugging and fouling of process equipment with carbonate salt solids. Although various grades of saleable NaHS exist (15 to 40+ wt%), the highest value grades typically have less than 3 wt% sodium carbonate and less than 4 wt% Na_2S. Other gas contaminants such as ammonia may also be present and may need to be separated from the NaHS to maintain product quality. Special caustic scrubber designs are required to treat these gas streams.

3 Important Considerations for Caustic Scrubber Design

There are many different possible designs for caustic scrubbers. In selecting a configuration for a caustic scrubber for H_2S removal, the following are some of the factors that should be considered:

- **H_2S abatement requirement (ppmv H_2S in product gas)** -- More stringent outlet gas H_2S contents may require special provisions including contact with fresh (high pH) caustic at the top of the contacting device or multiple treatment stages to maximize H_2S removal while producing a high quality NaHS product. The operating temperature and pressure of the system will also impact the achievable H_2S concentration in the product gas.

- **Amount of H_2S to be removed (tons/day of sulfur) –** Caustic scrubbers are most often applied in situations where there is a small amount of H_2S to scrub (e.g., less than about 10 ton/day). In comparison, other liquid and solid H_2S scavengers are typically exclusively used at lower sulfur tonnages (<0.1 ton/day). Regenerable processes (e.g., liquid redox and similar biological and chemical processes for combined H_2S removal and sulfur recovery) are most frequently used in the 0.2-15 ton/day range, and large scale amine/Claus/tail gas treating units are usually designed for capacities of at least 15 ton/day. (Note: the ranges are generally accurate, but with each category there are a few examples of applications well outside of the stated ranges.)

- **Other components in gas which may be scrubbed into the caustic –** The presence of CO_2 in the feed gas will result in the consumption of unnecessary caustic and can lead to the production of salts that can precipitate in the process. Careful evaluation of the amount of CO_2, relative to the amount of H_2S, is necessary. It is possible to design caustic scrubbers to selectively remove the H_2S and leave the majority of the CO_2 in the gas (based on slower CO_2 absorption rates). If ammonia is present in the feed gas, some may be absorbed into liquid phase in a caustic scrubber, although the high pH of caustic scrubbers limits this. Other contaminants, such as organic sulfur compounds and aromatic compounds, could also be absorbed into the caustic solution; if the spent caustic (NaHS) solution is to be marketed, the presence of small amounts of these contaminants could be important.

- **Utilization frequency of scrubber (continuous vs. occasional) –** This will impact the annual operating costs of the system including caustic replacement and electricity. In some cases, intermittent use may allow for design of a scrubber system that would be uneconomical under continuous operation.

- **Disposition of spent caustic (disposal or sale) –** NaHS solution is used in paper, mining, tanning and other industries, and the value of this product can vary locally and will also vary as a function of its strength (concentration of NaHS) and purity. As the application size becomes larger (with respect to the H_2S throughput rate), the value of the NaHS product becomes more important to the economic feasibility of applying caustic scrubbing. The possibility of blending poorer quality NaHS product streams with other higher quality NaHS streams at the refinery to make a saleable overall product should also be considered.

If there is no market for the NaHS, then disposal costs (e.g., trucked off site, injected in disposal well, dilution into a wastewater treatment system) need to be considered.

- **Cost of caustic** -- The cost of caustic can vary significantly over time and by physical location. Therefore, the expected life of the project and availability of caustic should be evaluated.

The challenge is to match the caustic process with the local conditions and constraints. Given all of these factors, a preliminary performance and economic evaluation should be conducted to determine feasibility and whether more detailed design of the process should occur.

4 Scrubber Designs for Sour-Gas Streams

Several caustic scrubber arrangements considered for refining applications are presented below to facilitate the discussion of this topic. Table 1 provides a brief summary of these designs and when they are typically used.

Table 1. Summary of Scrubber Designs for Sour-Gas Streams

Scrubber Design	Typical Use and Characteristics
Scrubbing using excess NaOH (single-loop design)	• Simplest design • Used with low CO_2 concentration relative to H_2S • Good for small capacity applications or infrequent use • Higher caustic consumption • Spent caustic quality may be poor
Scrubbing while minimizing excess NaOH (single or dual- loop design)	• More complex design and controls (dual-loop) • Use with low CO_2 concentration relative to H_2S • Minimizes caustic consumption • Potentially produces high quality, saleable NaHS product
Selective scrubber (short contact time)	• More complex design and controls • CO_2:H_2S ratio in gas is significant but not too high • Single-loop (also referred to as single-stage) design can make saleable NaHS product with less stringent treated gas H_2S specification • Multi-loop/stage design may be required to both i) meet deep H_2S removal and ii) produce saleable product
Special design for sour water stripper gas with H_2S and NH_3	• Used with sour water stripper gas containing H_2S and NH_3 • High operating temperature and low pressure make deep H_2S removal more difficult (need excess NaOH or dual-loop design) • Separated NH_3 vapor stream must be disposed of

Generally speaking, if the sour gas stream contains components that could also be absorbed in the caustic solution a special scrubber design may be warranted. In the case of sour gas with CO_2, a selective scrubber could be used to remove the H_2S while slipping most of the

CO_2 in a short-contact-time device with one or multiple stages, depending on the H_2S treatment specification and required product quality. Ammonia in a sour water stripper stream can be separated from the H_2S in a stripped caustic scrubber design, if it is required that the product NaHS be free of ammonia. If the sour gas is free of other unwanted soluble contaminants, then scrubbing can take place in either a single-loop design or in a dual-loop design. In the dual-loop design, a strong caustic section is used as a second treatment stage for the gas in order to achieve the desired H_2S removal.

Using excess NaOH in a single-loop design may allow for stringent outlet H_2S specifications to be met but results in a poor quality spent caustic product and high caustic usage. This may not be an issue if the spent caustic can be used elsewhere at the refinery or if the cost of the excess NaOH and disposal is not that detrimental. Minimizing excess NaOH usage in a dual-loop design with a strong-caustic section allows for deep H_2S removal and high product quality, but the design is more complex. A single-loop design can also be used while minimizing excess NaOH if deep H_2S removal is not required. The caustic scrubber designs are described below with examples of refinery applications and reasoning for their use.

4.1 Caustic Scrubbers with a Single Recirculating Loop

For small sulfur capacity, infrequent use, or situations in which deep H_2S removal is not required, a relatively simple single-loop design may be applied to caustic scrubbers. The single-loop design, shown in Figure 1, is a simple system in which the gas is passed through a tower (usually packed) countercurrent to a liquid stream of recirculating caustic. This type of unit would typically consist of a single packed tower with a surge tank, a circulation pump, an exchanger(s) (to heat system during startup and/or remove the heat of reaction), and the appropriate controls. A continuous makeup of fresh NaOH (with water for dilution of the caustic) and a continuous blowdown would be required, although for systems removing very small amounts of H_2S it may be practical to use a batch makeup and blowdown strategy.

A relatively large liquid recirculation flow rate from the column sump to the top of the column is typically maintained in order to achieve good contacting of the gas and liquid phases, and to provide the additional thermal mass needed so that the substantial reaction heat does not heat up the solution too much.

If deep removal of H_2S from the gas is not required, then this single-loop system can be designed to operate at moderate liquid pH values, minimizing caustic usage. At moderate liquid pH values, the removal efficiency H_2S from the gas may be limited by the equilibrium partial pressure of H_2S with the solution. The NaHS produced under this scenario can be of relatively high quality.

If deep removal of H_2S is required, then the single-loop design can still be employed, but operation of the solution at high pH would typically be required. This design strategy assures the maximum abatement of H_2S at the cost of excess NaOH usage. Excess amounts of NaOH (e.g., NaOH:$H_2S \geq 2:1$) are often required for deep H_2S removal. When large excesses of NaOH are used, the equilibrium partial pressure of H_2S of the solution is so low that it is typically negligible. The design of columns for this situation is straightforward. Well known strategies for evaluating the height of a transfer unit (HTU) of the column packing can be used, such as

packing vendor or literature HTU or K_ga data. Process simulators can also be used if they are known to adequately model the mass transfer rate in addition to the chemical equilibria. For single-recirculation-loop systems, the excess caustic utilization will be the primary factor determining the H_2S removal efficiency. Because of the high relative consumption of caustic and low value of the sulfidic caustic product, this type of scrubber is limited to very low sulfur throughputs and low CO_2 concentrations or intermittent use.

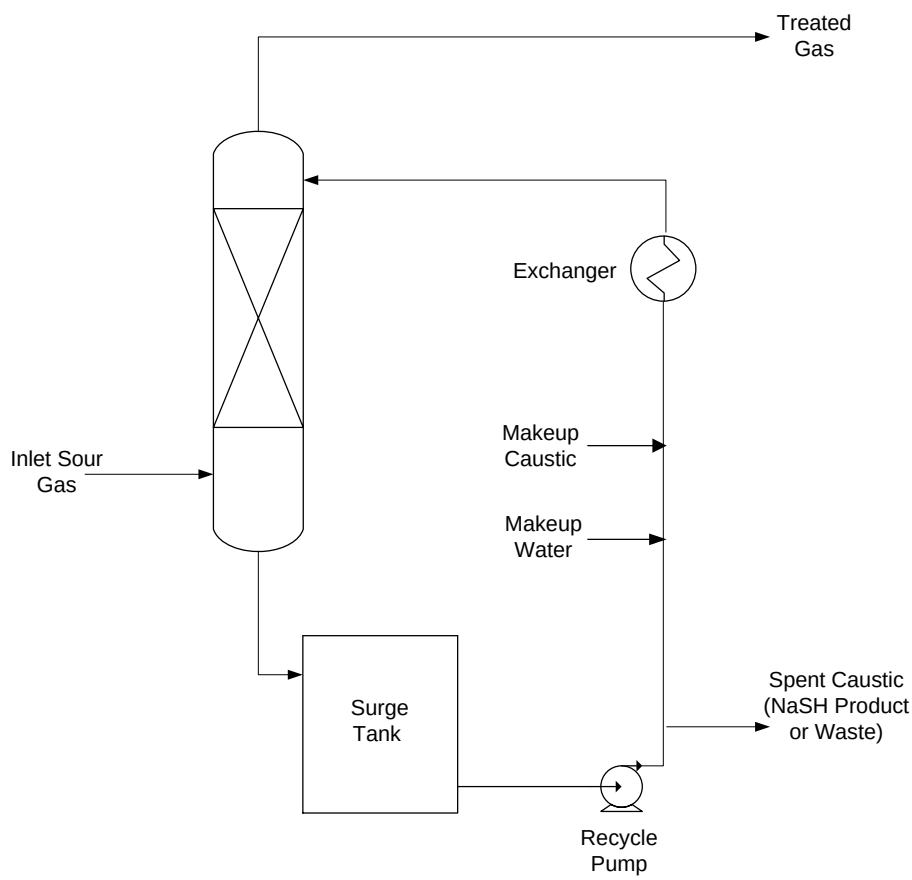

Figure 1. Typical Simple Caustic Scrubber

An example of the simple single-loop design is when a caustic scrubber is used as a backup to a Claus unit during shutdowns. Assuming that environmental and/or safety issues prohibit the flaring of acid gas streams, a backup method for H_2S disposition may be required if it is desired to continue to operate the amine plant during Claus unit outages. Short Claus outages may be accommodated by providing for some storage capacity for rich amine, but it is unlikely that it would be economically justified to provide enough rich amine storage to allow for Claus outages of more than roughly ½ hour. For longer Claus outages intermittent-use caustic scrubbers may be appropriate.

Backup Claus scrubber designs have been developed for very small applications to very large units (450 LTPD). Figure 2 shows an example flow scheme for a caustic scrubber applied as a Claus backup. The H_2S was generated in several hydrotreater units. In this design, a simple tray or packed tower is used. The tower has a large, tank-like sump at the bottom to hold a large volume of caustic solution. Since the scrubber is used as a backup, a small circulating pump circulates caustic over the trays to keep the internals of the tower wet when not in use. If the sulfur recovery unit (SRU) shuts down, a valve to the SRU closes and a valve to the scrubber opens sending the high-H_2S gas from the amine unit to the scrubber. When the scrubber inlet valve opens, the large circulating pump turns on to circulate caustic proportional to the H_2S flow. The caustic goes from the scrubber bottoms to the circulating pump, through a water-cooled heat exchanger to remove the heat of reaction, then to the top of the tower. Spent caustic exits from the pump discharge to spent caustic storage on specific-gravity control. The spent caustic may have a high Na_2S content because excess caustic is required to make treat. Fresh caustic enters the process on level control. There is also a condensate makeup line to supply more water if it is needed to adjust caustic strength.

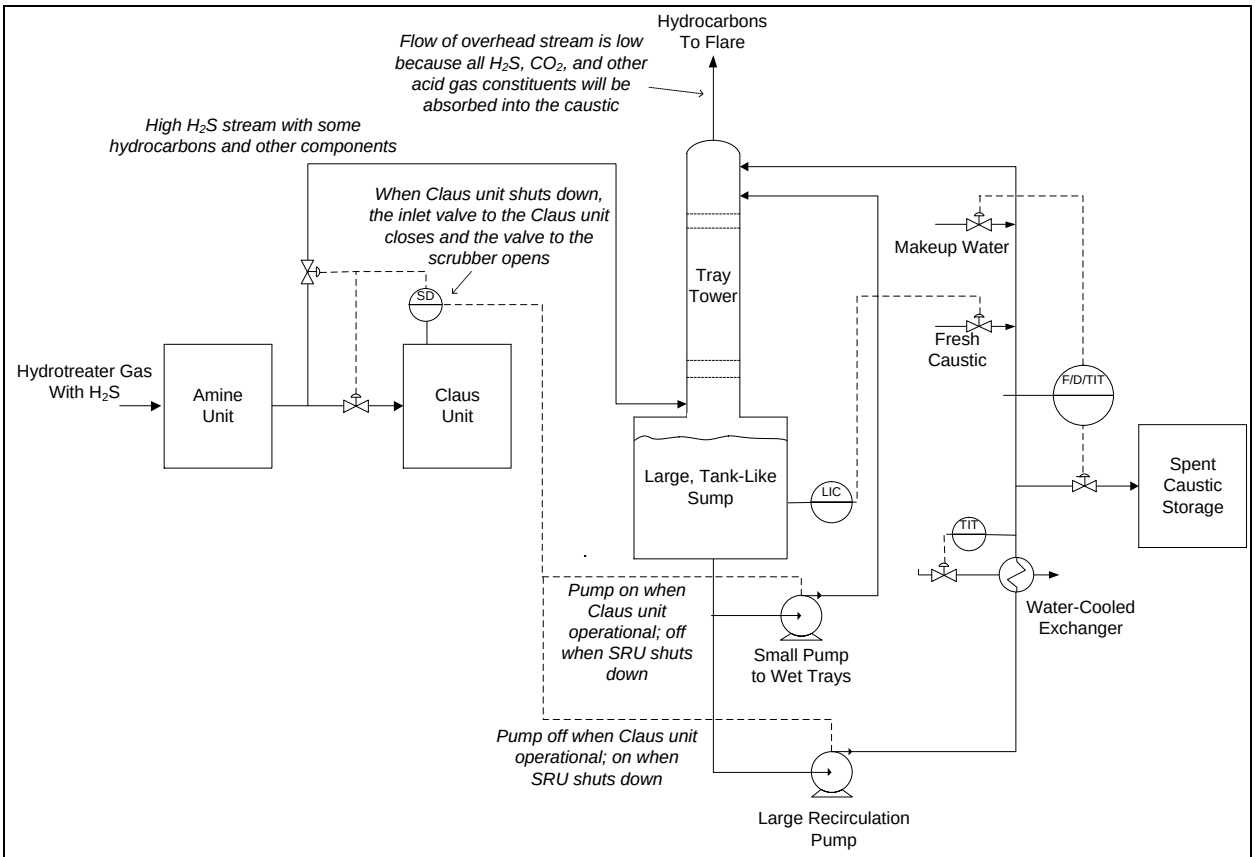

Figure 2. Caustic Scrubber Design for Backup Use to Claus Unit

A key aspect in the design of a typical backup Claus scrubber is that the gas flow drops significantly (to near zero) at the top of the tower as nearly all of the H_2S and other acid gas is absorbed in the caustic. Issues with mass transfer at the top of the tower due to low flow are

offset by keeping the pH high at the top of the tower. Since the high-strength caustic enters the top of the scrubber where there is little H_2S left, the equilibrium should drive the remaining H_2S to near zero (removal of 99+%), even though there is little gas flow. Any light hydrocarbons or other non-acidic species (e.g., NH_3) left in the overhead gas could be flared. Even though excess caustic would typically be used to meet treatment specifications, and a large amount of caustic must be used when in operation, the infrequent use of the unit can make caustic scrubbing a feasible option.

Backup scrubbers can also be designed to accommodate the continuous scrubbing of a small H_2S load (e.g., flash and storage tank vents) while being available (by turning on the large recirculation pump loop) to treat the full amine plant acid gas stream.

4.2 Caustic Scrubbers with Dual Recirculation Loops (Strong-caustic Section)

When deep removal of H_2S is required, and it is not desired to use a large excess of NaOH for economic or product quality reasons, a dual-loop system – containing two separate loops of recirculating caustic in the column – can be designed (Figure 3). Fresh caustic is fed to a top loop, which operates at a relatively high pH and serves as a polishing section to maximize H_2S removal. Caustic overflows from the top section to the bottom section. The bulk of the H_2S removal is done in the bottom recirculation loop which operates at a lower pH. The specification of dual-loop systems for H_2S removal is sometimes avoided because of their greater complexity and cost, but they offer the possibility of very low outlet H_2S concentrations with less caustic consumption and better product quality (i.e., more NaHS and less Na_2S) than would be the case with a single-loop system. Although dual-loop systems offer lower caustic consumption for H_2S removal than single-loop systems, dual-loop systems are not well suited for gas streams that contain a relatively large amount of CO_2, relative to H_2S.

In the design of the system – especially for the low pH loop and if the system is operated at higher temperatures – the chemical equilibrium of the system must be considered in design calculations. Particular care should be taken in the application of literature HTU/K_ga data to ensure that the data are applicable to the system being designed, and it must be recognized that the equilibrium partial pressure of H_2S above the liquid phase represents the minimum H_2S partial pressure that can be achieved in the treated gas.

As an example, a refiner had an existing caustic scrubber that produced a high quality NaHS product (up to 45 wt%) that was sold locally. The inlet gas contained 44% H_2S, 20% H_2, and the balance C_1-C_5 hydrocarbons; the gas flow rate was 830 Mscfd (14 LTPD) at 120°F and 80 psig. The outlet gas H_2S specification was only < 2% so a single-loop design was used while minimizing caustic consumption. The main unit experienced frequent shut downs on the order of 6 hours per week because of plugging issues. The contactor in this unit was operated in an unusual manner (liquid filled) to help minimize downtime. A second scrubber was designed by Trimeric for this gas stream. The scrubber was designed for multiple uses, including treating the 2% H_2S gas from the main unit down to 80 ppmv (total equivalent sulfur load of about 0.3 LTPD), and serving as a backup to the main scrubber when it shut down, thereby potentially treating the full 14 LTPD load. The new scrubber was originally designed to operate in a single loop with excess NaOH to ensure that the H_2S abatement is met and, thus, the ratio of Na_2S to

NaHS in the product would be high. A strong-caustic section (dual-loop design) was then evaluated with the goal of removing H_2S to 80 ppmv while producing a product with minimal Na_2S. However, when treating from 2% to 80 ppmv H_2S, the product stream is small (0.5 gpm) so it can easily be recycled to the main scrubber without concerns of negatively impacting overall product quality. Also, during times when the new scrubber acts as a backup to the main scrubber (producing a spent caustic product stream of 20 gpm), the poorer quality NaHS product can be stored and slowly bled back to the main scrubber when it comes on line. Since the product from the new scrubber is recycled to the main scrubber, the strong-caustic section was not required and the refiner opted to go with the simpler design.

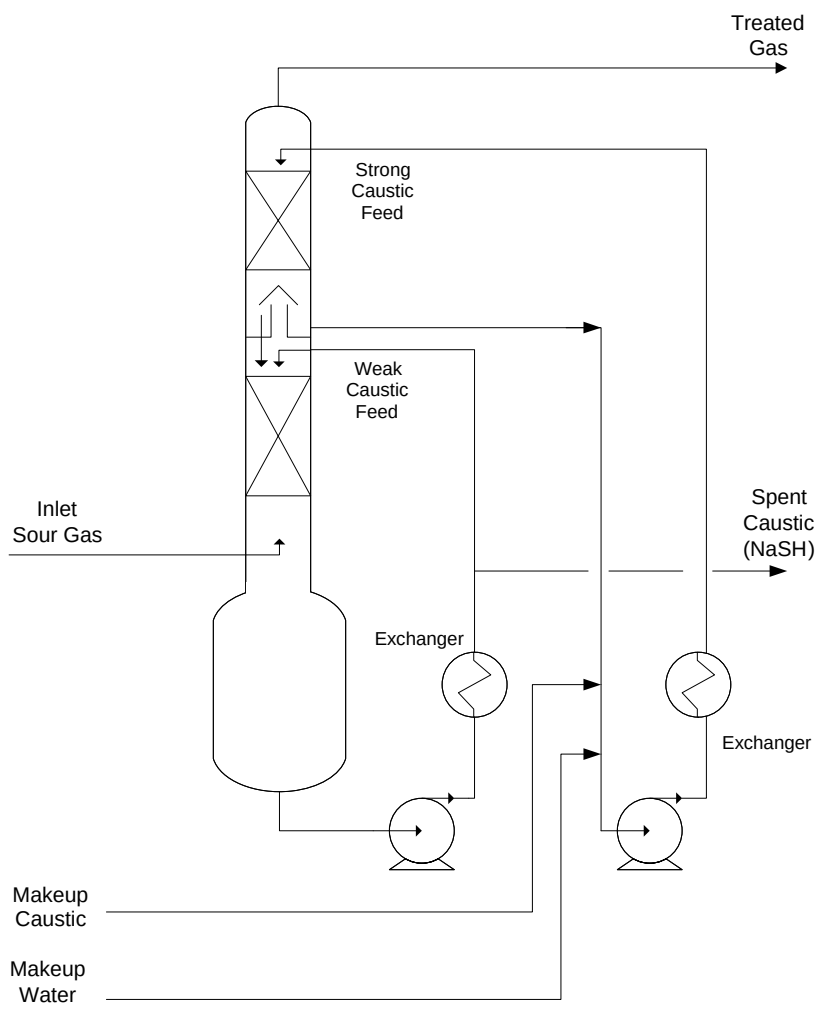

Figure 3. Caustic Scrubber Column with Dual-Loop Configuration

4.3 Selective Scrubbing of H2S in the Presence of CO_2

Figure 4 shows a flow diagram for a short-contact-time (SCT) scrubber designed for selective removal of H_2S from gases that contain CO_2. The SCT process can treat gas with percent levels of both H_2S *and* CO_2 at approximately ambient temperature and is designed to make the necessary H_2S removal while minimizing caustic consumption and CO_2 absorption. The CO_2 to H_2S ratios are typically less than 5:1 in this process, with lower ratios allowing for deeper H_2S removal while maintaining sufficient quality in the spent caustic product. Since H_2S can be absorbed much more quickly than CO_2 at high pH, selective H_2S removal is accomplished by limiting the contact between the gas and liquid, usually using a static mixer. The static mixers are usually implemented so that the gas and caustic solution flow through the contactor in the vertical, downward arrangement to better promote mixing of the gas and liquid phases, minimize pressure drop, and minimize unwanted extra piping that would provide undesired additional contact time after the contactor. Less CO_2 pick up helps avoid operating issues (potential for solid Na_2CO_3 formation and plugging), and minimizes unnecessary caustic usage while improving NaHS product quality.

Some key design features for a SCT system are discussed below.

- **Gas-Liquid Contact** – Venturis, concurrent spray towers, and in-line mixers are among the technologies that can be applied to the SCT system. Superficial contact time of the gas in a range of 0.01 to 0.2 seconds is typical.

- **Flexibility in Contactor Design** – Since limiting the contact of the gas and liquid phases is a critical design feature, if the gas flow rate and/or H_2S and CO_2 content of the gas are not well defined or known to vary greatly, it is important that the contactor device be designed with some flexibility. Static mixer contactors can be designed so that sections of contactor elements that can be added or removed after startup to meet the H_2S treatment specification, and can be readily modified to respond to changes in inlet gas conditions.

- **Vapor / Liquid Disengagement** – The gas and liquid leaving the contactor need to disengage quickly to stop mass transfer. Thus, the contactor must be mounted very closely to, or directly on the vessel. Any piping/fittings necessary between the contactor and the disengagement vessel should be as short as possible.

A high quality NaHS product can only be produced in a single-stage SCT unit when the CO_2:H_2S ratio is not too high and the H_2S content of the treated gas is not too low. If this is not the case, then a two-stage system may be necessary (Figure 5). For a two-stage design, various approaches can be taken, depending upon the H_2S removal requirements and the ratio of CO_2 to H_2S in the feed gas. In one approach, the product from the second stage can be overflowed to the first stage; in alternate approach, the product from the second stage can be removed as a low-quality NaSH or waste material. For cases when the ratio of CO_2 to H_2S in the feed gas is high and it is required to remove H_2S in the treated gas to very low levels, it may not be feasible to produce an acceptable quality NaHS product regardless of the number of stages used, resulting in the potential need to remove the spent caustic from the second stage (which would be high in carbonates) as a waste or low quality NaHS product.

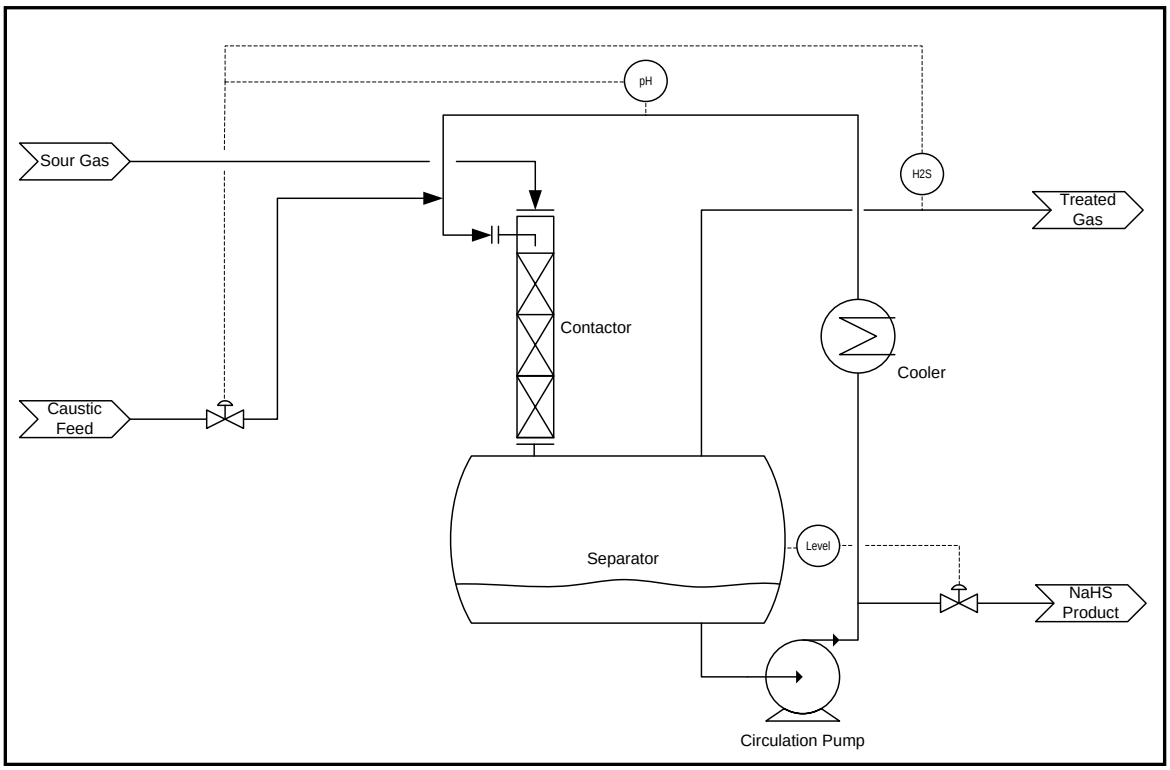

Figure 4. Short-Contact-Time Scrubber (Single Stage)

The two-stage SCT system is analogous to the dual-loop conventional scrubber column system. The fresh caustic would be fed to the second stage (relative to the gas flow path) and the second-stage spent caustic solution fed by overflow to the first stage. The second stage can thus be operated at a higher pH (e.g., 13-14) than the first stage (e.g., 10-12), resulting in the capability to achieve deeper H_2S removal. pH control in the first stage is critical since too high a pH can result in higher than desired Na_2S concentrations and possible precipitation of this solid from solution; too low a pH can result in poor H_2S removal and/or precipitation of sodium bicarbonate.

The key to designing a SCT unit is the selectivity predictions that involve complex calculations to determine the mass transfer enhancement factors for H_2S and CO_2 as well as the number of transfer units (NTUs) and removal efficiencies for these compounds. Calculation methods for the enhancement factors have been described in the literature. Trimeric recently used this approach to design the caustic scrubbers used for the selective treating applications described below.

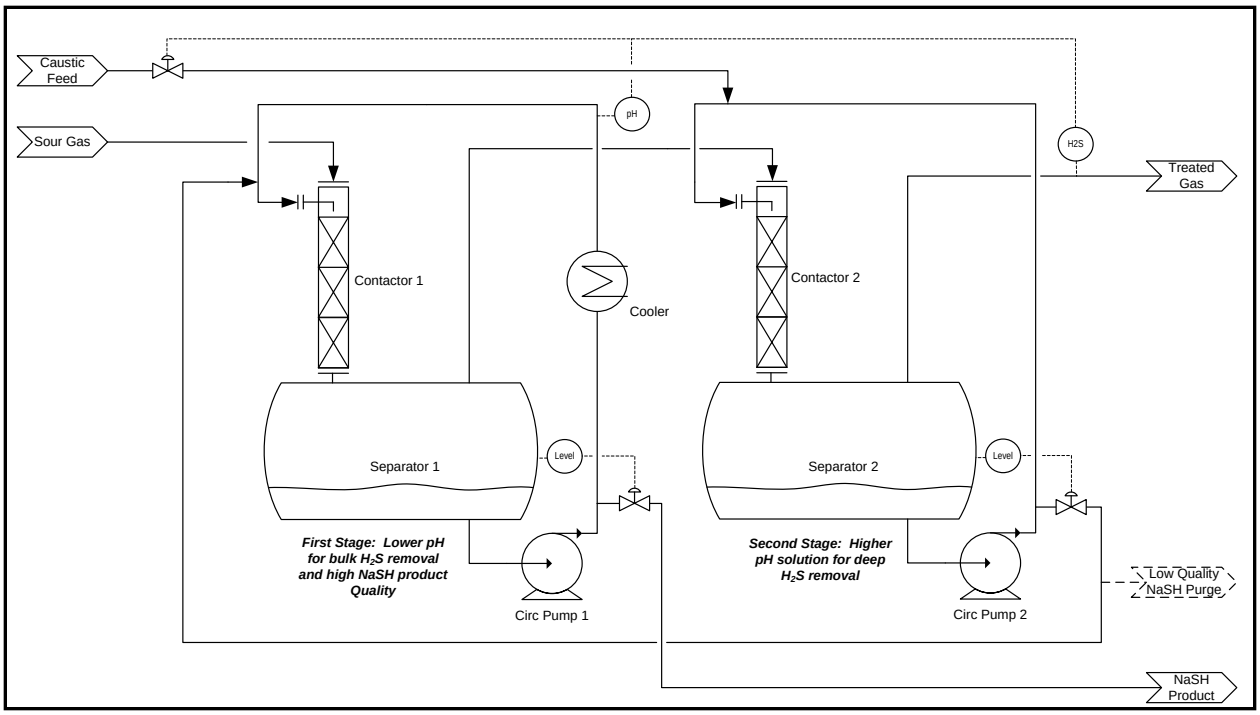

Figure 5. Two-Stage, Short-Contact-Time System

A SCT unit was designed for a fuel gas stream at a refinery that had highly variable flow rate (350 – 850 Mscfd), H_2S content (0.7 – 4%), and CO_2 content (2 – 3.5%) at 50 psig. The H_2S was to be removed to < 160 ppm. Initial calculations showed that a two-stage unit would allow for the required H_2S removal to be achieved while producing a good NaHS product. However, it was decided to initially build a single-stage unit to minimize capital cost and operating complexity. A high pH is required to meet the treatment specification in a single-stage unit, so more of the absorbed H_2S would be converted to Na_2S in the caustic solution potentially resulting in NaHS product specifications not being met. The unit also operates with a dilute solution (20% NaOH diluted to 10-15%) to minimize problems with the fluctuation gas feed composition and flow rate. The spent caustic from this unit is not of high quality, but it is blended with other higher quality NaHS streams so that it may be sold. The unit was designed with multiple (3) contactors to handle the large variation in gas feed flow rate and composition, and the contactors were designed with to be easily removed for modification or cleaning. The unit has been operating continuously for a few years with no significant downtime (the use of multiple contactors allow for cleaning precipitated solids out of the contactors occasionally as needed while the system is on-line). Data from the SCT unit were collected to compare to equilibrium and kinetic modeling predictions and to performance information provided by the static mixer vendor. Details of the selectivity modeling and comparisons with the SCT data from this unit are provided in the "Modeling Caustic Scrubbers" section of this paper.

Another SCT unit was designed for a refinery fuel gas stream with flow rates ranging from 160 to 230 Mscfd, H_2S at 1 to 10% and CO_2 at 0.2 to 1%. The unit operates at 50 psig and <160 ppm outlet H_2S is required. Again, a two-stage system was determined to be the best way to meet the low outlet H_2S specification and produce a NaHS stream that could be sold by itself

except for times when the H_2S:CO_2 ratio was particularly low or during low load. During these times, the Na_2S and Na_2CO_3 would exceed the product quality limits. Because of this, it was decided that the NaHS stream from the SCT unit would be combined with a NaHS stream from a different caustic unit at the refinery to make a consistently saleable product (e.g., 23% NaHS and less than 2% Na_2S and Na_2CO_3).

The design gas-liquid contact times in the SCT static mixer units discussed above ranged from roughly 0.06 sec to 0.11 sec. However, the gas/liquid contact must be carefully evaluated for each application in order to achieve a good design.

SCT units have also been designed for cases where the gas was almost entirely H_2S and CO_2 so that significant quantities of the H_2S were removed and the gas flow rate changed considerably. This can have an impact on the selectivity calculations as discussed later in this paper.

4.4 Specialty Design for H_2S Removal in the Presence of Other Gas Contaminants

Figure 6 shows a special design that was developed to remove H_2S from a sour water stripper overhead stream that also contains NH_3 and water vapor at low pressure and high temperature. A sour water stripper operates with reflux and produces an overhead stream at ~13 psig and 191°F. The sour off-gas is treated in a two-stage system. A caustic scrubber is used to remove H_2S from the gas, after which the spent caustic is sent to a second tower where steam strips physically absorbed ammonia out of the spent caustic solution in order to maintain spent caustic product quality. If the ammonia content of the spent caustic is too high, its value could be reduced and potentially eliminate sale in some markets. H_2S loss in the stripper is minimal because of the high pH of the solution. The treated vapor streams, now essentially free of H_2S but still containing large amounts of water vapor and NH_3, are combined and sent to an ammonia destruction device.

As shown in Figure 6, caustic (50 wt%) is fed to the caustic scrubber unit, and a cooler is operated on the recirculating liquid to condense some water vapor from the feed gas stream. Although low temperature operation is generally preferable for H_2S scrubbers (results in better H_2S abatement and lower corrosivity), it is not feasible to operate at lower temperatures when treating a sour gas that is mostly steam. Operation of the scrubbing solution at lower temperature would result in the condensation of most of the steam, and excessive dilution of the spent caustic NaHS product; excessive absorption of ammonia into the NaHS would also occur at these conditions. Excessive dilution of the product was not desired because dilute NaHS typically has little or no sales value, and the stream would have to be disposed of as a waste.

The cooler is designed to be controlled such that sufficient water vapor is condensed to dilute the caustic to the equivalent of approximately 20 wt%. The sulfur load for this case was 1 LTPD.

The high operating temperature in this design requires the use of a significant amount of excess caustic to achieve deep H_2S removal. The use of excess caustic results in the product having a relatively low quality, due to the high concentration of Na_2S. Another contributor to the poor product quality is the system operating pressure (~10 psig); more excess caustic (higher pH)

is required to achieve the same outlet H_2S concentration for a low pressure system compared to a high pressure system. For this particular application, a portion of the high pH partially-spent caustic product (partially spent caustic) stream would be used elsewhere in the refinery, and a portion of the stream could be sold as a low-quality / low-value product.

Another stripped caustic scrubber design (SCS) was produced for a different refinery that also needed to remove H_2S from fuel gas to <160 ppmv and then strip the ammonia from the caustic sulfide product stream using steam. The sulfur load for this case was on the order of 0.5 LTPD. The upstream sour water stripper in this case did not have a reflux system so the feed gas to the SCS unit was at 235°F and ~10 psig. The ammonia product was sent to a boiler firebox. The high pH product stream was used elsewhere at the plant to recover the alkalinity value and convert it to a typical NaHS product for sale.

The decision to operate the upstream sour water stripper with or without reflux should be evaluated when possible with respect to how the sour gas stream will be handled. Operating with a reflux lowers the temperature of the sour water overheads stream, which may allow for less expensive materials to be used in the stripped caustic scrubber system. It also produces a smaller overhead gas stream. However, if the SWS is refluxed, then more steam is required in the bottom of the sour water stripper tower, and more NH_3 gets absorbed into the caustic solution in the downstream caustic scrubber.

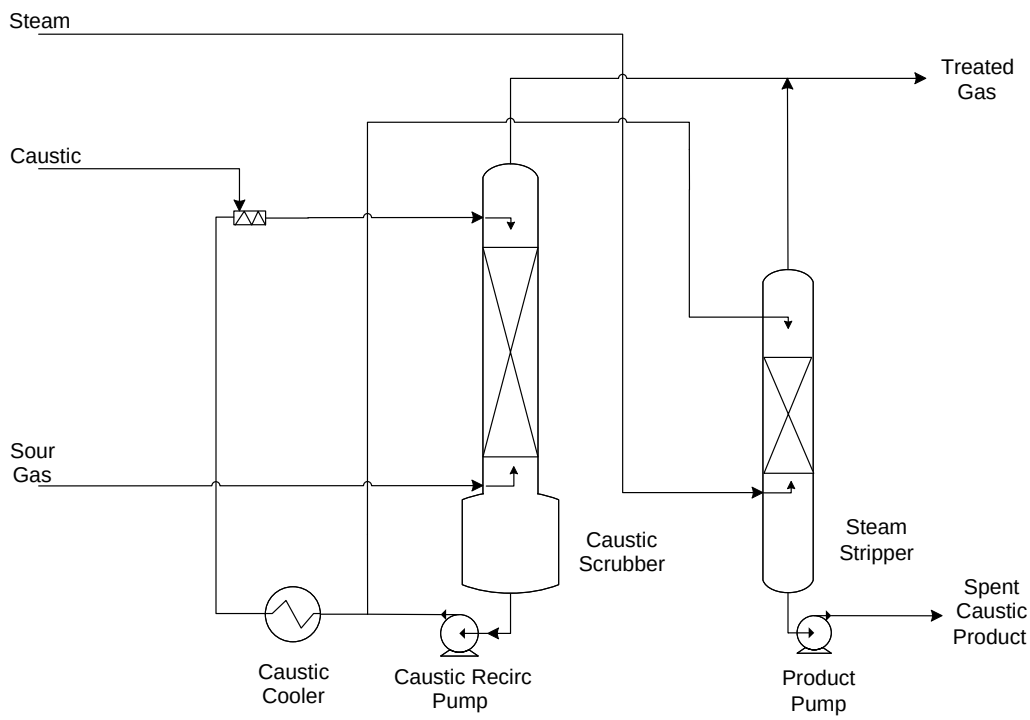

Figure 6. Stripped Caustic Scrubber for a Sour Water Stripper Overhead Stream

5 General Design Issues

Each of the scrubber systems discussed above has some unusual characteristics that were considered during the design phase of the work. These design issues are presented below.

5.1 Aqueous Equilibria and Solubility

One of the primary concerns in the design and operation of caustic scrubbing units is the precipitation of sodium salts of carbonate and sulfide. Knowing the solution properties at all operating conditions is critical to having a caustic scrubbing unit run smoothly, with minimal issues from solids precipitation. The equilibrium of the various forms of CO_2 and H_2S as a function of solution pH (based on their pKa in pure water at 25°C) are shown in Figure 7. NaHS product solutions are usually required to have low Na_2S content with less than 3 or 4wt% being common. For this reason, the pH of the caustic solution must be controlled so that the majority of the H_2S will be in solution in the HS^- form. If the pH is too high (roughly above pH 12 at 25°C), then a significant fraction of the HS^- converts to S^{2-}. Solubility of the reaction products is also a concern, since the salts of the different aqueous species of H_2S and CO_2 have different solubilities.

Figure 7 also shows the typical operating range for solution pH. Operation at lower pH ranges is associated with poor H_2S removal and excessive precipitation of carbonate solids (if there is CO_2 in the feed gas). Operation at higher pH ranges results in unnecessarily high caustic usage and the presence of high amounts of Na_2S in the product liquid.

Figure 8 shows the general trends of salt precipitation in the scrubbing solution as a function of: solution pH, temperature, CO_2 absorption amount (relative to the H_2S absorption), and the caustic feed strength (i.e., the concentration of NaOH in the fresh caustic). The precipitation line is this graph was created for a case when 22 wt% caustic was used absorbing H_2S and CO_2 at a ratio of 1.9:1. However, this is intended to be a general representation of behavior of the system in this region of conditions.

Figure 9 is similar to Figure 8, but would apply to systems where there is no CO_2 in the gas. It highlights the range of concentrations, pH, and temperature at which sodium sulfide precipitation can be an operating issue, particularly as it is attempted to make a higher concentration NaHS product.

A few conclusions from Figure 8 and 9 are:

- **Control of solution properties to prevent carbonate precipitation**. The pH and caustic strength strongly influence the solubility of the salts in the product solution. If there is a significant concentration of carbonate in the solution, it is important to maintain the solution in the basic region to avoid the precipitation of sodium bicarbonate salts; these salts are particularly troublesome since they tend to stick to metal surfaces and are not readily dissolved by raising the solution temperature.

- **Control of solution properties to prevent sulfide precipitation**. As shown in Figure 9, higher pH values increase the amount of sodium sulfide relative to NaHS. Because sodium sulfide has a limited solubility in water, operation at higher pH can result in the precipitation of sodium sulfide. Although the effect is not as dramatic as on the solubility of carbonate, it is still clear that very high pH values are better avoided since it raises the precipitation temperature. Higher caustic feed strength also decreases sulfide solubility. However, unlike with bicarbonate precipitation, higher solution temperature can be very useful for preventing sulfide precipitation. To minimize sulfide precipitation problems, caustic strengths of 20 wt% or less are typically employed. Higher caustic strengths can be (and are) used, but extra care should be taken to ensure that the unit will not operate under conditions that favor precipitation.
- **The absorption of CO_2 has a large impact on potential precipitation**. As the absorption of CO_2 decreases, the potential for carbonate salt precipitation is reduced. Achievement of a high selectivity of H_2S absorption over CO_2 absorption can therefore be important for a variety of reasons: maintenance of NaHS product quality, minimization of wasted caustic, and minimization of the potential for plugging of the system with carbonate salt solids.

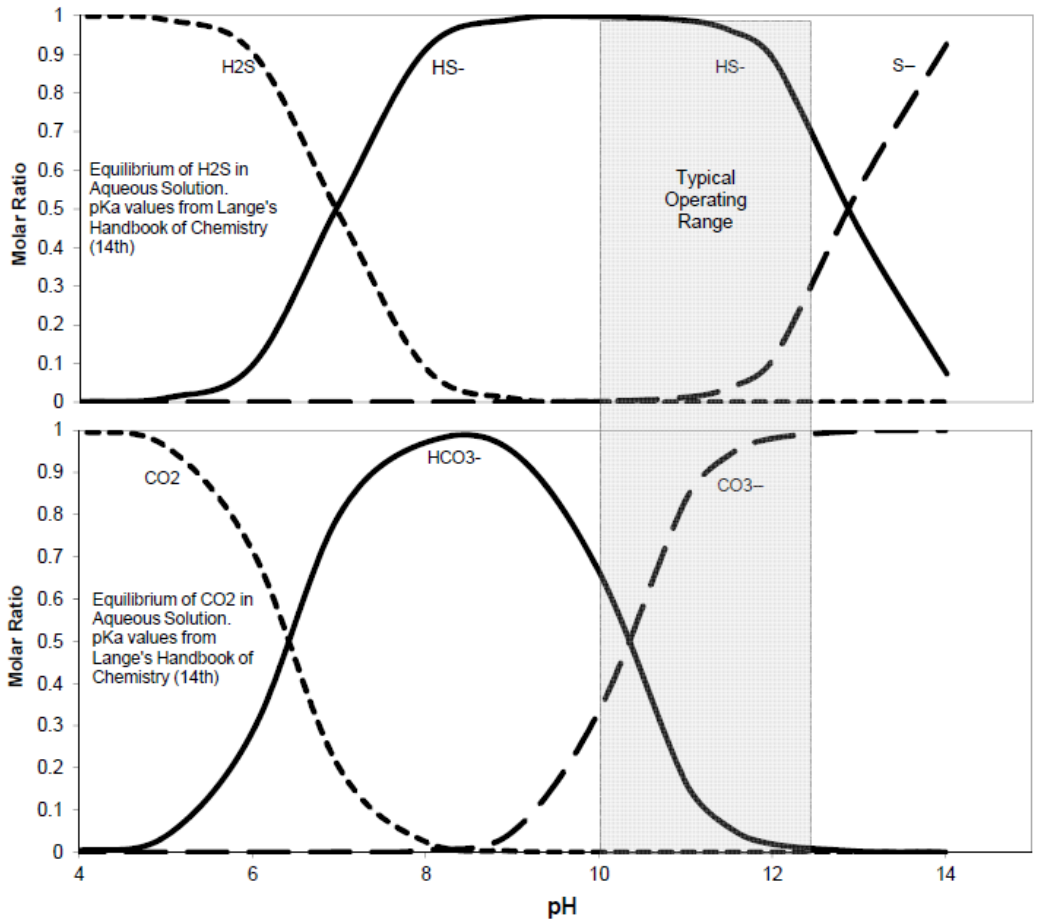

Figure 7. CO_2 and H_2S Speciation in Aqueous Solution (based on pKa values from Ref. 1)

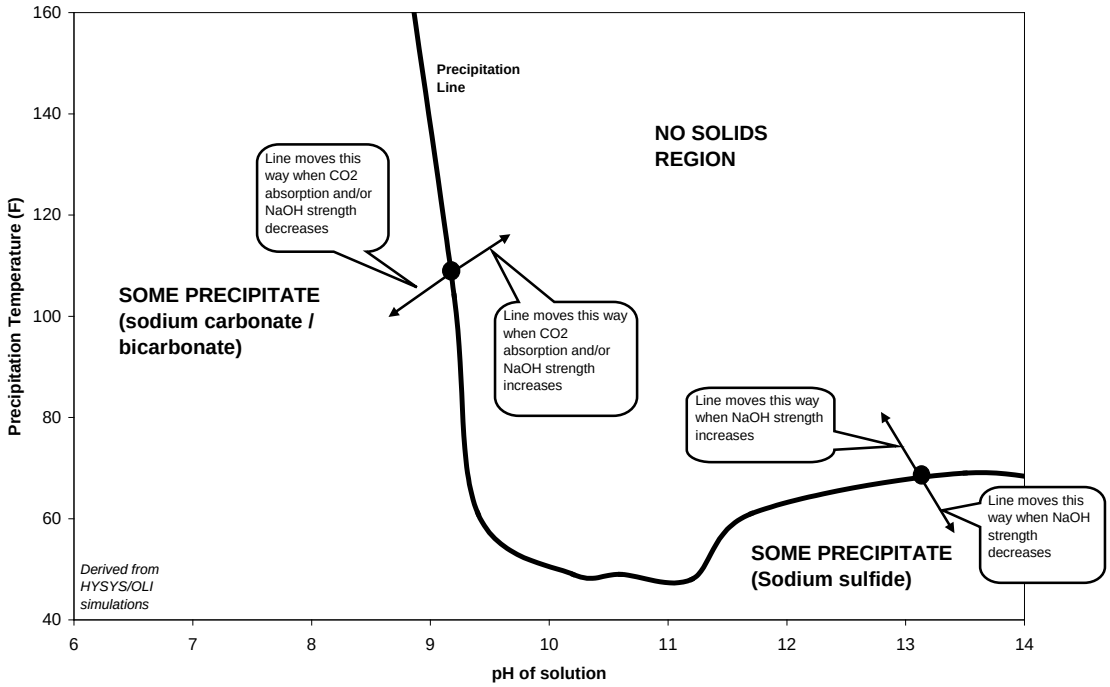

Figure 8. Example of General Trends of Solubility Limits for a Particular Scrubbing Solution. Systems where the gas contains both H_2S and CO_2.

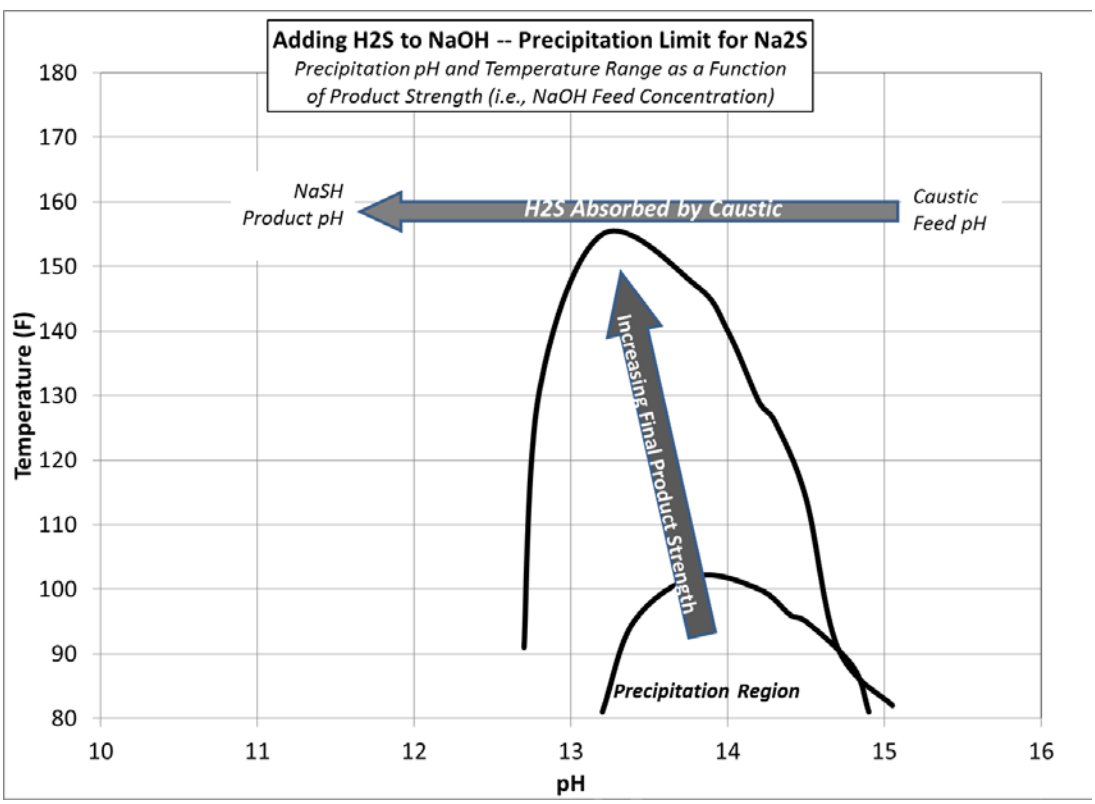

Figure 9. Example of General Trends of the Solubility Limit for a Particular Scrubbing Solution. System where the gas contains H_2S (no CO_2) showing the solubility limit of Na2S.

5.2 Enthalpy of Reaction

Absorption and neutralization of H_2S is highly exothermic (approx. -14 kcal/gmol for reaction 1). If a gas containing a high concentration of H_2S is scrubbed, cooling will usually be required on the circulating solution to maintain reasonable temperatures in the contacting device. The use of solution recirculation is important in the control of the reaction heat. The recirculation ratio of the solution (i.e., the relative amount of solution recirculated relative to the amount of fresh makeup solution) is typically dictated by two requirements: i) the need to keep the packing wetted or trays filled and achieve good gas-liquid contact, and ii) the need to provide thermal mass to absorb the reaction heat.

The solution recirculation rate, once the minimum rate has been established to provide for gas-liquid contacting, is generally set based on an assumed maximum allowable solution temperature in the column. This topic is discussed further in the following sections.

5.3 Operating Temperature and Pressure

Operating temperature, especially higher operating temperatures, can potentially limit both the maximum H_2S removal and the NaHS product quality. At higher temperatures, the need to achieve a specific requirement of H_2S content in the treated gas is often at odds with the need to produce a high quality NaSH product. The equilibrium partial pressure of H_2S in the gas phase increases with temperature, so at higher temperatures the removal of H_2S from the gas phase may be equilibrium limited. Additionally, if the pH range is kept low enough to produce NaSH solution with low Na_2S content, the equilibrium partial pressure of H_2S may limit the gas treatment efficiency. The operating temperature is also important with respect to the materials of construction that can be used, as discussed in the following section.

In general, equilibrium calculations predict that achieving a given H_2S removal from the feed gas requires more caustic at higher operating temperatures compared to lower operating temperatures.

The operating pressure of the scrubber may also be important. At a fixed scrubbing solution pH and temperature, and low to moderate total pressures, the partial pressure of H_2S in the gas at equilibrium conditions will be approximately constant regardless of the system pressure. The lowest concentration of H_2S in the treated gas that can be obtained is determined by the equilibrium condition, which can be expressed as: $y_i = P_i/P$, where P_i is the equilibrium partial pressure of the H_2S, P is the total pressure and y_i is the equilibrium concentration of H_2S in the treated gas. As the system pressure rises, the equilibrium-limit concentration of H_2S in the treated gas becomes lower. Therefore, higher operating pressures allow for H_2S removal goals to be met more easily.

Some predictive equilibrium calculations showing the effect of operating pressure and temperature on an example caustic scrubber is given in Table 2.

Effect of Operating Temperature						
Operating Temperature F	Operating Pressure psig	Inlet H2S lbmol/hr	Required NaOH lbmol/hr	pH	Deep Outlet H2S ppmv	Molar Na2S:NaSH Ratio
100	4.5	1.48	1.65	12.8	30	0.029
125	4.5	1.48	1.8	12.8	30	0.062
150	4.5	1.48	2.15	12.8	30	0.17
175	4.5	1.48	2.65	12.8	30	0.41
200	4.5	1.48	2.96	12.7	30	0.67
Effect of Operating Pressure						
Operating Temperature F	Operating Pressure psig	Inlet H2S lbmol/hr	Required NaOH lbmol/hr	pH	Deep Outlet H2S ppmv	Molar Na2S:NaSH Ratio
200	4.5	1.48	2.96	12.7	30	0.67
200	85	1.48	1.9	12.0	30	0.12

Table 2. Effect of Operating Temperature and Pressure on an Example Caustic Scrubber Case (based on calculated equilibrium data).

5.4 Corrosion and Materials of Construction

Although caustic is not highly corrosive to carbon steel at moderate temperatures, the presence of bisulfide and/or carbonates may cause significant corrosion rates, leading to a preference for stainless steels, or higher alloys, in liquid service. Chloride present in feed caustic may further limit metal selection.

The caustic strength and operating temperature must also be considered when selecting metals for the scrubber units. At temperatures greater than roughly 212°F, even 304 and 316 stainless steel alloys may experience significant caustic-induced corrosion rates, leading to a preference for higher alloys (e.g., AL-6XN, Alloy 20, Alloy 800) at higher temperatures. This is especially important for the stripped caustic scrubber design shown in Figure 6 since it can operate above 212°F. Additionally, "hot zones" may exist in 1) caustic scrubber towers where the sour gas enters the vessel especially hot [~235°F from the SWS without upstream reflux] and 2) the ammonia stripper tower due to the temperature of the stripping steam (50 psig at 298°F). These "hot zones" could cause erratic corrosion and may require special material of construction, more stringent corrosion allowances, and/or periodic inspections depending on the alloy used. Consultation with a corrosion scientist is recommended for such high-temperature caustic scrubber designs.

Furthermore, some refiners have experienced rapid corrosion in the in-line static mixers used to blend fresh 50 w% caustic with water or recirculating solution. Since it can be difficult to mix liquids of different densities such as these, static mixers are typically used. Because of the observed rapid corrosion, AL-6XN is sometimes selected for the material of construction of this small in-line mixer. Refiners should rely on their experience in selecting appropriate materials in this area.

5.5 System Control

The proper control of system variables greatly aids in the operation of a caustic scrubbing unit. One of the more important issues is how the addition of fresh caustic to the system is controlled. Addition of caustic can be done via pH control, H_2S concentration control on the outlet gas, or both. If the feed gas is highly variable in nature, then the use of pH as the primary control input may become particularly valuable.

pH probes must be routinely maintained (cleaned and recalibrated) in order to be accurate enough for use in process control. Probes of varying levels of automation are available: simple units where the operator performs manual maintenance/cleaning, and automated probes in which the cleaning and recalibration are automated. The materials used in the pH probe should be verified with a vendor as being suitable for caustic service. Outlet gas analyzers are also important to aid in controlling the caustic feed and also to ensure that the H_2S abatement requirements are met. If the outlet H_2S content is not continuously monitored, gas samples should be routinely taken and analyzed. It is usually not desired to greatly overshoot H_2S removal requirements from the feed gas; if more H_2S is removed from the feed gas than required, additional CO_2 could also be absorbed (if present in the inlet gas), and caustic consumption will be higher than necessary.

Other measurable parameters, such as solution density, can aid in troubleshooting and can also be used to control dilution of the caustic feed if desired. Coriolis flow meters are often specified for caustic scrubbers, because they can be configured to output fluid density and temperature in addition to the mass flow rate.

Control of the temperature of the circulating solution may be required. For the treatment of dry or cool gases with low concentrations of CO_2 and H_2S, cooling of the circulating solution may not be needed because the treated gas (and vaporization of some of the water from the caustic solution) may carry away the reaction heat. For more concentrated or hot acid gases, cooling of the circulating solution is usually required to maintain low enough solution temperatures to avoid material of construction issues, and to improve the H_2S removal efficiency. Air or water coolers can be used but provisions must be made to control the operation of the cooler so that temperatures cannot drop to the point where solids could precipitate from solution.

For a water-cooled exchanger, temperature control is usually achieved via the throttling of the cooling water flow rate, rather than throttling of the process side (caustic) flow rate. The control is done this way because the process side of the exchanger is considered to be more fouling-prone than the cooling water side. When doing this, care must be taken regarding the potential for achieving relatively high temperatures on the cooling water side due to low cooling water flow rates, which can result in fouling; if the higher cooling water temperatures in the exchanger may occur, changes to the cooling water treatment chemicals or the use of a separate tempered water loop should be considered.

For air cooled exchangers, it is critical to avoid overcooling of the process liquid – which would cause precipitation of salts – during cold weather. Air coolers would therefore be

equipped with VFD motors for fans, adjustable louvers, and/or warm air recycle. A startup heater or heater to maintain solution temperature when the unit is not processing gas may also be advisable in cooler climates, and if the unit is not expected to be continuously operating.

Precipitation of carbonate or sulfide salts can occur well above the normal freezing point of water. Therefore, even in warmer climates, heat tracing is essential for liquid-filled dead legs, and all small diameter liquid lines should be (as a minimum) well insulated. Complete insulation and thermostatically controlled heat tracing to maintain desired process temperatures in lines and vessels may be advisable.

Hard-piped flushing connections may also be a very good idea for caustic scrubbing systems. Equipment that is not in use, like a parallel contactor in the short-contact-time device, could be flushed with warm water to prevent salt crystallization.

6 Modeling Caustic Scrubbers

Multiple calculation tools are required for the design and performance prediction of caustic scrubbers. Apart from routine material balance calculations, two more complex issues are critical: equilibrium and kinetics. Accurate modeling is essential to the design of caustic scrubbing units because the chemistry and mass transfer of the process is rather involved. If solution properties are not well understood, it will be difficult to know the conditions to control the scrubber to avoid solids precipitation, make H_2S treat, and to selectively scrub H_2S in the presence of CO_2.

6.1 Equilibrium Prediction

Equilibrium calculations for caustic scrubbers define the limiting case for H_2S and CO_2 removal from the feed gas. Additionally, equilibrium calculations are also used to determine solubility of salts, and the distribution of the various ionic species in solution.

Although many software packages used to simulate refinery hydrocarbon systems aren't appropriate for use in the prediction of caustic scrubber equilibrium, some calculation tools are available to effectively model these electrolyte systems. In modeling these systems or parts of these systems, Trimeric has used an electrolyte equilibrium model, OLI properties package as an add-in in HYSYS, the electrolyte-NRTL properties package in HYSYS and Aspen Plus, and the sour-API model in WinSim DESIGN II.

A parameter that significantly impacts the H_2S removal predicted by calculations and simulations is the second dissociation constant for H_2S. The dissociation constants, for convenience referred to by the pK_a values, are defined below.

$$K_{a1} = \frac{[HS^-][H^+]}{[H_2S]_{(aq)}} \qquad K_{a2} = \frac{[S^{2-}][H^+]}{[HS^-]} \qquad (5)$$

$$pK_{a1} = -\log_{10} K_{a1} \qquad pK_{a2} = -\log_{10} K_{a2} \qquad (6)$$

There is a wide range of variability in the literature for the second dissociation constant (pK_{a2}) of H_2S with literature values (25°C) range from 11.97 to 19. The value of pK_{a2} has a significant impact on the equilibrium modeling of this system with respect to the H_2S removal that can be achieved, the amount of NaOH required to absorb a given amount of H_2S, the speciation (i.e., relative amounts of sulfide and bisulfide) of the product liquid, and the formation of solid sulfide species. A pK_{a2} value that is too low causes models to predict that a significantly greater-than-actual amount of caustic will be required to achieve the desired H_2S removal from a gas stream, while also causing models to predict a liquid product that has a considerably higher Na_2S to NaHS ratio than will actually be present.

A reference[2] presents work that was done to compare this range of pK_{a2} values to some literature and plant operating data. That paper provides a detailed discussion of the data and the comparisons that were made. Ultimately, a pK_{a2} value of 14.9 was determined to be reasonable for use in the in-house equilibrium model to design caustic scrubber units.

6.2 Kinetics Prediction for Short Contact Time Selective Scrubbers

As discussed previously, the difference in the kinetics of the absorption of CO_2 and H_2S is the primary reason for the potential selective absorption of H_2S in the short-contact-time unit (SCT) design. Selectivity is defined here as:

$$Selectivity = NTU_{H2S} / NTU_{CO2} \qquad (7)$$

A few different approaches can be used to determine the absorption rates of H_2S and CO_2, and define the selectivity of an SCT unit: predictive calculations based on absorption theory, equipment vendor calculations, and comparison with operating plant data.

It is typically desired to base the design of new equipment on models that have been proven by operating plant data. Given the relative scarcity of available data from operating SCT units and proven design techniques, Trimeric initially sought other methods for designing these contactor devices. One static mixer equipment vendor (Sulzer) has a proprietary method for designing SCT contactors and predicting CO_2 and H_2S selectivities. These vendor calculations were compared to a theoretically-based method from the literature as described below.

The calculation of the kinetics of the absorption of CO_2 and H_2S were estimated based loosely on the methods described by Bontozoglou and Karabelas[3,4]. The method involves numerically solving the differential equations that govern the diffusion and reaction kinetics and reaction equilibrium of the various chemical species, as they diffuse between the bulk liquid and the liquid/gas interface subject to appropriate boundary conditions. A reference[5] discusses the details of the selectivity model used by Trimeric.

The calculations done using the theoretical model gave results that predicted removal rates and H_2S selectivities of the same order of magnitude as those predicted by the equipment vendor; the equipment vendor estimates tended to be more conservative (i.e., predicted lower selectivity) by roughly 50 to 80%.

6.3 pK_{a2} and Selectivity Comparisons with Data from an Operating SCT Unit

Trimeric has designed SCT units for refinery fuel gas streams (see the "Selective Scrubbing of H_2S in the Presence of CO_2" section of this paper), and was able to collect some operating and analytical data from one of the units. The data were then compared with predictive methods that were used during design of the unit. A summary of operating data from the plant is shown in Table 3.

Table 3. Operating Data from an SCT Unit

Variable	*Units*	*Data Point 1*	*Data Point 2*	*Date Point 3*
Inlet Gas Properties				
Flow Rate	MSCFD	490	457	494
Pressure	psig	55.3	51.9	54.9
Temperature	F	89	93	94
H_2S	Vol %	2.73	1.74	1.63
CO_2	Vol %	3.36	3.4	3.43
Circulating Solution				
Temperature	F	129	135	138
Outlet Gas Properties				
H_2S	ppm	66	149	50
CO_2	Vol %	2.80	2.97	2.79
Gas Treatment Calculated Values				
H_2S removal	NTU	5.65	4.58	5.32
CO_2 removal	NTU	0.18	0.14	0.21
Selectivity		31	34	26
Circulating Solution Properties				
NaSH	Wt %	5	7.8	8.2
Na_2S	Wt %	7.3	6.8	5.9
Na_2CO_3	Wt %	2.4	2.7	3.8
pH		12.8	12.4	12.7

Using the kinetic modeling techniques discussed above, a selectivity of 31 was predicted with the typical operating conditions. As shown in the Table 3, the operating data agreed well with the mathematical model with respect to the selectivity of H_2S absorption over CO_2 absorption. Selectivities calculated from data for the three data sets were 26, 31, and 34. The table also shows that the H_2S is removed to below desired specifications, while little of the CO_2 is removed, which is what is desired in a selective scrubbing unit.

The operating data from the SCT unit were also used to back-calculate the pK_{a2} value for H_2S so that it could be compared with the values used in predictive calculations. The derived pK_{a2} value was ~14.7, which compared well with the pK_{a2} value that was used in the design calculations (14.9).

6.4 NTU Calculations for Different Caustic Scrubbing Scenarios

The number of transfer units (NTU) discussed previously in the selectivity calculations is a mass transfer concept that should be calculated in different ways depending on the situation for a caustic scrubber design. A simple relationship for the NTU is show in equation 8, where y_1 and y_2 are the inlet and outlet concentrations of the gas species being absorbed.

$$NTU = ln(y_1/y_2) \quad (8)$$

This simple relationship is only applicable when the equilibrium partial pressure of the component being scrubbed is zero and the bulk gas flow rate does not substantially change through the column (i.e., relatively low concentration of the gas component being scrubbed).

However, when the equilibrium partial pressure of the gas species being scrubbed is considerable, then there are two distinct cases that should be considered. The first is the case where the equilibrium partial pressure of the gas being absorbed can be assumed to be constant through the column. This is only a good assumption when the relative rate of the recirculation in the column is very high compared to the makeup/purge rate. Then, the NTU relationship in equation 9 can be used, where y_e is the equilibrium gas phase concentration of the species being absorbed.

$$NTU = ln\left(\frac{y_1 - y_e}{y_2 - y_e}\right) \quad (9)$$

The second case is when the equilibrium partial pressure cannot be assumed constant through the column. For situations where there is no solvent recirculation or it is relatively low, the equilibrium partial pressure of the gas being absorbed (y_e) cannot be assumed to be constant and the integral expression in equation 10 for NTU should be used.

$$NTU = \int_{y_2}^{y_1} \frac{dy}{y - y_e} \quad (10)$$

For cases where the bulk gas flow rate changes substantially (e.g., when greater than roughly 10 - 20% of the stream is being absorbed into the caustic solution), then the NTU analysis changes dramatically. The NTU expressions above assume constant bulk gas flow rate. When that is not the case, then equation 11 can be derived.

$$d(Gy)_i = -K_G a_i P y_i A_c dz \quad (11)$$

In equation 11, G is the gas phase flow rate (lbmol/hr). K_Ga is the overall mass transfer coefficient (lbmol/hr-ft^3-atm). A_c is the cross sectional area (ft^2). y_i is the mole fraction and P is the system pressure (atm absolute).

Equation 11 can be simplified to, where n_i is the molar flow of component i:

$$dn_i = -K_G a_i P y_i A_c dz \quad (12)$$

In the SCT design mentioned previously where the H_2S and CO_2 made up the bulk of the gas, equation 12 was used to numerically estimate the H_2S removal and selectivity. The value for K_Ga was obtained using data from the operating SCT unit discussed earlier.

7 Summary

Caustic scrubbers can be designed to effectively and economically remove H_2S from many different sour gas streams at refineries including fuel gas, sour water stripper gas, and off gas with high CO_2 content. The design of the scrubbing unit is determined from many different factors include the H_2S treatment specification and sulfur capacity, disposition for the spent caustic stream (e.g., sold, blended with other streams, disposed of), the gas composition and presence of other components that could be absorbed in the recirculating solution, and general operating temperatures and pressures. These factors must be evaluated through a preliminary performance and economic analysis to determine if caustic scrubbing is viable and, if so, the best flow scheme for the process.

Designs are available to scrub sour gas streams with little to no CO_2 in excess NaOH mode or by minimizing excess NaOH usage. Designs that use excess NaOH are fairly simple and involve recirculation a large amount of liquid to contact the gas in a single loop. The excess NaOH design can meet low outlet H_2S specifications but the spent caustic product quality is poor. Designs that minimize excess NaOH use two recirculation loops; the bottom loop does bulk H_2S removal and the top loop is feed fresh caustic to polish the H_2S to low levels. Special designs have been made to selectively scrub H_2S from off-gas with CO_2. The process minimizes the contact of the gas with the caustic so more H_2S is absorbed than CO_2, which has a slower kinetic rate. Ammonia can be separated from the H_2S in sour water stripper gas using the stripped caustic scrubber approach. It may be possible to develop new designs to separate other unwanted, soluble gas components from the caustic solution should the need arise.

The proper pH range and temperature of the operating solution must be maintained to avoid problems with salt precipitation, to ensure adequate H_2S treat, and to achieve the highest quality NaSH product. Good process control and frequent solution quality monitoring is key. Appropriate materials of construction should be used given the operating temperature and caustic strength used in the system.

Data from the operating SCT plant was used to show good selective removal of H_2S in the presence of CO_2. The selectivity predicted from a model developed based on literature findings compared well with the selectivities calculated from the SCT operating data. The pKa_2 value used in an in-house equilibrium simulator also compared well to the pK_{a2} values obtained with other commercial software using the SCT unit data. Simple relationships used to estimate the NTU for mass transfer cannot necessarily be used in all caustic scrubber designs.

8 References

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