Consider improved scrubbing designs for acid gases

Better application of process chemistry enables efficient sulfur abatement

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Scrubbing of hydrogen sulfide (H_2S) using sodium hydroxide (NaOH) solution is a well-established technology. Since this process uses a solvent that cannot be easily regenerated, caustic scrubbers are most often applied in situations where small volumes of H_2S must be removed. A review of various caustic-scrubber configurations and their applications highlights important criteria to consider when designing H_2S scrubbers for refinery applications.

Background. Using sodium hydroxide solution to remove acid gases including H_2S is a well-proven method that is practiced in many industrial applications. The process uses a solvent, which cannot be easily regenerated. Accordingly, caustic scrubbers are most often applied where low-acid gas (H_2S) volumes must be treated. However, high-quality aqueous sodium bisulfide (NaHS) product can often be sold. Depending on the value of the product solution, caustic scrubbing can be cost-effective at sulfur throughputs as high as about 10 tpd.

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

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

$$NaHS_{aq} + NaOH_{aq} \rightarrow Na_2S_{aq} + H_2O \qquad (2)$$
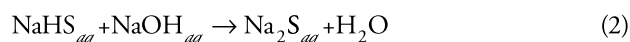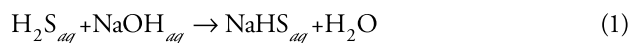
The extent of reactions 1 and 2 (Eqs. 1 and 2) depend on the strength of caustic, with higher pH favoring reaction 2. NaHS can be a valuable product. To maintain product quality, controlling the pH of the spent caustic solution is required so that NaHS is the predominant sulfide species. Carbon dioxide (CO_2) may also be present in gas streams. This compound complicates using caustic for H_2S scrubbing, because CO_2 is readily scrubbed into the caustic as well.

Despite the well-known chemistry of this process and that caustic scrubbers are common in low-sulfur tonnage ranges, there are significant gaps in the background knowledge necessary to design these units effectively. One of the more significant gaps is

the accuracy of the second dissociation constant, K_{a2}, of H_2S in solution that is used in models to predict H_2S removal. This paper will discuss considerations when designing caustic scrubbers for refining and oil and gas applications.

Scrubber designs for sour-gas streams. There are many different possible designs for caustic scrubbers. In selecting a configuration for a caustic scrubber for H_2S removal, several factors should be considered:
- H_2S abatement requirement (ppmv H_2S in product gas)
- Amount of H_2S to be removed (tpd of sulfur)
- Other components in gas that may be scrubbed, e.g., CO_2
- Utilization frequency of scrubber (continuous vs. occasional)
- Disposition of spent caustic (disposal or sale).

Four examples of caustic scrubber arrangements considered for refining and oil and gas applications will be presented.
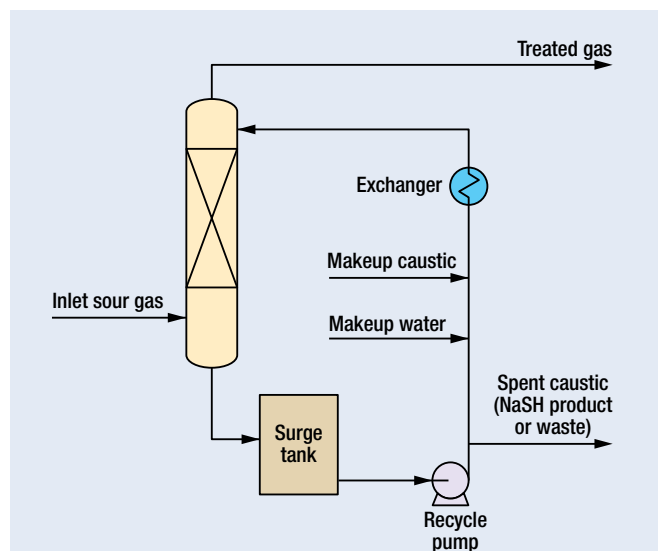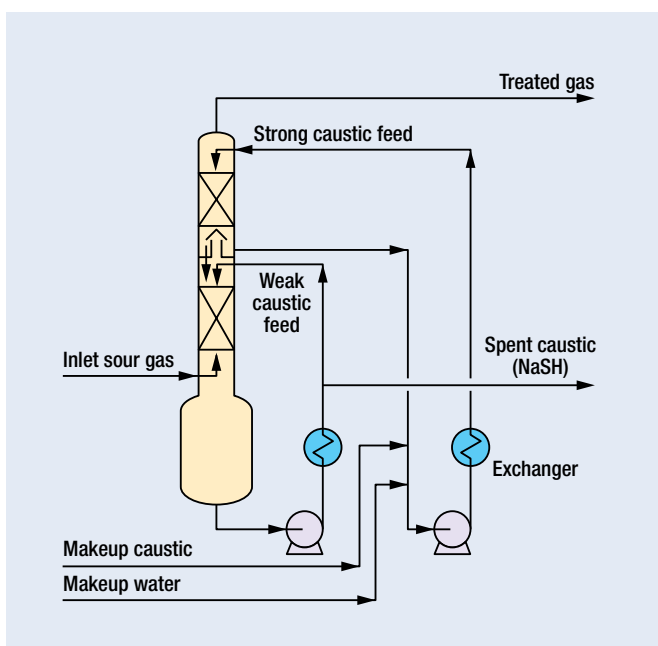

FIG. 1   **Typical simple caustic scrubber unit.**

Scrubbing using excess NaOH. For very small capacity or infrequent usage, caustic scrubbers may be designed to operate using a large excess amount of caustic. This design strategy assures the maximum H_2S abatement at the cost of excess NaOH usage. This unit would be designed as simply as possible; it would typically consist of a single packed tower with a surge tank, a circulation pump and a heat exchanger (Fig. 1). A large liquid recirculation flowrate is maintained to provide adequate contact with the gas phase. Makeup caustic is added, and spent caustic is withdrawn continuously or as needed.

Excess NaOH amounts would be used (e.g., NaOH:H_2S > 2:1). When large excesses of NaOH are used, the equilibrium partial pressure of the H_2S solution is so low that it is typically negligible. Column design 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 from a packing vendor, HTU literature, or K_ga data. Process simulators can also be applied if the software is known to adequately model the mass transfer rate in addition to the chemical equilibrium. For single recirculation-loop systems, the excess caustic utilization will be the primary factor in determining the H_2S removal efficiency. Because of the high caustic consumption and low value of the sulfidic caustic product, this scrubber is limited to very low sulfur throughputs and low CO_2 concentrations.

Scrubbing while minimizing excess NaOH. When a large excess of NaOH can not be used (e.g., NaOH:H_2S < 2:1) for economic or product quality reasons, the chemical equilibrium of the system must be considered in the design calculations, especially when operating at higher temperatures. At a lower pH, the literature HTU/K_ga data may not be accurate. 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.

One design strategy for these cases is applying two caustic recirculation loops (Fig. 2). Fresh caustic is fed to a top loop, which is used as a polishing section to maximize H_2S removal. The caustic overflows from the top to the bottom section. The bulk of the H_2S removal is done in the bottom recirculation loop, which operates at a lower pH. Double-loop systems are sometimes avoided due to greater complexity and cost, but this design can achieve very low outlet H_2S concentrations with less caustic consumption than would be possible using a single-loop system. Although double-loop systems offer lower caustic consumption, they are not well-suited for streams with high CO_2 levels.

Selective scrubber for H_2S with CO_2 present. Fig. 3 shows a flow diagram for a short-contact-time (SCT) scrubber designed for selective scrubbing. The SCT process treats gas with percent levels of both H_2S *and* CO_2 at approximately ambient temperature and is designed to achieve the desired H_2S removal while minimizing caustic consumption and CO_2 absorption. Since H_2S can be absorbed much more quickly than CO_2 at high pH levels, selective H_2S removal is accomplished by limiting the contact time between the gas and the liquid in a static mixer. The number of elements in the static mixer column can be varied to modify contact time. Less CO_2 pickup avoids operating issues including the potential for solid sodium carbonate (Na_2CO_3) formation and plugging, and minimizes unnecessary caustic usage while improving NaHS product quality.

The key to designing an 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.[1,2] A recent project used this approach to design a caustic scrubber for a selective treating application. Selectivity calculations are fundamental to the success of the treating process and to minimize caustic consumption/CO_2 pickup. In addition to limiting contact time, control of solution pH, flowrate and temperature are also important.

Design for H_2S removal with other contaminants. Fig. 4 shows a special design that was developed to remove H_2S from a sour-water stripper overhead stream that also contains

FIG. 2 | Caustic scrubber column with a two-loop configuration.
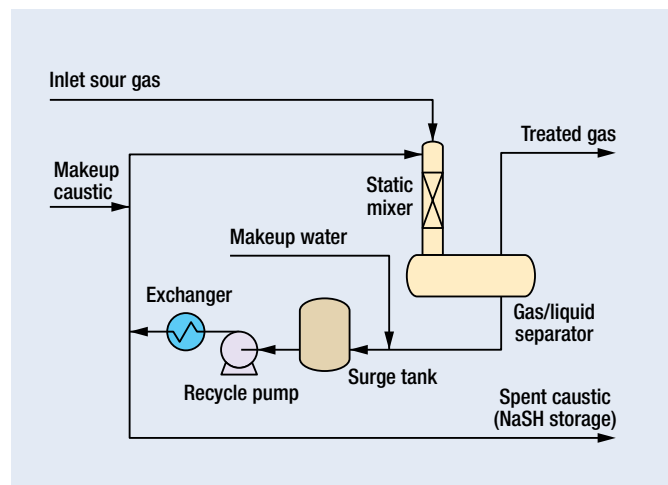

FIG. 3 | Short-contact-time caustic scrubber.

ammonia (NH_3) and water vapor at ~10 psig and 113°C. The sour offgas is treated in a two-stage system. A caustic scrubber removes H_2S from the gas, after which the spent caustic is sent to a second tower where steam strips the physically absorbed NH_3 from the spent caustic solution to maintain product quality. (H_2S loss in the stripper is minimal due to the high alkalinity of the solution.) The treated vapor streams, now H_2S free but still containing large amounts of water vapor and NH_3, are combined and sent to an ammonia destruction device.

As shown in Fig. 4, the 50-wt% caustic is fed to the caustic scrubber unit, and a cooler is operated on the recirculating liquid to condense water vapor from the feed gas. Temperature control of the recirculating solution is important. Although low-temperature operation is generally preferable (resulting in better H_2S abatement and lower corrosivity), it is not possible when treating a sour gas that is mostly steam. Excessive dilution of the spent caustic NaHS product is not desired. The cooler is designed to be controlled so that sufficient water vapor is condensed to dilute the caustic to the equivalent of approximately 20 wt%.

General design considerations. Each of the scrubber systems has some unusual characteristics that must be considered during the design phase and these include:

Corrosion and materials of construction. Although caustic is not highly corrosive to carbon steel at moderate temperatures, the presence of bisulfide may cause significant corrosion rates. Thus, a preference for stainless steels in this liquid service is desired. 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 about 100°C, even 304 and 316 stainless steel alloys may experience significant caustic-induced corrosion rates. Under these conditions, a preference for higher alloys (e.g., alloy 6XN, 20, 800) at higher temperatures is desired. This is especially important for the scrubber design shown in Fig. 4, which operates above 100°C.
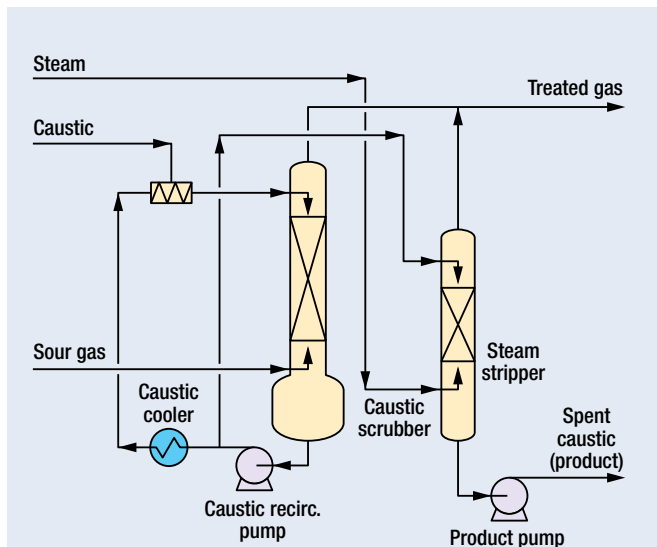
Enthalpy of reaction. Absorption and neutralization of H_2S is highly exothermic (approximately 14 kcal/gmol for Eq. 1). If a gas containing a high H_2S concentration is scrubbed, cooling may be required on the circulating solution.

Solubility. The solubility of sodium salts of H_2S and CO_2 are functions of pH and temperature. Sodium bisulfide has a high solubility in water (perhaps 40+ wt%), but sodium sulfide is a low solubility (13.6 wt% at 20°C). Sodium bicarbonate is even less soluble (9.6 wt%).[3] In mixed systems, the common-ion effect can further lower these solubilities.

In systems containing CO_2, sodium bicarbonate may precipitate readily in the lower pH range. At higher pH levels, hydrates of sodium sulfide (Na_2S) or sodium carbonate (Na_2CO_3) may precipitate. To minimize sulfide precipitation problems, caustic strengths of 20 wt% or less are typically applied.

Operating temperature and equilibrium limits. The previously mentioned scrubber systems described are intended to operate at significantly different temperatures (from ambient to about 110°C). Higher temperatures increase the vapor pressure of H_2S in the caustic solution, thus making treatment specifications more difficult to meet. For this reason, it becomes even more important to understand the equilibrium limitations so that models used in calculations can be verified. (Note: It is imperative that the computer models and simulations always be verified, especially with aqueous systems.) However, there is a limited amount of equilibrium data available for model verification with these particular systems. Since the H_2S equilibrium is an important aspect to the design of caustic scrubber units (at any temperature), the remainder of this article will focus on the solution equilibrium data for H_2S.

Solution equilibrium of H_2S. 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 as:
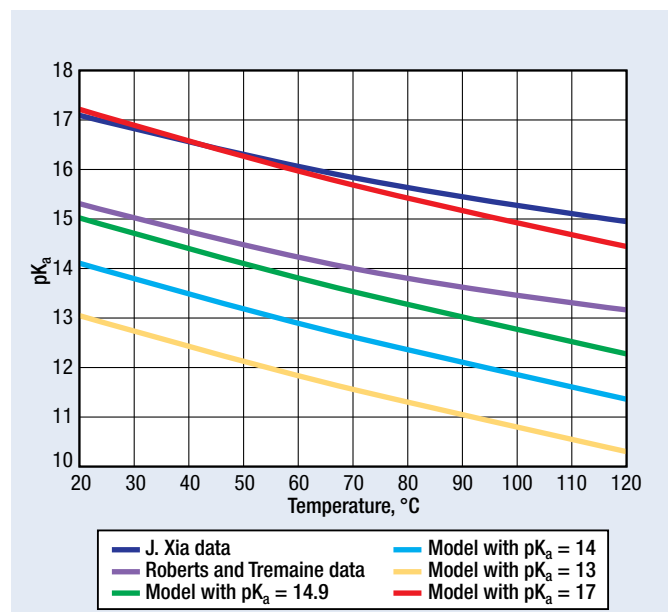
FIG. 5 pK_{a2} values of H_2S from various literature sources and calculated by models.

$$K_{a1} = \frac{[HS^-][H^+]}{[H_2S]_{aq}} \qquad K_{a2} = \frac{[S^{2-}][H^+]}{[HS^-]} \qquad (3)$$

$$pK_{a1} = -\log_{10} K_{a1} \qquad pK_{a2} = -\log_{10} K_{a2} \qquad (4)$$

Eq. 3 is the form commonly used, and is correct for infinite dilution. But these equations are actually approximations, and are more correctly expressed in terms of the activities of the species. As concentration of the system increases, Eq. 3 will become less accurate. Nonetheless, the pK_a values are useful.

The value of pK_{a2} affects the vapor pressure of H_2S over solutions that have moderately high pH, such as concentrated NaHS solutions. Although the pK_{a1} for H_2S is known to be 6.97, with little variation among sources, the same cannot be said for the pK_{a2}. As shown in Table 1 from the literature, more values of the second dissociation constant for H_2S at 25°C ranged from 11.97 to 19.

As demonstrated in Table 2, lower pK_{a2} values cause models to predict that a significantly greater amount of caustic will be required to achieve the same H_2S removal from a gas stream, while also predicting a liquid product that has considerably more Na_2S than NaHS. Gas conditions for Table 2 were 40°C and 50 psig.

To determine which pK_{a2} value should be used in designing the caustic scrubber units, the model results were compared to 1) actual plant operating data from an existing caustic scrubber that was being used to create an NaHS product, and 2) available literature data. The existing NaHS unit operates at approximately 82°C and 50–75 psig and is known to produce 40 wt% to 45 wt% NaHS with maximum treated gas H_2S content of 16,000 ppmv. Assuming that this scrubber has a very high approach to equilibrium, the model predictions using a pK_{a2} value of 17 agreed with the scrubber data in that very little excess NaOH would be required to match the H_2S slip and produce a high-purity NaHS product. Conversely, a low pK_{a2} value of 13 would require 75% more caustic than stoichiometric and the product was predicted to have a significant amount of Na_2S, which is not supported by operating data. This suggested that the lower pK_{a2} values may not be correct.

Data found in the literature showed the H_2S content in the gas phase over different NaHS solutions at 20–21°C and atmospheric pressure. One particular dataset was very useful since it reported the specific NaHS concentration (36.4% NaHS with 5.4% Na_2S), solution pH, and gas-phase H_2S content (240 ppmv measured and approximately 300 ppmv in curve fit of

experimental data). Calculations were done—using both pK_{a2} of 13 and 17—to predict the gas phase H_2S composition based on the liquid phase conditions. As shown in Table 3, the lower pK_{a2} results again did not compare well with the measurements. The model with pK_{a2} equal to 17 gave fairly reasonable results, although the H_2S concentration was one-third of this particular literature data source.

The calculations used to model the equilibrium were then "calibrated" to this data to determine the value of pK_{a2} that is consistent with these data. A pK_{a2} of 14.9 was estimated, which yielded a pH of 12.7 and an outlet H_2S content of 377 ppmv. Fig. 5 shows that this pK_{a2} value (14.9) compares reasonably well with other literature data over the specified operating temperatures. The H_2S removal predicted at high temperatures was also compared to another literature source and was within a factor of two (lower) than the measured values.[4]

Obviously based on the reported pK_{a2} values in the literature, there is much debate on the most appropriate value for the second dissociation constant for H_2S, which may be further complicated by applying different activity coefficient models and limitations at high ionic strengths. In this particular case, it was decided that using a pK_{a2} value of 14.9 in the model was reasonable for design use since it most closely matched available data for similar applications.

Observations. As discussed here, there are many different design considerations when designing a caustic scrubbing system. The composition and operating conditions of the inlet gas stream, as well as the specifications and disposition of the resulting NaHS stream, tend to dictate the flow scheme for the unit as well as the materials of construction. Simulators are useful tools, but it is very important to understand the fundamental basis behind the calculations, especially for complex electrolyte systems, to ensure that the unit is reasonably designed. It is always important to investigate the equilibrium data and/or the basis for the selectivity calculations used in simulation software to avoid unknowingly under- or over-designing with respect to H_2S treat. This could result in unnecessary capital and operating expense, in addition to creating operational issues with the unit. **HP**

TABLE 1. Second dissociation constants for H_2S found in the literature

Source	pKa₂
CRC,[5] 64th Ed., 983-1984	11.97
Lange's Handbook of Chemistry,[6] 1992	12.97
Christensen,[7] Proton Ionization Heats, 1976	12.97
Beutier and Renon,[8] I&EC, Vol. 17, pp. 220–30, 1978	14
Lange's Handbook of Chemistry,[9] 1952	14.92
Roberts and Tremaine,[10] 1985	15.2
J. Xia, et al.,[11] 1999	17
CRC,[12] 86th Ed., 2005–2006	19

TABLE 2. Example comparison of results with pK_{a2} = 17 and pK_{a2} = 13

Parameter	Model with pK_{a2} = 17	Model with pK_{a2} =13
H_2O content of caustic, moles	41.66	41.66
Total absorbed H_2S, moles	3	3
NaOH required to reduce H_2S in treated gas to 80 ppmv, moles	3.03	5.25
pH	11.96	11.28
Mass ratio Na_2S to NaHS	0.01	3.9

TABLE 3. Model comparison to literature data

Parameter	Literature data	Model w/pK_{a2} = 17	Model w/pK_{a2} = 13
pH	12.5	13.15	9.7
H_2S, ppmv	240-300	80	~220,000

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