Sour Water Stripper Performance in the Presence of Heat Stable Salts[1]

Nathan A. Hatcher
Optimized Gas Treating, Inc.
142 Cimarron Park Loop, Suite C
Buda, TX 78610
(512) 970-5019
nate.hatcher@ogtrt.com

R. Scott Alvis
Optimized Gas Treating, Inc.
12337 Jones Rd., Suite 432
 Houston, TX 77070
(281) 970-2700
scott.alvis@ogtrt.com

Ralph H. Weiland
Optimized Gas Treating, Inc.
P.O. Box 125
Clarita, OK 74535
(580) 428-3535
ralph.weiland@ogtrt.com

ABSTRACT

Sour water strippers (SWS) have traditionally been almost exclusively designed using equilibrium stages. However, tray efficiencies remain obscure with quoted values over a factor-of-three range from 15% to 45% which leaves designers with less than complete confidence in the reliability of their final design. Recently a mass transfer rate-based simulation model has become available for designing and troubleshooting sour water strippers.

In this paper, we use the new mass transfer rate model to show (a) the effect of heat stable salts on ammonia and H_2S stripping, (b) where to inject caustic soda for remediation, and (c) what effect excess caustic injection has on stripper performance as measured by residual ammonia and H_2S levels in the stripped water.

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Nathan A. Hatcher, Optimized Gas Treating, Inc., Buda, TX
R. Scott Alvis, Optimized Gas Treating, Inc. Houston, TX
Ralph H. Weiland, Optimized Gas Treating, Inc., Clarita, OK

Introduction

The sour water generated in refineries comes from numerous sources. Most refinery sour water systems contain very little CO_2, but H_2S levels can become very high. The capacity of ammonia solutions for H_2S is a direct result of the weak acid-weak base reactivity between H_2S and ammonia. The potentially high H_2S content can make sour water extremely foul, and H_2S removal from the sour water to quite low levels is mandatory to avoid unacceptable pollution levels. Many sour water sources have been noted in the excellent review article by Asquith and Moore (2000).

Sour water is generally classified as phenolic or non-phenolic. Non-phenolic water contains almost exclusively NH_3, H_2S, and possibly a trace of CO_2. It is generated by refinery hydro-treating (hydrodesulphurisation or HDS) units. When stripped of contaminants, non-phenolic water can typically be recycled for reuse in the HDS unit as wash water, or it can be used as makeup water to the crude desalting process. Phenolic (or more broadly, non-HDS) water typically contains HSSs, phenols, and caustic.

It may be useful to point out that ammonia and hydrogen sulphide have almost unlimited solubility in water when they are present together. This is an interesting consequence of the fact that the reactive component of the solvent, ammonia, is volatile and, if present in the gas phase, it will continue to absorb as long as it becomes protonated as a result of H_2S co-absorption. Thus, it is conceivable that a particular sour water stream may be a lot more concentrated than the solubility of either ammonia or H_2S by itself might suggest.

Sour water stripping uses either steam generated by a reboiler, directly injected steam, or even a hot hydrocarbon stripping vapor to shift chemical reaction equilibria by applying heat. Stripping vapour is the "gaseous solvent" used to remove and carry the ammonia and H_2S out of the system. It functions by:
1. Heating the sour water feed to the boiling point
2. Reversing chemical reactions
3. Diluting the partial pressure of the gases stripped by furnishing excess vapour

Figure 1 shows a typical SWS column with live steam injection and with the plumbing to allow caustic soda injection onto one of the trays in the column. Typical energy usage in the stripping process is in the range 1.0–1.5 lb of 50 psig equivalent saturated steam per gallon of sour water.

To minimize heat exchange surface, an external reboiler often uses higher pressure (temperature) steam than is typical in an amine regenerator because amine thermal degradation is not a limiting factor. However, there is a practical limit of 400-450°F where

coking heavy hydrocarbons can lead to fouling and solids deposition in the reboiler, and, of course, corrosion and vapor blanketing become increasingly of concern at higher temperatures.
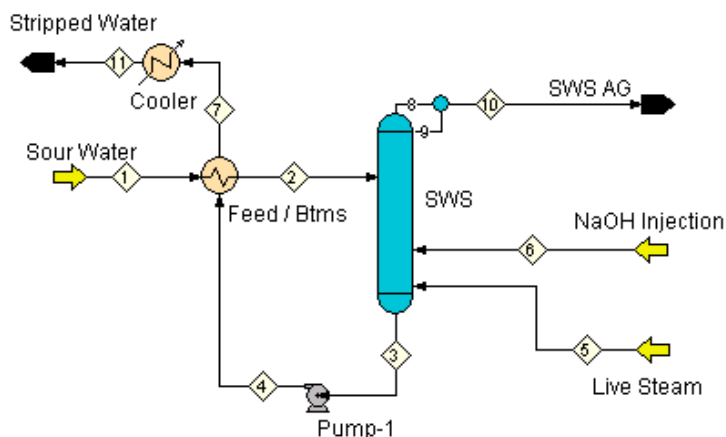

Figure 1   SWS Using Live Steam and Caustic Injection

Stripped sour water specifications for NH_3 and H_2S can be highly dependent on local regulatory requirements. Typical targets for NH_3 are 30–80 ppmw in the stripped water versus undetectable to less than 0.1 ppmw for H_2S. Typical recent installations (Quinlan and Hati, 2010; Asquith and Moore, 2000) involve 35-45 actual trays.

It is common in refinery cracking units (FCCs and Cokers) for the sour water generated to contain organic and inorganic acid impurities from heat stable salt precursors and, just as for amine units, ammonia partially in the protonated form. It cannot be thermally regenerated because the HSS responsible for the protonation is completely nonvolatile and cannot be removed by boiling it into the stripping steam. In such cases, it is quite common to inject a small amount of strong base (NaOH) to shift the pH into a range where ammonium ion (NH_4^+) shifts back to NH_3. Spent caustic from Merox-type units is commonly used for this purpose, but care must be taken to ensure that disposal of the spent caustic is not completely reliant on this destination, or the tail will begin to wag the dog.

When adjusting the pH of the water to spring ammonia chemically, the adjustment is usually made by metered injection of caustic onto a tray far enough down the column that most of the H_2S has already been stripped out and ammonia is the main remaining component. The metering rate is normally set to control the pH in the stripped water after it has been cooled. Caustic injection on a lower tray generally works better than injection directly into the SWS feed itself because the H_2S concentration is already small on lower trays. However, pH is extremely responsive to caustic addition, so the measuring and control elements should be as close together as feasibly possible if rather large fluctuations in pH are to be avoided. As we shall see, no more caustic than absolutely necessary should be injected because excess caustic can permanently bind H_2S into the solution, and eventually this will

find its way into biological treatment ponds, either reducing the efficacy of the microbial population, or unnecessarily increasing the biological oxygen demand.

Traditionally, SWSs have been modeled as a series of equilibrium stages with stage efficiencies being quoted anywhere in the range from 15% to 45%, i.e., ranging over a *factor of three*. However, since the mid to late 1980s the mass transfer rate-based approach to simulating amine contactors and extractive, azeotropic and reactive distillation has been in very successful commercial use. The extension to sour water stripping is a natural progression and, in December, 2011 the ProTreat® simulation package saw the addition of a commercial mass transfer rate-based sour water stripper model. The remainder of this article uses the ProTreat simulator's SWS model to explore how HSSs affect the performance of SWSs and how caustic addition can be tailored to provide the optimal stripping of H_2S and ammonia from HSS-laden sour water.

Case Study

Figure 1 shows the simplest possible configuration of a sour water stripper with caustic injection. For this case study, the same stripper as outlined previously in Weiland and Hatcher (2012) was used. It contained 40 one-pass valve trays on 2-ft spacing with 2-inch weirs. Sour water was fed at 235°F to Tray 6 (from the top), live steam saturated at 50 psig entered below the bottom tray, and in all cases the column was sized for 70% of jet and downcomer flood. Caustic could be injected on any tray in the column. Table 1 gives the conditions of the sour water used for this case study.

Table 1   Sour Water Feed Conditions

Temperature (°F)	135
Pressure (psia)	70
Total flow (lb/hr)	150,000
Water (mol%)	96.4
Hydrogen sulphide (mol%)	1.5
Carbon dioxide (mol%)	1.1
Ammonia (mol%)	2.0
Formate (ppmw)	200
Thiocyanate (ppmw)	100

Effect of Heat Stable Salts on Stripped Water Quality

Figure 2 shows the effect of stripping steam rate and the absence versus presence of 300 ppmw HSSs (composition indicated in Table 1 on the simulated stripped water quality with respect to residual ammonia and H_2S content. It is readily apparent from the plot on the left that the presence of heat stable salts forces the retention of a corresponding concentration of ammonia, and *no matter how much steam is injected into the stripper there is a residual ammonia level that simply cannot be removed when there are heat stable salts in the sour water*. Heat stable salts have a negative effect on ammonia stripping. However, they have a *beneficial* effect on H_2S removal because they are generally stronger acids. A *two order-of-magnitude reduction* in residual H_2S is possible with only a modest amount of HSS present.
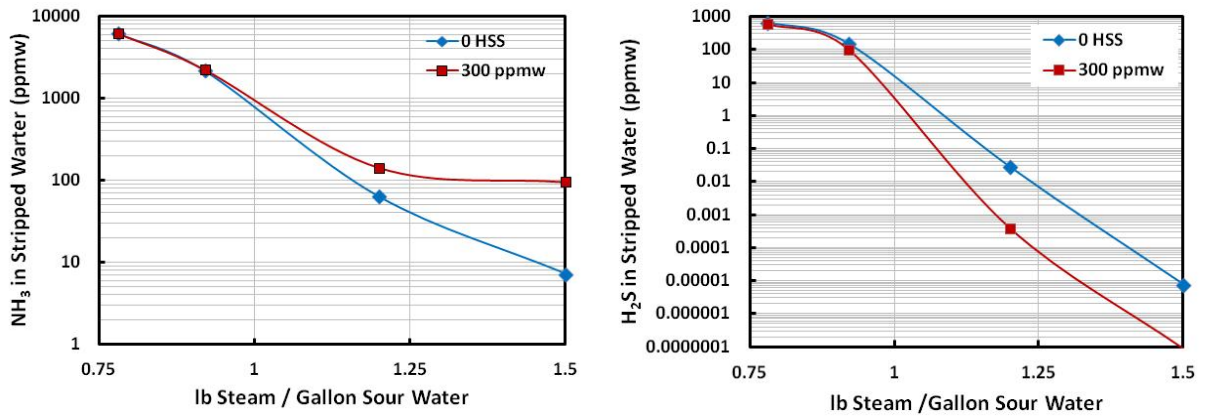
Figure 2   Effect of Heat Stable Salts on Stripped Water Quality

One way to improve ammonia removal is to inject caustic soda, a stronger base than ammonia, onto a tray somewhere in the column. At the risk of oversimplification, if the right amount is added, the caustic will then bind all the HSSs that would otherwise be neutralized with ammonia, without negatively affecting H_2S stripping. If too much used, the excess would be expected to permanently bind H_2S; if too little, then less than the full potential for ammonia release would be realized. In a broad sense, this is indeed what happens, but for accurate answers one must account for the pK_a and reaction equilibria of the weak acids and bases involved as well as considering the finite mass transfer rates of ammonia and hydrogen sulphide by using a genuine mass transfer rate model of the tower and its trays. There are two questions to be answered: where to inject ammonia, and how much optimally to inject.

Injecting Neutralizing Caustic on Various Trays

As a first approximation one might expect that the optimal caustic injection rate will be just sufficient to completely neutralize the HSSs in the feed. This is a *Neutralization Ratio of NaOH to HSS* of unity. Less than unity is under-neutralized, greater than unity is over-neutralized. Figure 3 shows the effect on the stripped water residual ammonia and H_2S levels with injection of an amount of caustic soda just enough to neutralize the HSS onto various trays. Two live stripping steam rates are considered.
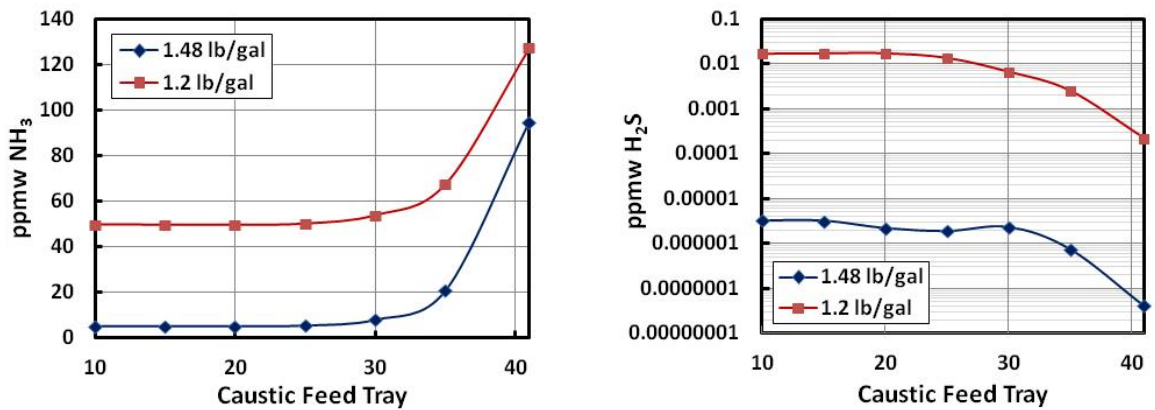

Figure 3   Effect of Heat Stable Salts on Stripped Water Quality

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As far as ammonia removal is concerned, caustic injection at or *above* tray 30 results in the optimal degree of improvement. However, H_2S removal is improved only if caustic is injected *below* tray 30. Indeed, if caustic is not injected at all (below Tray 40 is equivalent of the tower sump and no stripping is assumed to take place there) the best possible H_2S removal is obtained, but no improvement to ammonia stripping results. Interestingly (and in contradiction to conventional wisdom…), caustic might as well be injected right into the sour water feed itself—*there is no real benefit from injecting it onto a mid-tower tray*—at least not in this case study! The benefit to H_2S from injecting below tray 30 is probably because by that tray most of the H_2S has been removed anyway, and there is too little left in the water to be held by the caustic. On the other hand, the further below tray 30 one injects caustic, the fewer stripping trays that are left to remove the ammonia released; thus, spiking the water with caustic is increasingly pointless the further below tray 30 one injects. We note in passing that some of this discussion becomes increasingly more academic as the H_2S levels being considered fall below detectible limits (<< 1 ppmw).

The Effect of Caustic Injection Rate

The effect of the extent of HSS neutralization on ammonia stripping is fairly clear cut. As the plot on the left side of Figure 4 shows, caustic injection at a rate just sufficient to neutralize the HSSs springs the maximum possible amount of ammonia, although at low stripping steam rates, a slightly larger amount helps. With H_2S, however, the effect of under- versus over-neutralization is spread over a wide range of neutralization ratios. When the neutralization ratio reached 0.5, the H_2S residual had already started to rise and by the point where a ratio of about 1.25 was reached, the residual H_2S had attained its highest level. However, if exact neutralization is not exceeded by much, quite satisfactory residual H_2S levels in the stripped water can be achieved. Note though, that these results pertain only to the conditions presented in this case study—they should not be generalized; rather, the ProTreat SWS model should be run for the conditions pertinent to the specific installation.
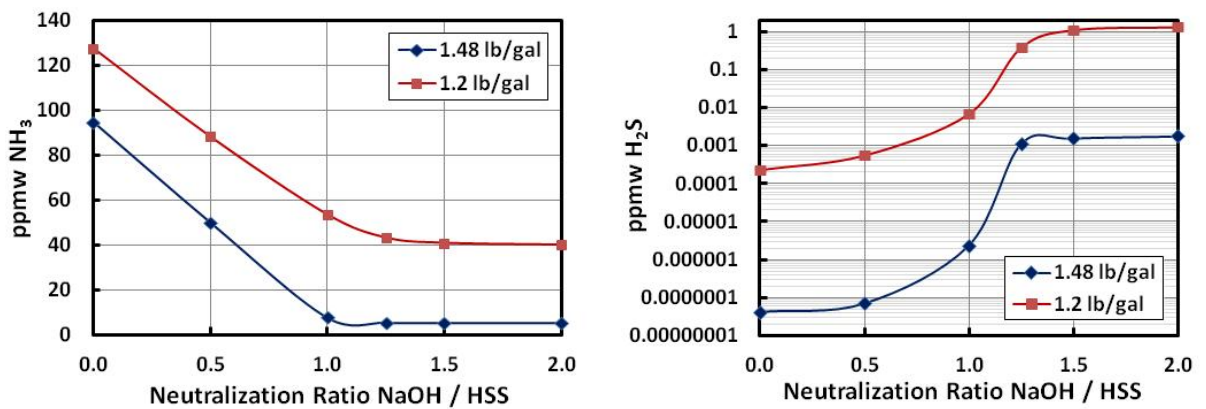

Figure 4   Effect of Extent of Neutralization on Stripped Water Quality. Caustic Injection Ws onto Tray 30 from the top of the Column

The Set-point for pH Control and Optimal Stripping

When using caustic injection with phenolic sour waters, it is common practice to manipulate the caustic flow to control a pH set-point. The question is, what should the set-point value be? The answer almost certainly depends on the amounts and kinds of contaminants and HSSs present, and probably also on the levels of ammonia and hydrogen sulphide in the sour water. For the case being examined here, assuming injection at Tray 30, the stripped water pH at 120°F is shown as a function of neutralization ratio in Figure 5 for two stripping steam rates. If the target caustic injection rate is 100% neutralization of the HSSs, the treated water pH at 120°F is 9.0–9.1. If the set-point in actual use were 8.0, say, no caustic at all would be injected at a steam rate of 1.2 lb/gal and only 70% neutralization would be achieved at 1.48 lb/gal, leaving 35 ppmw ammonia in the stripped water rather than the 5 or so ppmw actually achievable. The value of the pH set-point to achieve the best ammonia removal without needlessly poor H_2S stripping is rather an important parameter. It does not seem to depend to any significant extent on the stripping steam rate, but it is a parameter whose value can be predicted and verified accurately only by using a genuine mass transfer rate model for sour water stripping.
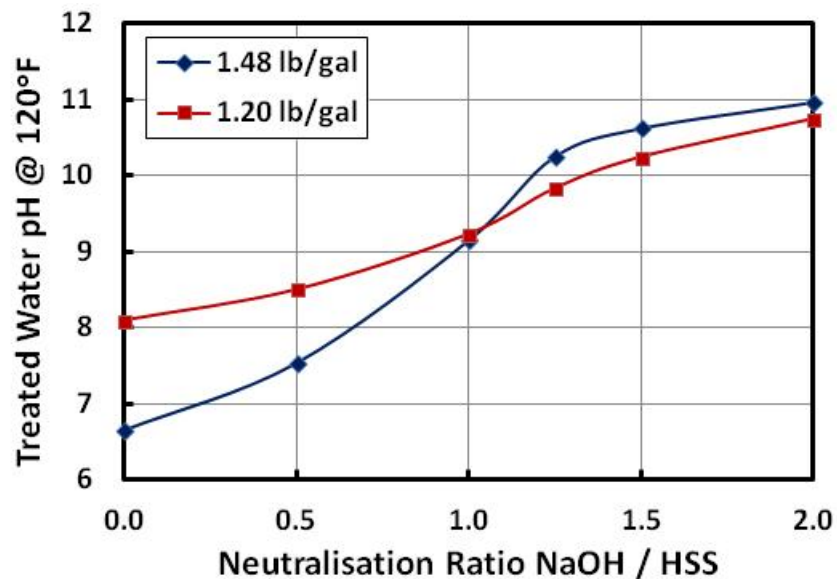

Figure 5   Setting the pH Control Point for Optimal Stripping

An additional observation from the simulations was that when 500 ppmw of MDEA was added to the sour water (steam rate of 1.48 lb/gal) and the caustic was added to tray 30 with a neutralizing ratio of 1.0, essentially all the MDEA reported to the stripped water. However, the higher consequent pH (9.48 versus 9.08) caused *less* ammonia (5.5 versus 7.8 ppmw) but *more* H_2S (0.0000548 versus 0.0000235 ppmw) to remain in the stripped water. The lesson to be learned here is that sporadic or varying levels of contamination (amine losses would be a case in point) may wreak havoc on attempts to practically implement pH control in the field.

Summary

Perhaps the most important message of this paper is that genuine mass transfer rate-based modeling allows the construction of a virtual plant on a computer. There is no reliance on what might be termed "fudge factors" to achieve agreement between calculations and reality. The power of the ProTreat sour water stripper model is the ability to analyze a given tower under specified conditions in such detail that the optimal caustic injection rate and even the pH control point can be very accurately assessed beforehand. This can go far in taking the guesswork out of plant process optimization.

A mass transfer rate-based sour water stripper model provides a virtual SWS on a computer. Engineers can now design, analyze and optimize SWS units with unprecedented accuracy and reliability. Plant operations personnel can answer a wide range of what-if questions to troubleshoot operations and to optimize existing units with considerably more confidence in the results. Some possibly valuable lessons of this work include:

- The optimal caustic injection rate is primarily dictated by the kind and concentration of heat stable salts in the sour water.
- No matter how much caustic is injected to spring ammonia, it will have a deleterious effect on stripping hydrogen sulphide.
- The tray selected for caustic injection is unimportant as long as it is far enough up the stripper for there to be sufficient trays below the injection point to strip the additional ammonia.
- As long as caustic is added to the sour water a reasonable number of trays up from the bottom, the precise tray for injection is immaterial to the outcome. In other words, even adding caustic directly to the feed water itself produces stripped water of the same quality as obtained by injection into the column. Some practitioners advise to add caustic to the feed water; others say always to add it to a tray. In fact it makes no difference, so one might as well save a feed nozzle.
- The presence of amine in the sour water results in higher pH and better ammonia stripping, but slightly poorer H_2S removal. All amine remains in the stripped water.

In conclusion, this article has revealed several aspects of stripping phenolic sour water that do not seem to have been recognized heretofore. It also highlights the benefits that can be obtained from simulating sour water strippers without taking shortcut assumptions of tray efficiencies, ideal stages, or phony residence times per theoretical stages.

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