Stripping sour water: the effect of heat stable salts

Mass transfer rate-based simulation models sour water stripping and assesses the distribution of ammonia in conventional amine treating systems

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In a recent article dealing with a live steam-injected stripper (*PTQ*, Q3 2012), we discussed how steam usage affected the stripped water residual ammonia and hydrogen sulphide levels, how ammonia distributed itself within the stripper in an unexpected way, and how Murphree (1925) vapour efficiencies varied with location within the tower at various stripping steam rates.[4] The discussion was limited to non-phenolic sour water. In the present article, we examine the effect of heat stable salts (HSS) on sour water stripper (SWS) performance, how the injection of caustic soda can spring ammonia from the sour water, and how caustic injection can worsen H_2S stripping if it is injected at the wrong place, or too much caustic is injected. The analysis uses a mass transfer rate-based simulation model for sour water stripping and for assessing the distribution of ammonia in conventional amine treating systems.

Sour water sources

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.[1]

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 hydrotreating (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 make-up water to the crude desalting process. Phenolic (or more broadly, non-HDS) water typically contains HSS, phenols and caustic.

Finally, 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.

SWS uses either steam generated by a reboiler, directly injected steam, or even a hot hydrocarbon stripping vapour 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:

- Heating the sour water feed to the boiling point
- Reversing chemical reactions
- Diluting the partial pressure of the gases stripped by furnishing excess vapour.

Figure 1 shows a typical SWS column with heating by the injection of live steam and with the possibility of injecting caustic soda to one of the trays in the column. Typical energy usage in

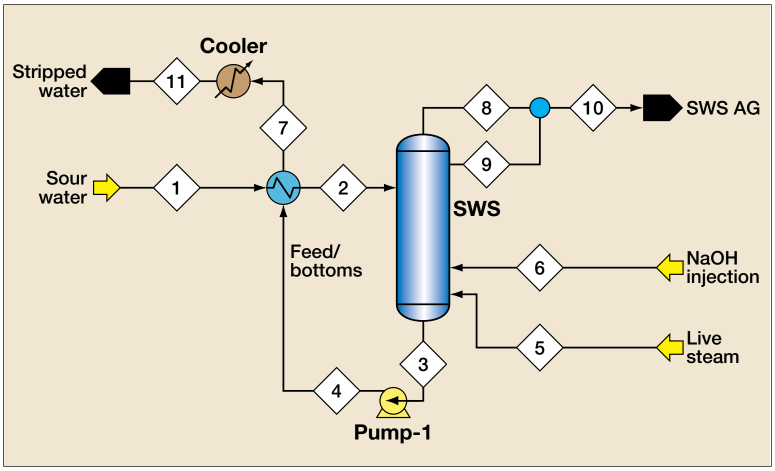

Figure 1 SWS using live steam and caustic injection

the stripping process is in the range 1.0-1.5 lb of 50 psig equivalent saturated steam per gallon of sour water.

To minimise 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 is always a concern.

Stripped sour water specifications for NH_3 and H_2S can be highly dependent on local requirements. Typical targets for NH_3 are 30-80 ppmw in the stripped water and undetectable to less than 0.1 ppmw for H_2S. Typical recent installations involve 35-45 actual trays.[1,3]

It is common in refinery cracking units (FCCs and cokers) for the sour water generated to contain organic and inorganic acid impurities from HSS 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 non-volatile 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 controlled to a set point on the pH measurement 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 in time as possible if rather large fluctuations in pH are to be avoided. As we shall see, no more caustic than is 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 modelled as a series of equilibrium stages, with stage efficiencies being quoted anywhere in the range from 15% to 45%, that is 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 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 SWS model. The remainder of this article uses this model to explore how HSS affect the performance of SWSs and how caustic addition can be tailored to provide the optimum amount of stripping of H_2S and ammonia from HSS-laden sour water.

Case study

Figure 1 shows the simplest possible configuration of a SWS with caustic injection. For this case study, the same stripper as outlined previously was used.[4] It contained 40 one-pass valve trays on 2ft 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.

Sour water feed conditions

Total flow, lb/h	150 000
Temperature, °F	135
Pressure, psia	70
Water, mol%	96.4
Hydrogen sulphide, mol%	1.5
Carbon dioxide, mol%	0.1
Ammonia, mol%	2.0
Formate, ppmw	200
Thiocyanate, ppmw	100

Table 1

Effect of HSSs on stripped water quality

Figure 2 shows the effect of the stripping steam rate and the absence versus presence of 300 ppmw HSS (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 upper plot that the presence of HSS 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 HSS in the sour water. HSS 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.

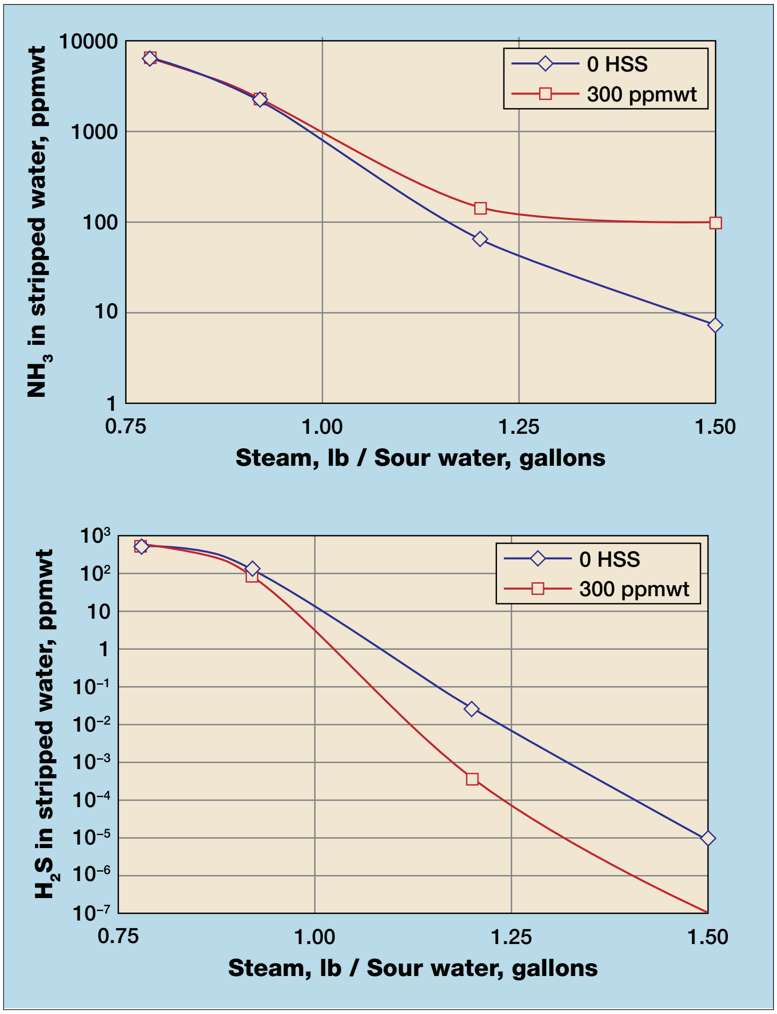

Figure 2 Effect of HSS on stripped water quality

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 HSS that would otherwise be neutralised with ammonia, without negatively affecting H_2S stripping. If too much is 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 realised. In a broad sense, this is indeed what happens, but for accurate answers one must account for the pKa of the weak acids and bases involved, as well as considering the finite mass transfer rates of ammonia and H_2S by using a genuine mass transfer rate model of

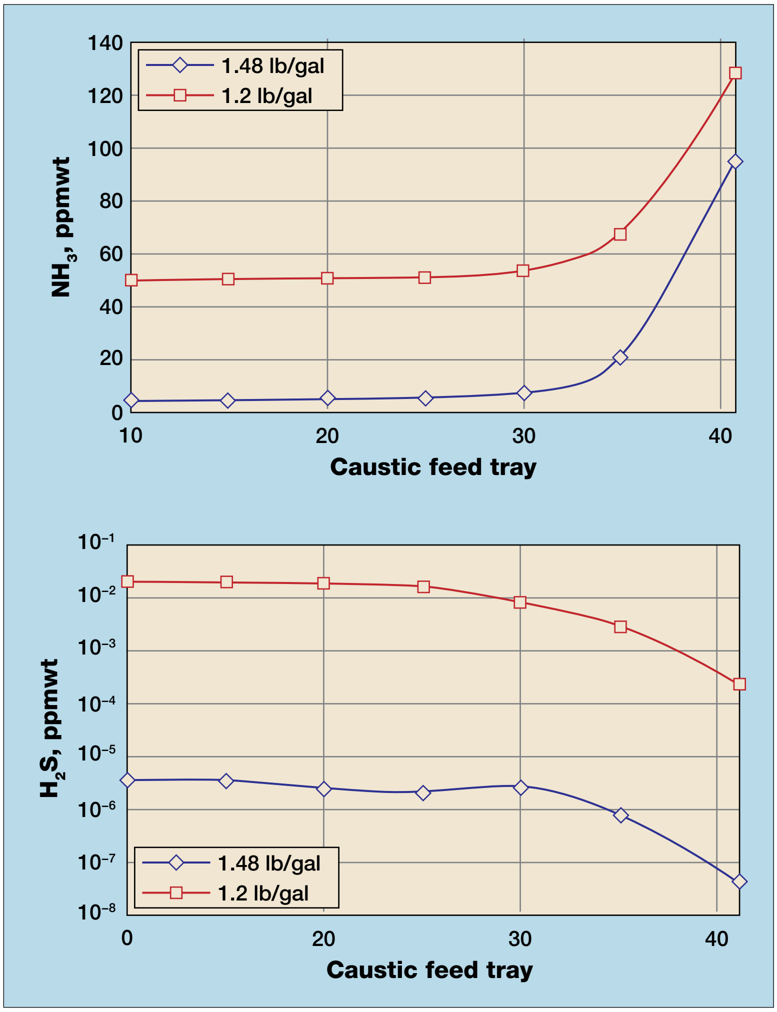

Figure 3 Effect of caustic injection on stripped water quality

the tower and its trays. There are two questions to be answered: where to inject ammonia, and how much optimally to inject.

Injecting neutralising caustic on various trays

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

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 the 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, as 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, in this case, 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 detectable limits (<<1 ppmw).

Effect of caustic injection rate

The effect of the extent of HSS neutralisation on ammonia stripping is fairly clear cut. As the upper plot of Figure 4 shows, caustic injection at a rate just sufficient to neutralise the HSS springs the maximum possible amount of ammonia, although at low stripping steam rates, a slightly larger amount helps. With HSS, however, the effect of under- versus over-neutralisation is spread over a wide range of neutralisation ratios. When the neutralisation 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 neutralisation 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 generalised; rather, the ProTreat SWS model should be run for the conditions pertinent to the existent installation.

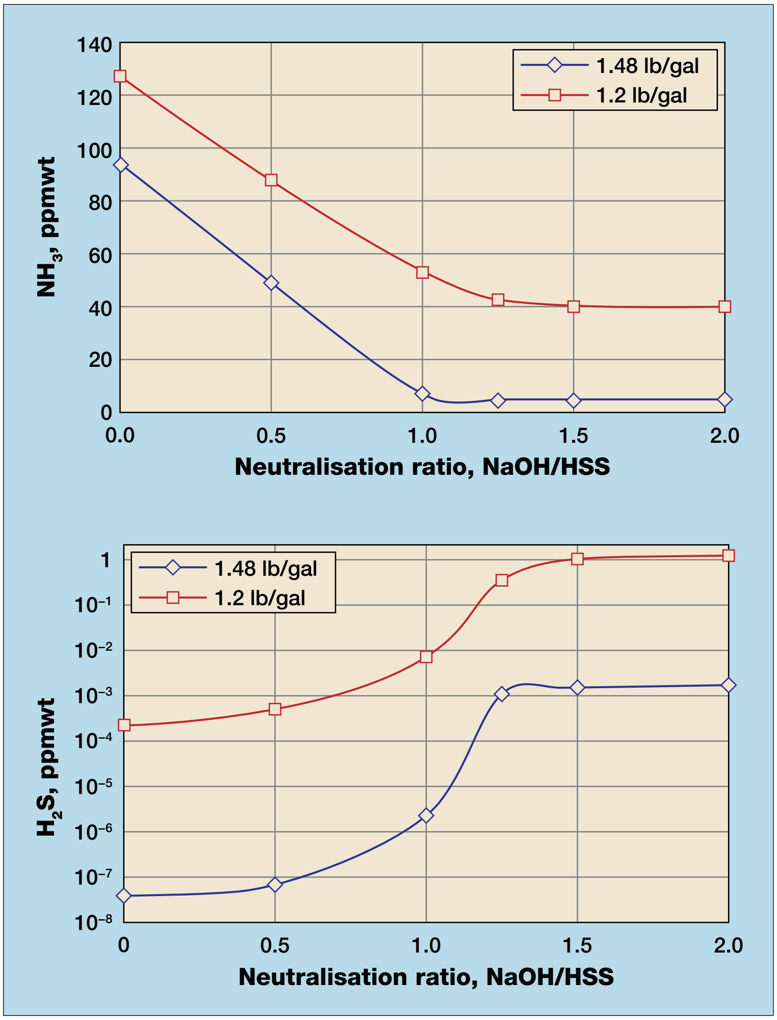

Figure 4 Effect of extent of neutralisation on stripped water quality. Caustic injection was onto tray 30 from the top of the column

Set point for pH control and optimal stripping

When using caustic injection with phenolic sour waters, it is common practice to control the caustic flow to 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 HSS present and probably on the levels of ammonia and H_2S in the sour water as well. For the case being examined here, and injection at tray 30, the stripped water pH at 120°F is shown as a function of neutralisation ratio in Figure 5 for two stripping steam rates. If the target caustic injection rate is 100% neutralisation of the HSS, 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% neutralisation 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 SWS.

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 neutralising 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.

Conclusion

Perhaps the most important message here is that genuine mass transfer rate-based modelling 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 SWS model is the ability to analyse a given tower under specified conditions in such detail that the optimal caustic injection rate and

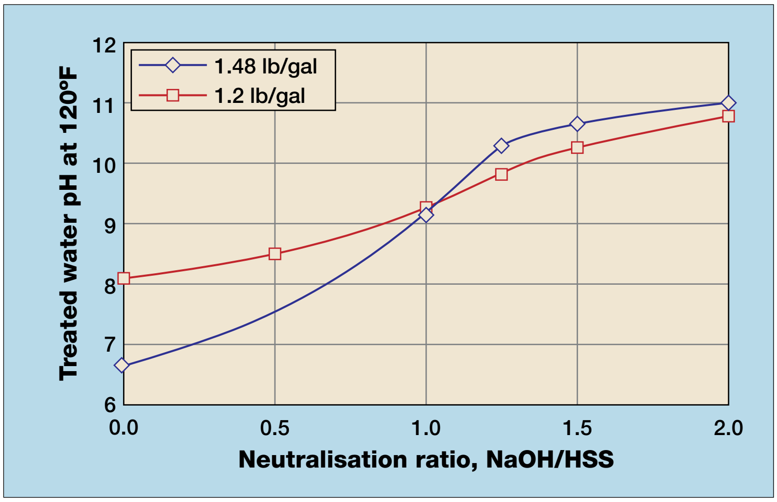

Figure 5 Setting the pH control point for optimal stripping

even the pH control point can be very accurately assessed beforehand.

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

- The optimal caustic injection rate is primarily dictated by the kind and concentration of HSS in the sour water
- No matter how much caustic is injected to spring ammonia, it will have a deleterious effect on stripping H_2S
- 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 recognised heretofore. It also highlights the tremendous benefits that can be obtained from simulating SWSs the right way — using a genuine mass transfer rate model.

ProTreat is a mark of Optimized Gas Treating, Inc.

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