

# SOUR WATER STRIPPERS EXPOSED<sup>1</sup>

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## **Abstract**

Sour water strippers (SWS) are moderately-large reboiled or live-steam-injected towers (30 to 60 trays) in which ammonia and other gases are removed from the sour water by steam stripping. Heretofore they have been designed using equilibrium stages. However, tray efficiencies have remained obscure with quoted values anywhere from 15% to 45%, a factor of three range. Designers therefore have less than complete confidence in the reliability of their final design. The consequence of uncertainty is either overdesign and, therefore, excessive costs or sleepless nights because of an underperforming unit.

Recently a mass transfer rate-based simulation model has become available for designing and troubleshooting sour water strippers. In this paper, we use the model to determine tray efficiencies for ammonia and H<sub>2</sub>S stripping, how they vary across the height of a tower, and what operating variables affect them. We also predict quantitatively how the presence of heat stable salts affects the treat-ability of sour water to specified residual levels of ammonia and H<sub>2</sub>S.

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## Introduction

Oil refining always generates sour water, and within a refinery there are numerous sources. Most refinery sour water systems contain very little CO<sub>2</sub>. H<sub>2</sub>S content makes sour water “sour”, and H<sub>2</sub>S levels can become very high. The capacity of ammonia solutions for H<sub>2</sub>S is a direct result of ammonia’s ability to accept the proton liberated by H<sub>2</sub>S when it enters the solution and dissociates. In principle, and with enough H<sub>2</sub>S partial pressure, there can be more H<sub>2</sub>S than ammonia. This potentially high H<sub>2</sub>S content can make sour water extremely foul, and if the H<sub>2</sub>S is not recovered, pollution levels would be completely out of hand. Many sour water sources have been noted in the excellent review article by Asquith and Moore (2000). Sources include:

- Many refining units use live steam and heat for fractionation, and live steam for velocity assist and temperature control in fired heaters. Nitrogen in the presence of heat and a hydrogen source (such as a hydrocarbon) forms ammonia. The steam is condensed and recovered in the O/H circuit of the crude unit, FCC unit, or Coker unit.
- In the case of refinery hydrotreating, hydrogen gas and a metal catalyst are used to saturate olefins. Hydrotreating also converts sulfur-containing hydrocarbons to H<sub>2</sub>S, and nitrogen-bearing hydrocarbons to ammonia.
- Although ammonia is considerably more volatile than most alkanolamines, it has a high affinity for water. Ammonia is removed from hydrocarbon products by injecting wash water into the gas and cooling the mixture at elevated pressure to condense the water. This provides an irresistible invitation for ammonia to enter the aqueous phase.
- Additionally, the wash water serves to prevent the accumulation of salts and the corrosion of heat exchange surfaces. Accumulation is especially prevalent in areas where there are gas liquid interfaces and where there are sudden temperature changes on heat transfer surfaces such as when heat transfer is controlled by liquid level in an exchanger.
- Amine regenerator reflux water purges can also be a significant source of ammonia.

The sour water generated in refineries is generally classified as being either phenolic or non-phenolic. Non-phenolic water contains almost exclusively NH<sub>3</sub>, H<sub>2</sub>S, and possibly a trace of CO<sub>2</sub>; it is generated by refinery hydro-treating (hydrodesulphurization or HDS) units. When stripped of contaminants, non-phenolic water can typically be recycled for reuse in the HDS as wash water, or it can be used as makeup water to the crude desalting process. Phenolic (or more broadly, non-HDS) water contains compounds that can harm upstream units if used in them as wash water. Typical contaminants include salts, phenols, and caustic. However, makeup water to processing units first must be treated, so there are attendant operating costs; thus, maximizing water reuse is desirable.

Other sources of water to SWS units are process drums, crude desalting units, scrubbing of hydrocarbons following caustic treatment for mercaptans, COS and final H<sub>2</sub>S

removal, TGU quench columns, and various effluent drains for removing the water used to prevent salt deposition in equipment (Stevens et al., 2007).

Finally, it may be useful to point out that ammonia and hydrogen sulfide 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<sub>2</sub>S co-absorption. Thus, it is conceivable that a particular sour water stream may be a lot more concentrated than the solubility of ammonia itself would suggest.

## Basic Stripping Process

Sour water stripping is a fairly simple process in which either external steam, steam generated by a reboiler, or even a hot hydrocarbon stripping vapor is used to shift chemical reaction equilibria by heating the sour water. The steam is the “gaseous solvent” used to remove and carry the ammonia and H<sub>2</sub>S out of the system. In other words, the application of heat generates internal stripping steam (equivalently, live steam injection can be used) and carries ammonia, H<sub>2</sub>S, and CO<sub>2</sub> out of the water by:

1. Heating the sour water feed to boiling point
2. Reversing chemical reactions
3. Diluting the partial pressure of the gases stripped by furnishing excess steam

This sounds a lot like an amine regenerator, and it is. Figure 1 shows a typical SWS column with heating by the injection of live steam. Because a sour water stripper does not form a fully

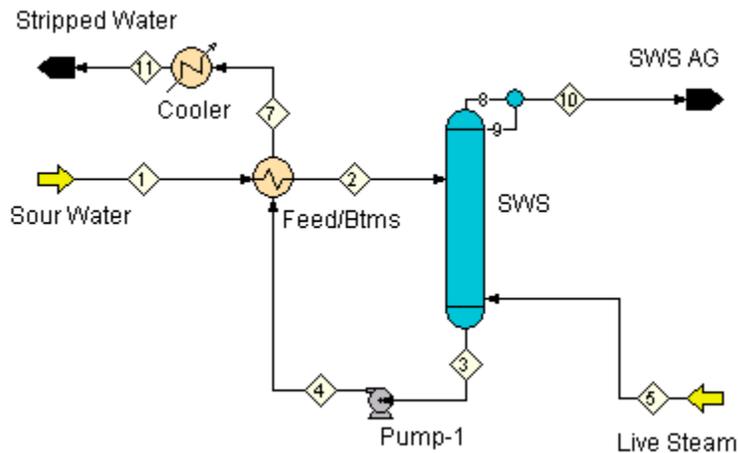


Figure 1 Sour Water Stripper with Live Steam Injection

closed loop like an amine regenerator does, maintaining a water balance is unnecessary. This means that live steam can be used as a stripping agent either alone or in conjunction with a conventional reboiler and the additional water added by the condensate simply added to the refinery’s water inventory. 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.

When an external reboiler is used, steam pressure is often higher than in an amine regenerator to minimize heat exchange surface. In an amine regenerator, amine degradation limits temperatures. In a sour water stripper, ammonia recycle in the stripped sour water is undesirable to begin with, so these concerns do not exist. 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 corrosion is always a concern.

Higher NH<sub>3</sub> and H<sub>2</sub>S concentrations require more stripping energy, but a higher concentration is also a more efficient way to store and transport the NH<sub>3</sub> and H<sub>2</sub>S removed from upstream units. Because high H<sub>2</sub>S solubility relies on the presence of ammonia, the molar concentration of H<sub>2</sub>S very rarely exceeds that of ammonia, and then usually only in dilute systems. A typical molar ratio of H<sub>2</sub>S to ammonia is 0.5-0.8 in the combined SWS feed water of a typical refinery. Ammonia levels in the water are often determined by upstream process conditions, and they can be highly specific to the process licensor and crude slate in operation. Obviously, higher concentrations of NH<sub>3</sub> and H<sub>2</sub>S are preferred from a water consumption perspective. However, there is a practical limit of between one and several weight percent ammonium bisulfide equivalent in the sour water feed before metallurgy must be significantly upgraded.

Trays have historically been used in SWSs, but random packing is beginning to see use in units processing relatively clean water. Trays with directional, fixed valves have been reported to be more resistant to fouling because the horizontal velocity imparted as the gas leaves each valve tends to sweep clean the area near the valves (Hauer and Kirkey, 2003).

Stripped sour water specifications for NH<sub>3</sub> and H<sub>2</sub>S can be highly dependent upon the locale where the unit is installed and the final discharge requirements. NH<sub>3</sub> is harder to strip than H<sub>2</sub>S and typical targets for NH<sub>3</sub> are 30-80 ppmw in the stripped water versus undetectable to less than 0.1 ppmw for H<sub>2</sub>S. Typical recent installations (Quinlan and Hati, 2010; Asquith and Moore, 2000) involve 35-45 actual trays with tray efficiencies quoted anywhere from 25 to 45%.

In some cases, other alkaline contaminants besides ammonia may be present in sour water. Amine can carry over into the regenerator purge or it can be present from injection into the crude unit overhead for corrosion control. Sodium, potassium, and magnesium may also be present from impurities in the makeup water (hardness) or by water-contacting various products containing these compounds within the upstream units. These species can chemically trap additional H<sub>2</sub>S and prevent the H<sub>2</sub>S from being stripped. In order to spring the H<sub>2</sub>S, acid then must be added to the water. Other contaminants and their effect will be deferred to the next section on the chemistry of ammonia-acid gas systems.

## Chemistry of Ammonia with Acid Gases

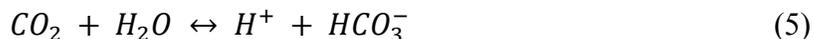
Ammonia is a relatively weak base capable of being mono-protonated. For example, in aqueous solution it forms ammonium ion (protonated ammonia) to a limited extent:



This reaction is in perfect parallel with amine protonation, so in this sense ammonia can be thought of as nothing more than just another reactive amine. There is a great deal of nonsense written in various books and other publications concerning the reactions of H<sub>2</sub>S and CO<sub>2</sub> with ammonia. With the exception of carbamate formation by the direct reaction of CO<sub>2</sub> with NH<sub>3</sub>, all other reactions involve only ionic species. Ions do not form ionic compounds except possibly when materials begin to precipitate. As long as all species are in solution, they exist

as ions and in no sense are they associated with each other, forming compounds. All ions are freely floating and the only associations are ones that result in solution nonideality. Thus, there is no such thing as ammonium carbonate, ammonium bicarbonate, ammonium bisulfide or diammonium sulfide. Such compounds are pure fictions, and it is very hard to make sense of reaction equilibria unless one discards such notions.

The reactions that occur when H<sub>2</sub>S and CO<sub>2</sub> dissolve in solution are the same as in any other aqueous, primary or secondary amine system. The reactions are:



Ammonia influences all these reactions by serving as a proton sink per reaction (1). Understanding sour water strippers, understanding the way ammonia behaves as a solvent for acid gases, and understanding what happens to ammonia in amine regenerators depends on knowledge of

- vapor-liquid equilibria,
- kinetics of the carbamate forming reaction, Equation (7), and
- an appreciation for mass transfer as a rate process where Henry's law applies.

The thermodynamic framework on which the vapor-liquid calculations are based involves a model for the activity coefficients via extended Debye-Hückel theory. Thus, the basic modeling approach for ammonia is the same as for any other amine with one exception: Ammonia is highly volatile and this leads to different distributions in absorption and especially regeneration equipment compared with amines. Its volatility is responsible for it getting into the sour water system (through condenser water blow down, for example) but volatility also allows it to be recovered relatively easily from the same sour water. Heat stable salts and alkali salt contaminants also affect the distribution of ionic species in solution and their presence must be considered, too.

It is very 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. Just as for amine units, ammonia will be converted into 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 these 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<sub>4</sub><sup>+</sup>, shifts back to NH<sub>3</sub>. 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<sub>2</sub>S has already been stripped out and ammonia is the main remaining component. The metering rate is 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<sub>2</sub>S 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. It is important to avoid injecting any more caustic than absolutely necessary because excess caustic injection permanently binds H<sub>2</sub>S 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.

## Simulating Sour Water Strippers

Traditionally, SWSs have been modeled as a series of equilibrium stages with stage efficiencies quoted anywhere in the range from 15% to 45%, i.e., ranging over a *factor* of three. However, the mass transfer rate-based approach to the simulation of amine contactors and such hard-to-model distillation processes as extractive, azeotropic and reactive distillation have been in commercial use since the mid to late 1980s. Their extension to sour water stripping is a natural progression and, in December, 2011 a commercial mass transfer rate-based sour water stripper model became available as part of the ProTreat™ simulation package. The remainder of this paper uses the ProTreat simulator's SWS model to reveal some rather surprising facts and behaviors of sour water strippers.

### Phase Equilibrium

The vapor pressure of ammonia and acid gases above sour water plays a key (but by no means the only) role in determining the extent to which a given column and process configuration will purify sour water and how the process operating conditions affect the separation. We have developed an activity coefficient model for phase behavior for sour water that uses the Deshmukh-Mather (1981) approach for activity coefficients, and the Peng-Robinson equation of state for the vapor. The thermodynamic model has been fitted to the data of Rumpf et al. (1999), Wilson (1990), van Krevelen et al. (1949), Badger and Silver (1938), Carroll and Mather (1989); Carroll et al. (1991), Otsaka et al. (1985), Goppert (1985), Muller et al. (1987), Miles and Wilson (1975), Cardon and Wilson (1978), Gillespie et al. (1985), Clifford and Hunter (1933), Butler (1998), Kohl and Riesenfeld (1985), Edwards et al. (1978), and Beychok (1967), a total of some 550 separate experiments, most involving ammonia and either one or both of the acid gases H<sub>2</sub>S and CO<sub>2</sub>. Figure 2 is a set of parity plots indicating partial pressure ranges and the goodness of fit.

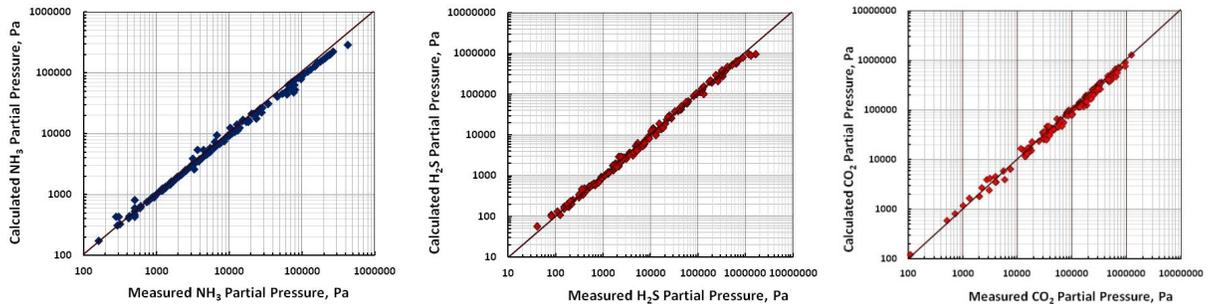


Figure 2 Parity Plots of VLE Data for the system NH<sub>3</sub>-H<sub>2</sub>S-CO<sub>2</sub>-H<sub>2</sub>O

### *Mass Transfer Rate Model*

The sour water stripper model in ProTreat deals with the separation of ammonia, the acid gases, and water as governed by the particular *mass transfer rate* of each individual component. Ammonia is treated as reactive towards CO<sub>2</sub> in the same sense that any other primary or secondary amine is reactive and transfer rates are determined by individual (vapor and liquid) phase mass transfer coefficients, interfacial areas, and concentration difference driving forces. The details of mass transfer rate modeling have been described at length elsewhere (Weiland et al., 2003; Weiland and Dingman, 2001) and will not be repeated here. Suffice it to say the kinetics of the NH<sub>3</sub>-CO<sub>2</sub> reaction (Eq. 7) have been properly accounted for using known kinetic parameters and the usual enhancement factor approach. The resulting process model is a virtual plant on a computer in which all the fundamental physical and chemical processes occurring are properly accounted for. The computer simulation is a direct one-for-one prediction of both column and process performance completely without recourse to user estimates of any parameters whatsoever. All that is required is the actual process flow sheet configuration, tower internals details, and values for process parameters corresponding to such operating conditions as sour water flow and composition, tower pressures and imposed heat loads.

The SWS model itself has been validated against at least a half-dozen sets of stripper performance data by two refining companies and an engineering firm, with what were reported by them as excellent results. Using a virtual plant in the form of a precise computer model, the remainder of this paper examines the effect of steam to water ratio, the presence of heat stable salts, and stripper operating pressure on SWS performance as measured by such parameters as Murphree tray efficiency and residual ammonia and H<sub>2</sub>S in the stripped water. Consideration also is given to how caustic injection strips ammonia, and the fact that one can simulate a little more complex water stripping scheme such as the Chevron WWT process. The bulk of the simulation cases have used live steam injection as the source of stripping vapor because this tends to be the most effective approach to providing thermal energy for stripping; however, reboiled strippers add less makeup water, and they can be simulated just as easily.

## **Exploring Strippers**

Figure 1 shows the simplest possible configuration of a sour water stripper. For this exercise, the stripper contained 40 one-pass valve trays on 2-ft spacing with 2-inch weirs. Sour water was fed 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. Except for the case study involving stripper pressure where a fixed temperature approach of 20°F was used, the sour water feed to the stripper was kept at 235°F. Table 1 gives the conditions of the sour water used for this case study.

### *Ratio of Steam to Sour Water*

Four steam rates were used: 0.78; 0.92; 1.20 and 1.48 lb/USgal, covering the range normally used in sour water stripping<sup>2</sup>. One of the performance parameters of interest is the

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<sup>2</sup> Gantz (1975) shows performance data for steam rates from 0.6 to 4.0 lb/USgal although, commercially, rates at and above 1 lb/USgal are more usual.

computed tray efficiency. For H<sub>2</sub>S, Figure 3 shows the Murphree (1925) vapor-phase efficiency,  $E_{i,n}^{MV}$ , defined (Taylor and Kooijman, for component  $i$  on tray  $n$  (from the top) as:

$$E_{i,n}^{MV} = \frac{y_{i,n} - y_{i,n+1}}{y_{i,n}^* - y_{i,n+1}} \quad (8)$$

It should be noted that this is *not* an overall tray efficiency. Overall efficiencies are based on equilibrium stage calculations to determine the number of theoretical stages. ProTreat<sup>®</sup> studiously avoids such calculations because when combined with the averaging that is done through overall efficiencies, they completely obscure what is really going on in SWSs. The Murphree vapor efficiency provides a quantitative measure of how close to equilibrium each real tray operates. There is *no* relationship between Murphree and overall tray efficiencies.

Table 1 Sour Water Feed Conditions

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

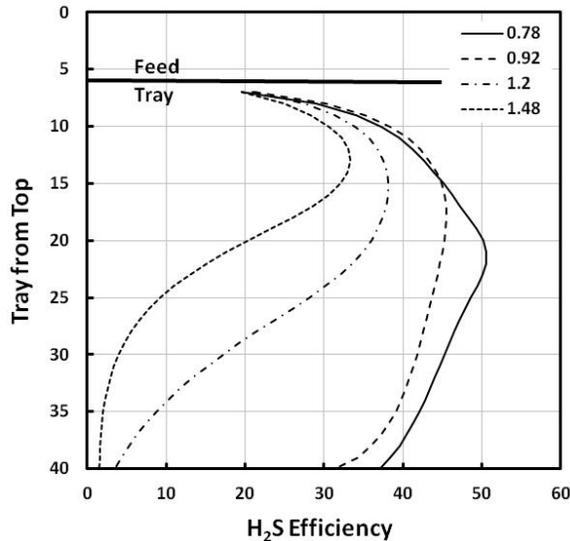


Figure 3 Calculated Murphree Vapor Tray Efficiencies for H<sub>2</sub>S

As can be seen from Figure 3, H<sub>2</sub>S efficiency varies enormously throughout the tower and is a very sensitive function of the steam-to-sour-water ratio. Generalizing H<sub>2</sub>S component efficiency is utterly impossible because it varies from a few percent to 50%.

Obviously the tray count and the steam required depend heavily on the treated-water specifications to be met. Thus, the designer is faced with a difficult decision because *more trays and more stripping energy lead to lower efficiency!* These effects cannot be modeled or accounted for with an equilibrium stage model, even when an efficiency is used. Providing optimal, cost-effective designs using theoretical stages is a rather seat-of-the-pants enterprise.

Before tackling corresponding efficiencies for ammonia, it is revealing to look at the vapor- and liquid-phase concentration profiles of ammonia, as well as the *simulated* vapor profile compared directly with the *equilibrium* vapor composition. Figure 4 shows tray-by-tray profiles of the liquid and vapor phase mole percentages of ammonia. The surprising thing is the bulge, or maximum, displayed at boil-up rates at the low end of the range.

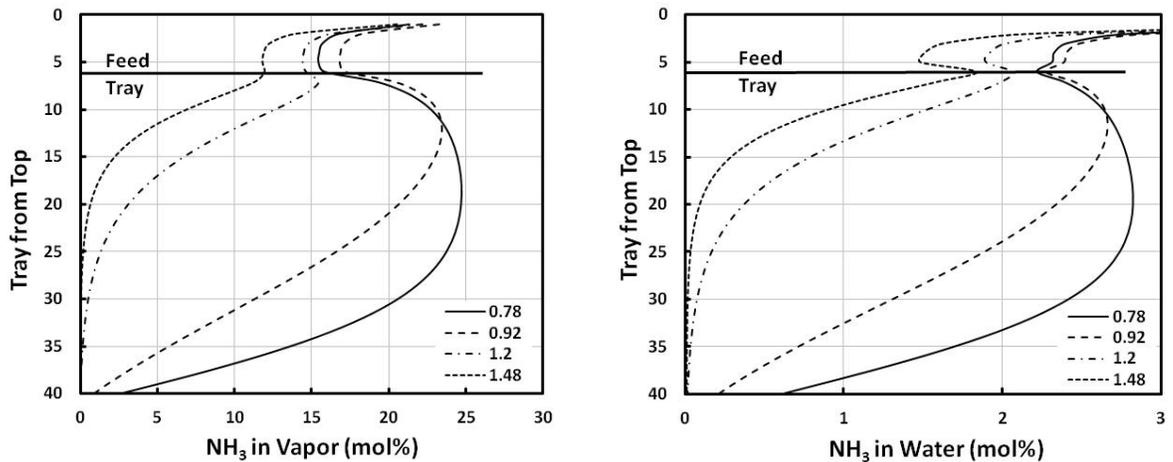


Figure 4 Ammonia Concentration Profiles in the SWS

We have observed and reported the existence of similar maxima in ammonia concentration in the context of ammonia control in refinery amine units (Hatcher and Weiland, 2012). Indeed, there it was found that in an amine regenerator, only the bottom few trays were effective in stripping ammonia. In the present case of a SWS, ammonia stripped in the lower part of the column is actually reabsorbed in the upper part because the  $H_2S$  is high enough there to react with and fix a significant part of the ammonia back into the liquid. When the steam to sour water ratio is high enough, however, the  $H_2S$  concentration is everywhere too low to remove enough ammonia to result in a maximum in the ammonia concentration. We note in passing that there is a strictly monotonic decrease in  $H_2S$  concentration as the sour water moves down the column.

When the boilup rate is at the lower end of the spectrum and a maximum in ammonia concentration occurs away from the ends of the stripper, the Murphree vapor efficiency for ammonia exhibits seemingly odd behavior. Figure 5 shows very surprising efficiency trends from tray-to-tray at stripping steam rates of 0.78 and 0.92 lb steam/USgal. At the lowest steam rate, the apparent efficiency ranges from -100% to +120% and at 0.92 lb/USgal the apparent efficiency reaches +200%. The reason is that the lines corresponding to actual and equilibrium vapor phase mole fractions cross (as they must do because a bulge implies that stripping gives way to absorption at some point in the column) and they have a maximum on immediately adjacent trays rather than on the same tray. Figure 6 shows the actual ( $y$ ) and equilibrium ( $y^*$ ) lines for the steam rate of 0.92 lb/USgal from which it can be seen that both

exhibit a maximum, the lines cross, and they have peak values on different trays. Referring to Equation (8) (definition of efficiency), it is easy to see that if the numerator or denominator changes sign, or the concentration difference in the denominator becomes very small, apparent efficiencies can become not only large, but negative.

At first glance, much of this odd efficiency behavior may seem a little academic; however, when a constant efficiency is applied to an equilibrium stage model, the maximum in ammonia concentration in the interior of the column, well away from the ends, will *not* be revealed and *simulation results will tend to be quite optimistic* in terms of sour water quality and stripped gas ammonia levels. *This may go some way to explaining the wide variations reported in tray efficiencies (15 to 45%) in this application.* It is worth noting that when stripping steam rates are moderate to high, the efficiency turns out to be between 35 and 40%, with variations of only one or two percentage points across the whole column.

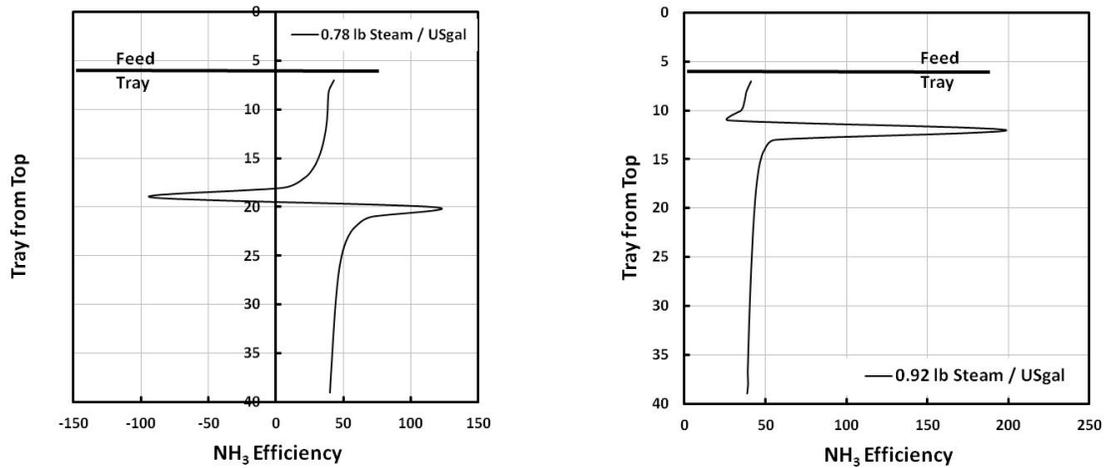


Figure 5 Murphree Vapor Efficiencies for Ammonia at Low Steam Rates

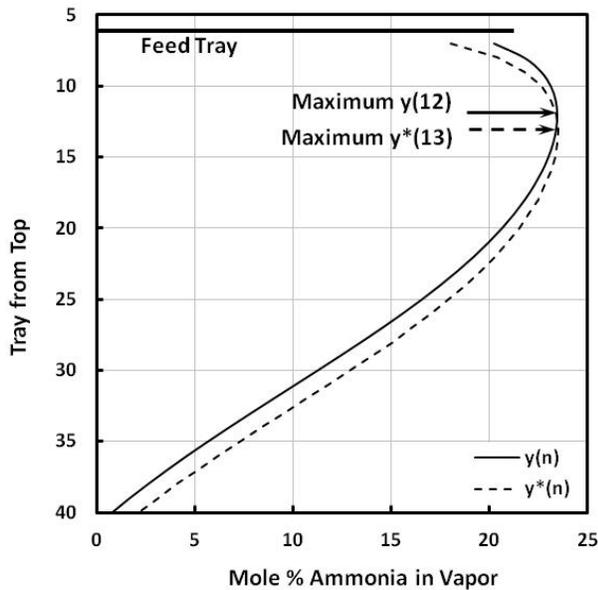


Figure 6 Actual and Equilibrium Ammonia Concentrations in the Vapor Phase at Low Steam Rates

### *Effect of Stripper Pressure*

From time to time, one hears it stated that higher stripper pressures favor sour water stripping so we decided to put this old wives' tale to the test. Table 2 shows the effect of column head pressure in residual ammonia and H<sub>2</sub>S levels in stripped water for the same process configuration and sour water composition shown in Figure 1 and Table 1, respectively. The simulated performance corresponds to a steam rate of 25,000 lb/h of 50 psig steam (1.40 lb/USgal) with the cross exchanger set to a temperature approach of 20°F to minimize the effect of temperature differences across the stripping section. The table shows that contrary to anecdote, higher pressure has a negative (albeit relatively small) effect of water quality with respect to ammonia, but can cause an 80-fold increase in residual H<sub>2</sub>S content of the stripped water (890% loss in performance) under these conditions. *Higher pressures do not seem to favor ammonia stripping, and they certainly have a negative effect on stripped water quality vis à vis H<sub>2</sub>S.*

Table 2 Effect of Stripper Pressure on Residual NH<sub>3</sub> and H<sub>2</sub>S levels in Stripped Water

Stripper Head Pressure (psig)	Treated Water	
	Ammonia (ppmw)	H <sub>2</sub> S (ppmw)
10	17.2	0.00002
15	21.1	0.00013
20	26.0	0.00058
25	31.5	0.00197

### *Effect of Heat Stable Salts on Stripped Water Quality*

Figure 7 shows the effect of stripping steam rate and heat stable salt level on the simulated stripped water quality with respect to residual ammonia and H<sub>2</sub>S content. The stripper is the same 40 tray unit shown in Figure 1 and the sour water has the composition of Table 1, with and without the heat stable salts and levels indicated there. 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<sub>2</sub>S removal because they are generally stronger acids. A two order-of-magnitude reduction in residual H<sub>2</sub>S is possible with only a modest amount of HSS present.

The beneficial effect of HSS on H<sub>2</sub>S removal is at least partially connected to the fact that when caustic is used, it is injected fairly low in the column. *By injecting caustic on one of the bottom few trays, the benefit of the HSS on H<sub>2</sub>S removal is retained.* The ammonia released from the HSSs by caustic can be adequately removed using only a few trays right near the bottom of the column. Although no results are reported here, the mass transfer rate-based SWS model is perfectly capable of quantitatively predicting the effect of caustic injection, the caustic strength or injection rate and the injection position. The highly accurate pH prediction also provides a way to assess reliably the efficacy of pH control.

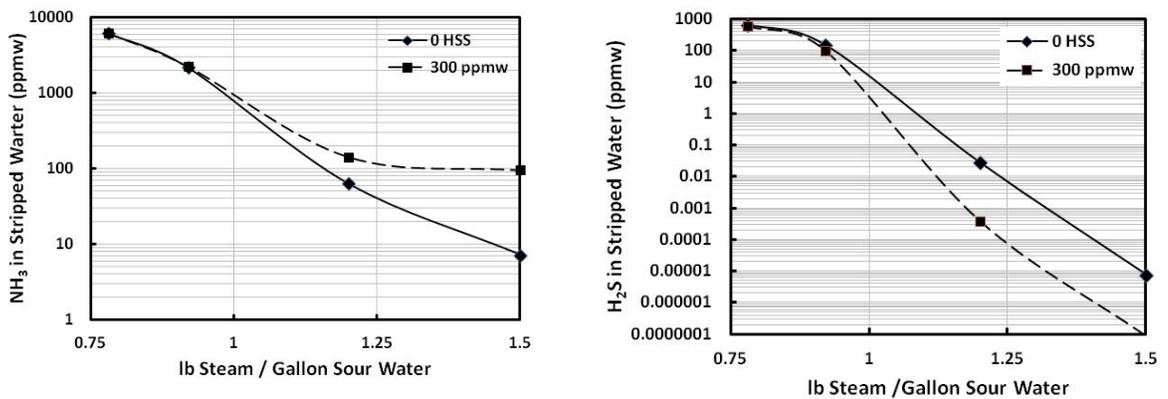


Figure 7 Effect of Heat Stable Salts on Stripped Water Quality

## 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.

A mass transfer rate-based sour water stripper model provides a virtual SWS on a computer. Engineers can now design 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 complete confidence in the results.

Murphree tray efficiencies are probably the most commonly used type of efficiency for tray calculations. They are an invention of the 1920’s developed to allow ideal stage *distillation* calculations to approximate reality more closely, and as 90 year old technology they have served the distillation business well. However, the whole equilibrium stage approach was superseded by mass transfer rate calculation methods in the mid to late 1980s, already nearly 25 years ago. The gas treating industry deals with far more complex separations processes than distillation but, unfortunately, it has been remarkably slow to catch on to the new technology. Genuine mass transfer rate-based simulation is an extremely powerful tool in gas treating.

From this paper there are several other “take-home” messages that pertain directly to sour water stripping:

- $\text{H}_2\text{S}$  efficiency varies enormously from tray to tray throughout a SWS, and it is a very sensitive function of the steam-to-sour-water flow rate ratio. Any attempt to generalize  $\text{H}_2\text{S}$  component efficiency is utterly futile because of its huge variation from only a few percent to 50% across a column and its dependency on the particular operating conditions of each unique situation.
- With respect to efficiencies pertinent to  $\text{H}_2\text{S}$  stripping, the tray count and the steam required depend heavily on the treated-water specifications to be met. Thus, the designer is faced with really quite a difficult decision—*more trays and more stripping energy lead to lower efficiency!* What and where is the balance? Should one use more or less steam, and more or fewer trays? These effects cannot be accounted for

with an equilibrium stage model, even when it uses efficiency. The process is too complex.

- At stripping steam rates in the lower half of the normal range used in practice, it is quite possible for the ammonia concentration in a SWS to show a bulge or maximum in some part of the stripping section well away from the ends. At this bulge, the SWS changes from acting as an ammonia stripper to an ammonia absorber. When (and where) the bulge occurs, there is a high enough H<sub>2</sub>S concentration in the liquid to attract ammonia into the water phase and bind it there as ammonium bisulfide. Again, equilibrium stage models even with efficiency do not show this kind of behavior, and they can lead to either gross overdesign or to a complete mis-design, depending on the relative H<sub>2</sub>S and ammonia concentrations in the sour water feed.
- Murphree plate efficiencies for ammonia in SWSs operating at low to moderate stripping steam rates can vary from large *negative* values to positive values well over 100%. At high stream rates, on the other hand, Murphree vapor efficiencies for ammonia stripping are typically 35 to 40%. This huge variation depending on steam rate and H<sub>2</sub>S to NH<sub>3</sub> ratio may go a long way towards explaining the wide range of 15% to 45% overall efficiency often quoted by practitioners.
- Contrary to a commonly repeated anecdote, higher stripper pressures do *not* favor better ammonia stripping, and they certainly do *not* favor H<sub>2</sub>S stripping where a *factor of 80 loss in performance* was predicted even for the setup in this study.
- When there are heat stable salts in the sour water there is a residual ammonia level that simply cannot be removed from the water no matter how much steam is injected into the stripper. HSSs neutralization is needed to reduce the ammonia level further.
- Caustic can be used to spring ammonia bound to HSSs. However, it should be injected as far down the column as possible so as not to interfere with the benefits that the HSSs have on H<sub>2</sub>S stripping.

In conclusion, this paper has pointed out several aspects of sour water stripping that either do not seem to have been recognized heretofore, or that offer solid scientific explanations for previously observed and reported characteristics.

## References

Asquith, J., and Moore, A., *Sour Water Processing – Balancing Needs*, Proceedings of the 2000 Brimstone Sulphur Recovery Symposium, Vail, CO.

Beychok, M.R., *Aqueous Wastes from Petroleum and Petrochemical Plants*, John Wiley & Sons, New York, p 199, 1967.

Badger, E. H. M. and Silver L., *J. Soc. Chem. Ind.*, 57, 110-112 (1938).

Butler, J. N., *Ionic Equilibrium: Solubility and pH Calculations*, John Wiley & Sons., 1998.

Cardon, D. L. and Wilson, G. M., API Publication 955, American Petroleum Institute, Washington D.C. (1978).

Carroll, J. J. and Mather, A. E., *The Solubility of Hydrogen Sulphide in Water from 0 to 90°C and Pressures to 1 MPa*, *Geochimica Cosmochimica Acta*, 53, 1163-1170, (1989).

Carroll, J. J., Slupsky, J. D. and Mather, A. E., *The Solubility of Carbon Dioxide in Water at Low Pressure*, *J. Phys. Chem. Ref. Data*, 20(6), 1201-1209 (1991).

- Clifford, I. L. and Hunter, E., *J. Phys. Chem.*, 37, 101 (1933).
- Deshmukh, R. D. and Mather, A. E., *A Mathematical Model for Equilibrium Solubility of Hydrogen Sulfide and Carbon Dioxide in Aqueous Alkanolamine Solutions*, *Chem. Eng. Sci.*, 36, 355-362 (1981).
- Edwards, T. J., Maurer, G., Newman, J., Prausnitz, J.M., *Vapor-Liquid Equilibria in Multicomponent Aqueous Solutions of Volatile Weak Electrolytes*, *AIChE Journal*, 24(6), 966-976 (1978).
- Gantz, R. G., *Sour Water Stripper Operations*, API Special Report, Hydrocarbon Processing, May, p. 83, 1975.
- Gillespie, P. C., Wilding, W. V. and Wilson, G. M., *Vapor-Liquid Equilibrium Measurements on the Ammonia-Water System from 313 K to 589 K*, Research Report RR-90, Gas Processors Association, Tulsa, OK (Oct 1985).
- Goppert, U., Dissertation, Universität Karlsruhe, Fed. Rep. Germany (1985).
- Hatcher, N. A. and Weiland, R. H., *The Fate of Ammonia in Refinery Amine Systems*, *Hydrocarbon Engineering*, January, 2012 (in press).
- Hauser, R. and Kirkey, R.T., *Refinery Tests Demonstrate Fixed Valve Trays Improve Performance in Sour Water Stripper*, *AIChE Spring National Meeting*, March 31, New Orleans, LA T1-2E.
- Kohl, A., Riesenfeld, F., *Gas Purification*, 4th Edition, Gulf Publishing, 1985.
- Miles, D.H., Wilson, G.M., *Vapor-Liquid Equilibrium Data for Design of Sour Water Strippers*, Annual Report to API for 1974 (Oct. 1975).
- Muller, G., Bender, E., Maurer, Paper Submitted for Publication in *Berichte Der Bunsengesellschaft für Physikalische Chemie.*, Universität Kaiserslautern, Germany (1987).
- Murphree, E. V., *Graphical Rectifying Column Calculations*, *Ind. Eng. Chem.*, 17, 747-750 and 960-964 (1925).
- Otsaka, E., Yoshimura, S., Yokabe, M. and Inque, S., *Kogyo Kagaku Zasshi*, 63, 1214-1218 (1960).
- Quinlan, M. P. and Hati, A. A., *Processing NH<sub>3</sub> Acid Gas in a Sulfur Recovery Unit*, *Proceedings of the 2010 Laurance Reid Gas Conditioning Conference*, Norman, OK.
- Rumpf, B., Kamps P.-S., Sing, R. and Maurer, G., *Fluid Phase Equilibria*, [158-160] 923-932 (1999)
- Taylor, R. and Kooijman, H., *ChemSep Tutorial: Efficiencies*, [http://www.chemsep.com/downloads/docs/ChemSepTutorial\\_Efficiencies.pdf](http://www.chemsep.com/downloads/docs/ChemSepTutorial_Efficiencies.pdf), downloaded 4 January 2012.
- Van Krevelen, D. W., Hoftijzer, P. J., and Huntjens, F. J., *Recueil Des Travaux Chimiques Des Pays-BAS.*, 68, 191-216 (1949).
- Weiland, R. H., Sivasubramanian, M. S. and Dingman, J. C., *Effective Amine Technology: Controlling Selectivity, Increasing Slip, and Reducing Sulfur*, *Laurence Reid Gas Conditioning Conference*, Norman, OK, 2003.

Weiland, R. H. and Dingman, J. C., *Column Design Using Mass Transfer Rate Simulation*, Laurence Reid Gas Conditioning Conference, Norman, OK, 2001.

Wilson, G. M. and Eng, W. W. Y., "GPSWAT GPA Sour Water Equilibria", Research Report RR-118, Gas Processors Association, Feb 1990.