

## **Sour Water Strippers – Reliable Tools Translate to Reliable Design**

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### **1. Abstract**

Sour water is a common byproduct from petroleum refining and gas processing. Sour water generated from oil refining primarily contains H<sub>2</sub>S which makes the water “sour” and NH<sub>3</sub>, but it can also contain a wide variety of other components such as CO<sub>2</sub>, phenols, cyanides and heat stable salts. Some of the sources of sour water include hydrotreating units, fractionators using live steam, TGU quench columns, ARU reflux purge, crude salting units, scrubbing of hydrocarbons following caustic treatment for mercaptans, COS, and H<sub>2</sub>S removal, and many other processes. Sour water generated from gas processing contains mostly H<sub>2</sub>S originated from cooling, water washes and fractionation processes. Sour water stripping (SWS) is a fairly simple process which involves providing heat and a diluent gas/vapor to remove and carry H<sub>2</sub>S and NH<sub>3</sub> out of the system. The interesting sour-water chemistry involves NH<sub>3</sub> behaving as a “hydrogen ion sink” and acting like a reactive amine for acid gases. Most of the models are based on ideal stages, where the interacting ionic nature of the solution is not accounted and the installed column internals (real stages), are evaluated by extreme tuning or introducing “correction factors” to represent system non-ideality to meet plant performance. Often designers use tray efficiency or packing HETP factors to translate simulated ideal stages into actual, or “real” number and type of installed trays or packing height. This leads to process designs that are unreliable and non-versatile because they are too localized based on a specific operating condition. This design methodology typically presents these deficiencies: (1) Ionic species in aqueous phase are ignored, (2) Simulations cannot qualitatively predict stripping as vapor, liquid loads and energy inputs change, and (3) Innate stripping performance of trays and packings are not accounted; these internals exhibit different contact area and mass transfer and liquid/vapor contact characteristics.

The conventional method of tray calculations has been based on overall efficiency and Murphree tray efficiencies. However, the range of tray efficiencies is very obscure quoted within a vague range of 15% to 45%. In this work, we present case studies where we analyze the treated water NH<sub>3</sub> and H<sub>2</sub>S levels in SWS stripper from the lower end of 93 kg to the upper end of 177 kg of steam/cum stripping stream rate. It has been illustrated that H<sub>2</sub>S efficiency is a sensitive function of the steam-to-sour water flow rate ratio and its efficiency can hugely vary from a few percent to 50% across the column depending on different operating conditions. In addition, the designers often must assess the effect of more trays and more stripping, leading to lower efficiency. Therefore, generalizing H<sub>2</sub>S efficiency is utterly futile, and designing a SWS process based on the concepts of overall and component efficiency is complicated and inefficient. It has also been observed that at certain stripping steam rates, there is a possibility of NH<sub>3</sub> concentration trap, showing a bulge in some part of

the stripping section. The SWS section changes from acting as NH<sub>3</sub> stripper to NH<sub>3</sub> absorber at this bulge, where the H<sub>2</sub>S concentration is high enough to bind more NH<sub>3</sub> into the aqueous phase; a peculiar phenomenon that cannot be captured by equilibrium stage models. Ignoring such complex behaviors in the aqueous solution could lead to gross over-design depending on H<sub>2</sub>S and NH<sub>3</sub> concentration in the sour water feed.

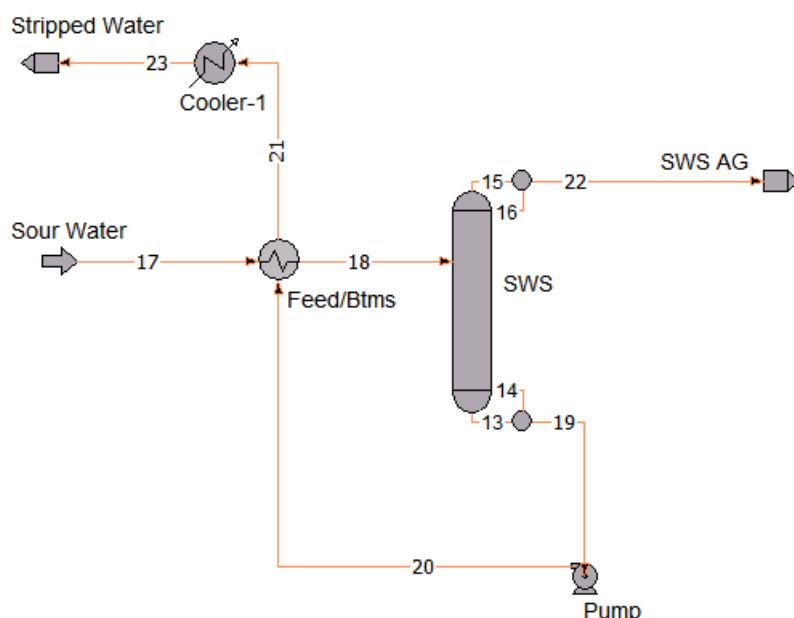
An optimal and efficient SWS design should capture such peculiarities. A genuine mass-transfer rate-based model coupled with an accurate vapor-liquid equilibria (VLE) thermodynamic framework that considers the aqueous ionic chemistry representing the high non-ideality of the sour-water system is needed to have reliable SWS simulation models for unit process design and operational troubleshooting. In this work, we have also illustrated the proprietary thermodynamic model and the rate-based mass-transfer model from OGT | ProTreat® to simulate different SWS configurations. OGT's thermodynamic model has been extensively validated against 550 experimental data points to accurately capture the non-ideal behavior exhibited by the NH<sub>3</sub> – H<sub>2</sub>O – CO<sub>2</sub> – H<sub>2</sub>S system. Depending on the design/rating methodology, engineers can evaluate different SWS unit design configurations with unprecedented accuracy and reliability using ProTreat's rigorous rate-based mass-transfer model. In addition, the model could also be effectively used for predicting stripping performance at varying operating conditions, troubleshooting operations, and optimizing existing units with complete confidence in the results.

## 2. Introduction

Sour water is a common byproduct from petroleum refining and gas processing. Sour water generated from oil refining primarily contains H<sub>2</sub>S which makes the water “sour” and ammonia (NH<sub>3</sub>), but it can also contain a wide variety of other components such as CO<sub>2</sub>, phenols, cyanides, and heat stable salts. Sour water is always found in refineries, and less often in natural gas processing. In the case of refinery hydroprocessing, hydrogen gas and a metal catalyst are used to crack heavier fractions, to saturate olefins along with converting sulfur containing hydrocarbons to H<sub>2</sub>S, and nitrogen bearing hydrocarbons to NH<sub>3</sub>. Another common source of sour water is fractionation using live steam. 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 NH<sub>3</sub>. The steam is condensed and recovered in the O/H circuit of the crude unit, FCC unit, or Coker unit. NH<sub>3</sub> 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 NH<sub>3</sub> to enter the aqueous phase. NH<sub>3</sub> finds its way into amine systems, and if not purged via a reflux purge, will eventually escape from the system with the acid gas often at high concentrations. 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.

### 3. Basic Sour Water Stripping (SWS) Process and Configurations

Sour water stripping (SWS) is a fairly simple process where the general approach to stripping is to provide heat, and a diluent gas/vapor to remove and carry the stripped components (primarily H<sub>2</sub>S and NH<sub>3</sub>) out of the system. The heat raises the sour water to the bubble point and reverses any solubility equilibrium reactions. It may also provide the diluent gas as a stripping carrier by boiling off some of the water. Heat and stripping carrier are commonly delivered either by a reboiled stripper system, or by direct injection of live steam. An alternative to steam is using a hot stripping gas such as methane or nitrogen to provide the heat and the diluent carrier. But regardless of the approach, the basic process remains the same.



**Figure 1:** Schematic of Single Stage Sour Water Stripper (SWS)

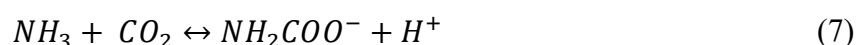
Figure 1 shows a schematic of a typical reboiled SWS configuration. Energy usage is generally quoted as kg of steam per cubic meter of water or lb of 50 psig steam per gallon of water, since steam is an abundant heat media available. NH<sub>3</sub> levels range from 1 to several wt.% on an ammonium hydrogen sulphide (NH<sub>4</sub>.HS) equivalent basis. A typical H<sub>2</sub>S to NH<sub>3</sub> ratio in the combined SWS feed water is 0.5 – 0.8. Higher concentrations of NH<sub>3</sub> and H<sub>2</sub>S are preferred from a water consumption perspective for a more efficient way to store and transport NH<sub>3</sub> and H<sub>2</sub>S removed from upstream units, although it would also require more stripping energy and risks ammonium bisulfide deposits causing upstream units operational problems. Due to high fouling service, stripper columns are most commonly equipped with trays, preferably with directional valves for self-cleaning. The target levels expected during SWS stripping process is generally few 10s of ppmw for NH<sub>3</sub>, with almost negligible H<sub>2</sub>S concentration (< 0.1 ppmw).

The most common configuration of SWS is a single column in which both H<sub>2</sub>S and NH<sub>3</sub> are removed from the sour water and discharged overhead to a sulfur plant. However, a two column system could offer advantages, separating the H<sub>2</sub>S on the first column (the H<sub>2</sub>S stripper) while NH<sub>3</sub> comes from the second column. It is important to note that when high Sulphur and Nitrogenated crudes are processed, the amounts of NH<sub>3</sub> produced can be high enough to consider worth recovering NH<sub>3</sub> as a saleable product rather than just routing it to the SRU furnace. Further, removing NH<sub>3</sub> from the Claus plant unloads the Claus plant hydraulically, reduces front-end air requirement, and allows for a thermodynamically higher Sulphur recovery.

SWS condensing systems are either overhead condenser or pump around type. Pumparound configurations have an advantage since it minimizes the salts deposition in the overhead system, whereas an overhead condenser system has a risk of plugging by very high concentrations of NH<sub>4</sub>SH through salt deposition. Although pumparound condensers are not completely immune to plugging problems, their coolers work on a single-phase water system and hence tend to operate at lower process fluid velocity, thereby lessening the plugging effects. Caustic is injected to adjust the pH of the water and to chemically strip NH<sub>3</sub> bounded with HSS as explained below.

#### 4. Chemistry and Speciation Involved

Reactions (1) to (7) represent all the critical molecular and ionic species involved in a typical SWS process.



Sour water chemistry is quite interesting with the fact that each of these reactions except Reaction (1) is a producer of hydrogen ions. The first reaction is a consumer of hydrogen ions and therefore, NH<sub>3</sub> acts as a proton (or hydrogen ion) sink. So NH<sub>3</sub> allows all the other reactions to keep picking up acid gases, and when NH<sub>3</sub> gets a bit depleted, more is absorbed which allows even more acid gases to dissolve into the water. This makes it possible for both NH<sub>3</sub> and acid gases to reach high concentrations.

Except for 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. All the species in the solution exist as ions, they are freely floating and are not associated with each other. Understanding sour water strippers requires

understanding the way  $\text{NH}_3$  behaves as a solvent for acid gases, and understanding what happens to  $\text{NH}_3$  in amine regenerators depends on knowledge of:

- 1) Vapor-liquid equilibria
- 2) Kinetics of the carbamate forming reaction, Reaction (7), and
- 3) Appreciation for mass transfer as a rate process where Henry's law applies.

In our current work, we have used the activity coefficient framework of extended Debye-Hückel theory to describe the vapor-liquid equilibria of all the species involved in a SWS process.

Thus, the basic modeling approach for  $\text{NH}_3$  is the same as for any other amine with one exception:  $\text{NH}_3$  is highly volatile and this leads to different distributions in absorption and especially regeneration equipment compared with amines. Its volatility leads to it entering the sour water stream through condenser water blowdown but volatility also allows it to be recovered relatively easily from the same sour water. It is also worth mentioning that the presence of heat stable salts and alkali salt contaminants can affect the distribution of ionic species in solution and thus their presence should be taken into consideration.  $\text{NH}_3$  converted into its protonated form 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  $\text{NH}_4^+$  shifts back to  $\text{NH}_3$ . Therefore, presence of organic and inorganic contaminants in a typical SWS could affect the distribution of molecular and ionic species, and should be handled with additional care.

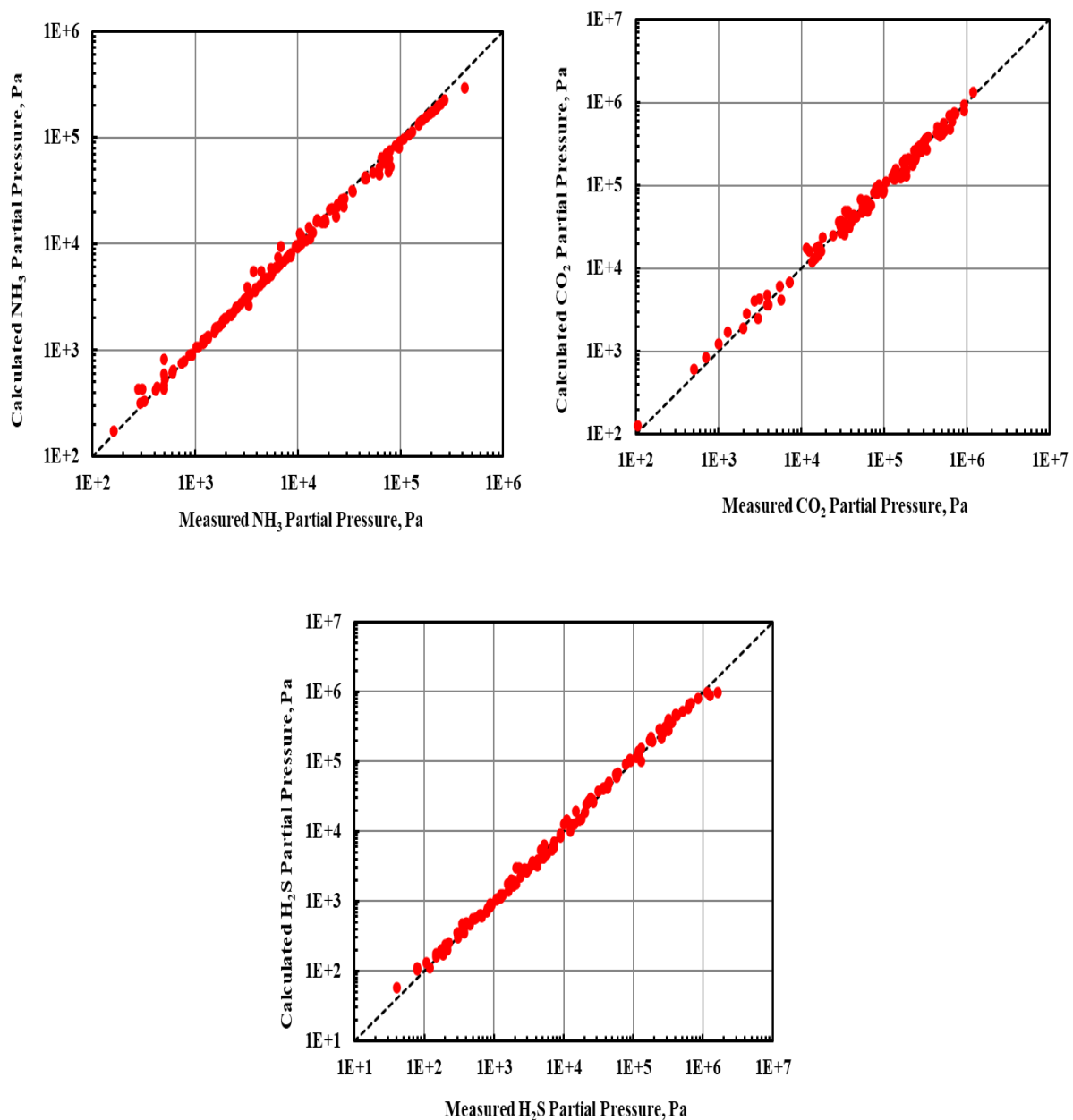
## 5. Simulating Sour Water Strippers

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 as a rule of thumb. Although the mass transfer rate-based approach has been in commercial use since the mid to late 1980s, their extension to sour water stripping is not straightforward and the rest of the paper uses the ProTreat simulator's SWS model to reveal some surprising behaviors of SWSs.

### 5.1 Phase Equilibrium

The vapor pressure of  $\text{NH}_3$  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. Therefore, it is critical to have a correct representation of distribution of each species between vapor and liquid phases. A majority of the process simulators in the literature assume the sour water chemistry to be ideal by assigning activity coefficient of unity for all species. They typically use methods such as Kent-Eisenberg and API-Sour models where the solutions are essentially ideal and the equilibria amongst components ignores the interacting ionic nature of the species. This leads to models with inherently flawed designs which are unable to match plant performance without some extreme tuning that is very localized or introducing "correction factors" to a very specific operating range. So, these legacy models could be inaccurate and presence of HSS in the solutions will make the predictions even worse.

OGT's Proprietary gas treating thermodynamic model was developed to account for all the sour water system non-idealities. The thermodynamic framework is analogous to extended Debye-Hückel theory and uses the Deshmukh-Mather (1981) equation to represent liquid phase activity coefficients and the vapor phase is described using the Peng-Robinson equation of state. The thermodynamic model has been fitted and validated against 550 experimental data points which includes data of Clifford and Hunter (1933), Badger and Silver (1938), van Krevelen et al. (1949), Beychok (1967), Miles and Wilson (1975), Cardon and Wilson (1978), Edwards et al. (1978), Gobbert et al. (1985), Gillespie et al. (1985), Kohl and Riesenfeld (1985), Muller et al. (1987), Carroll and Mather (1989), Wilson (1990), Carroll et al. (1991), Butler (1998), and Rumpf et al. (1999). Figure 2 shows a parity plot showing comparison between experimental and calculated partial pressures of NH<sub>3</sub>, and acid gases CO<sub>2</sub> and H<sub>2</sub>S.



**Figure 2:** Comparison between experimental and calculated data for NH<sub>3</sub> – H<sub>2</sub>S – CO<sub>2</sub> – H<sub>2</sub>O system



## 5.2 Mass Transfer Rate Model

The SWS model in ProTreat deals with the separation of NH<sub>3</sub>, the acid gases, and water as governed by the particular mass transfer rate of each individual component. NH<sub>3</sub> 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 in detail by Weiland et al., (2003) and Weiland and Dingman, (2001). The kinetics of the NH<sub>3</sub> – CO<sub>2</sub> reaction (Equation 7) has been properly accounted for using known kinetic parameters and the usual enhancement factor approach.

## 6. Exploring Strippers

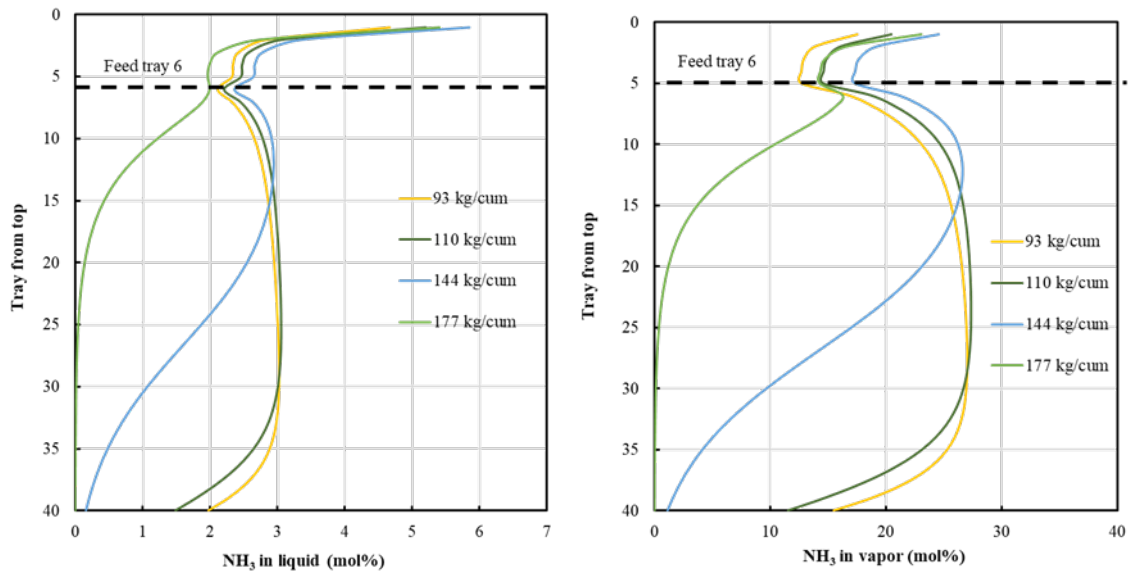
Figure 1 shows the schematic of the standard SWS configuration. For this case study, the stripper contained 40 one-pass valve trays on 2-foot spacing with 2-inch weirs. Sour water was fed to Tray 6 (from the top), return of the reboiler driven with saturated steam at 50 psig entered below the bottom tray, and in all cases the column was sized for 70% of jet and downcomer flood. Table 1 gives the conditions of the sour water used for this case study. We have examined a few cases from the lower end of 93 kg to about 177 kg of steam/cum of stripping steam ratio. The treated water spec is to have less than 20 ppmv of NH<sub>3</sub> and undetectable levels of H<sub>2</sub>S.

Table 1: Typical 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 shows the profiles of NH<sub>3</sub> in both the vapor and the liquid phases in the SWS across the four different steam rates. The surprising thing is the bulge, or maximum shown in the middle section of the column especially at lower steam rates. NH<sub>3</sub> stripped in the lower part of the column is reabsorbed in the upper part because the H<sub>2</sub>S is high enough to react with and revert a significant part of the NH<sub>3</sub> back into the liquid. When the steam to sour water ratio is high enough, the H<sub>2</sub>S concentration is everywhere too low to remove enough NH<sub>3</sub> to

result in a maximum in the NH<sub>3</sub> concentration. It is also worth noting that there is a strictly monotonic decrease in H<sub>2</sub>S concentration as the sour water moves down the column.



**Figure 3:** NH<sub>3</sub> concentration profiles in liquid and vapor phase in SWS.

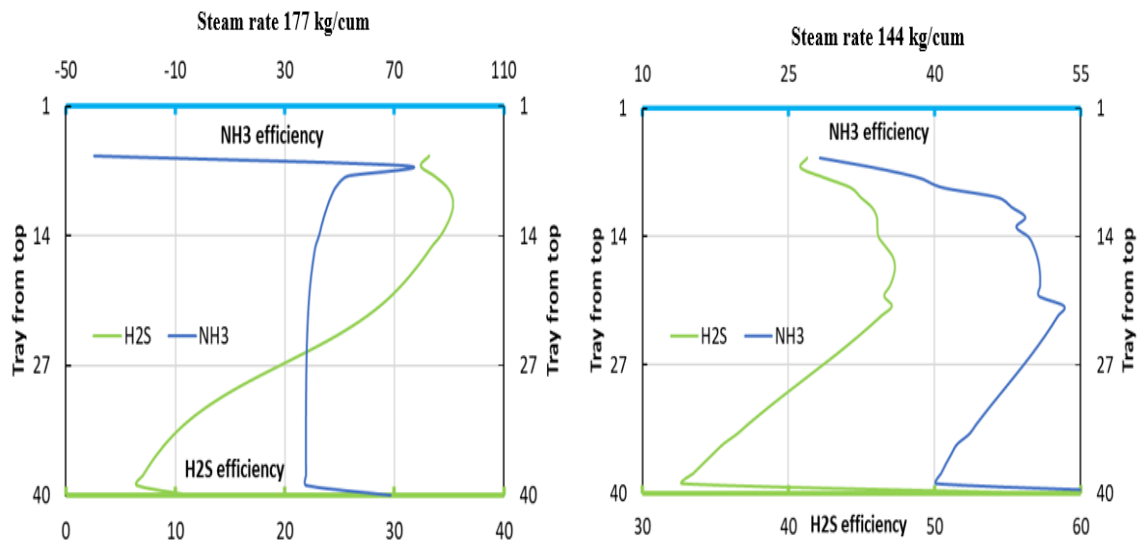
One of the performance parameters of interest used by majority of simulators is the Murphree vapor-phase efficiency defined as follows:

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

Another common definition of efficiency is the overall column efficiency defined by number of equilibrium stage/number of actual trays and is generally used to convert from ideal to real trays. The value of overall efficiency could be between 0 to 100% and lumps all non-idealities into one factor, whereas Murphree vapor efficiency is the efficiency of a given component on a particular tray and could have values anywhere between negative infinity to positive infinity. It should be noted that there is no correlation between overall efficiency and Murphree vapor efficiency. ProTreat<sup>®</sup> studiously avoids measuring the effectiveness of its mass transfer model based on these efficiencies because these numbers do not have any predictive abilities and lumping the non-idealities into these efficiencies leads to obscurity as to what is happening in SWSs.

Figure 4 shows the profiles of Murphree vapor efficiencies of NH<sub>3</sub> and H<sub>2</sub>S at different steam flow rates. As can be seen from the figure, H<sub>2</sub>S efficiency varies enormously throughout the tower and is a very sensitive function of steam flow rate. Generalizing H<sub>2</sub>S efficiency based on one steam flow rate is utterly impossible because it varies from a few percent to 50%. Similarly, if we notice the scale of NH<sub>3</sub> efficiency, it varies from -50% to positive values as high as 70%. It is worth noting here that if we take mean equilibrium stages based on H<sub>2</sub>S and NH<sub>3</sub> from one steam flow rate scenario (for example 177 kg/cum) and apply it to another steam flow rate (144 kg/cum), we will end up with different answers of efficiency. In such a case, a designer is left with complicated choices to make; either increase the steam rate at a given stage count or increase stage count at a given steam rate, either way the efficiency could not be generalized.





**Figure 4:** Murphree efficiencies for NH<sub>3</sub> and H<sub>2</sub>S at different steam flow rates.

This may go some way to explaining the wide variations reported in tray efficiencies (15 to 45%) reported in the literature. 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. It is important to understand here that designing or rating a SWS should not be left to guess work. SWS has components which are both absorbed and stripped at the same time, and therefore using the right simulation tools such as ProTreat<sup>®</sup> is critical for successful design and operation of a SWS.

## 7. Conclusion

We have presented the key limits in using the widely practiced overall and Murphree vapor efficiency for designing SWS. A crucial take home message from this work is that a genuine mass transfer rate-based model coupled with an accurate VLE thermodynamic framework is necessary for the construction of a virtual plant model on a computer for benchmarking. The correction factors used to lump all idealities into a factor like efficiency to achieve an agreement between calculations and reality is an oversimplification which could lead to gross overestimation or design failures.

H<sub>2</sub>S efficiency varies enormously from tray to tray throughout a SWS, and is a very sensitive function of steam flow rate, hence any efforts to generalize H<sub>2</sub>S efficiency could be utterly futile. Another interesting observation is the presence of a bulge in NH<sub>3</sub> concentration in a SWS. At this bulge, the SWS changes from acting as an NH<sub>3</sub> stripper to an NH<sub>3</sub> absorber. The bulge shows the point where H<sub>2</sub>S concentration is high enough in the liquid to attract NH<sub>3</sub> into the liquid phase and bind it as ammonium sulfide. Again, oversimplified equilibrium stage models or pseudo rate models could not detect such a behavior. Therefore, it is imperative to address the complex sour water chemistry using a true rate-based model as ProTreat<sup>®</sup>.

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