

# Sour Water: Where it comes from and how to handle it

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## **ABSTRACT**

Sour water strippers are common in gas processing facilities, sulfur recovery units, wellhead facilities, and refinery applications. Understanding the variables allows engineers to better optimize the initial design and operation. This paper reviews options for sour water stripper configuration and presents a method to optimize stripper operation by finding the most efficient operating parameters. Options investigated include: single or double column for increased product purity; addition of acid or caustic for improved performance; refluxed or non-refluxed columns to mitigate water in the overhead gases; condenser or pump-around and their effects on overhead composition; reboiler, direct steam injection, or a combination of these and the effect they have on corrosion concerns. In addition, optimization of the steam rate is investigated. Overall stage efficiency for trayed strippers, HETP for packed strippers and individual component efficiencies are discussed based on available sour water stripper operating data.

# Sour Water: From where it comes and how it is handled

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## Section 1: Sources of Sour Water

### Gas Processing

Water is the single largest waste stream in oil and gas production worldwide. Wastewater streams come from a variety of sources, the largest of which is associated or production water. Other sources of wastewater include water used during startup and industrial hygiene, purge water from amine sweetening units (ASU), and wash water used in the tail gas treating section (TGTU) of the sulfur recovery unit (SRU). Of these sources, associated water is the largest in total volume; however, the latter two are the largest sources of sour water.

Water always exists in oil and gas reservoirs, often sitting towards the bottom of the production zone. While production may be relatively dry at the beginning of a field's life, water-to-hydrocarbon ratios will increase over the life of a well as hydrocarbons are depleted and water begins migrating upwards to areas of production. The United States averages around ten barrels of associated water per barrel of oil produced [1].

There are a variety of impurities found in this associated water, such as oil and grease, suspended solids, BTEX/VOCs, as well as sulfur and ammonia. Table 1 lists the concentration of typical contaminants in associated water from sources in the Gulf of Mexico [2] and in Pennsylvania [3]. Notice that the largest concentration of contaminants is the suspended solids while the smallest is typically sulfur species and ammonia, those components typically removed in a sour water stripper.

Table 1 : Typical associated water contaminant concentrations

	Gulf of Mexico (mg/L) [2]	Venango County, Pennsylvania (mg/L) [3]
<b>Oil and Grease</b>	26.6	2.74-78
<b>Suspended Solids</b>	141	20-614
<b>BTEX/VOCs</b>	20	1-1,000
<b>Sulfur</b>	42	1-584
<b>Ammonia</b>	12.2	2.22-17

As a waste stream, associated water is disposed of in a variety of ways, depending on the production site's geographical location, geological concerns, the types of contaminants in the water, and whether production is onshore or offshore. The overwhelming majority of associated water is reinjected into either the production reservoir for Enhanced Oil Recovery (EOR) or into depleted or unused underground reservoirs. As much as 95% of onshore associated water is disposed of in this way [4]. The implication is that although associated water is a huge waste, much of it is minimally treated and readily disposed of back into reservoir rock.

The remaining uninjected associated water is either used beneficially or disposed of on the surface in evaporation ponds. Beneficial uses include agricultural use when circumstances allow, such as US

onshore reservoirs that produce water with a low salt content and lie west of the 98th meridian [5]. Some water is also treated and reused in gas processing facilities [6]. Evaporation ponds, as a means of onshore disposal, are falling out of favor due to the additional processing needed and environmental concerns such as salt contamination of surface soil and erosion [7]. Table 2 provides a summary of US onshore associated water disposal practices.

**Table 2 : Summary of Disposal Practices for Onshore Produced Water [4]**

<b>Method</b>	<b>Percent of Onshore Produced Water</b>
<b>Injected for Enhanced Recovery</b>	57%
<b>Injected for Disposal</b>	36%
<b>Beneficial Use</b>	4%
<b>Evaporations</b>	2%
<b>Treat and Discharge</b>	1%
<b>Others</b>	<1%

Offshore water disposal practices for associated water vary from onshore practices. Drilling injection wells and setting up the infrastructure to get the produced water from the platform back to the injection site can be cost prohibitive, so associated water is not typically reinjected offshore [4]. Some production water is treated and reused; however, the majority is simply treated and discharged into the sea [1]. The primary contaminants of concern for this discharged water are suspended solids, oil, and BTEX/VOCs. Removal of these contaminants, by means of coalescers or degassing units, often results in the by-removal of any sour components. This wastewater, therefore, does not need to be introduced to a sour water stripper. The net result is that the primary source of sour water being sent to sour water strippers in upstream applications is not comprised of associated water.

In rare cases, amine sweetening units in upstream applications may be sources of sour water. In most cases, the sweet gas temperature is higher than the inlet gas temperature due to absorption of acid gas components in the absorber. The increase in gas temperature results in water actually being removed from the amine solution. If, however, the sweet gas temperature is lower than the inlet gas temperature, water may actually build up in the amine solution and be removed from the sour liquid condensate in the amine regenerator. This could occur if the inlet gas contains little acid gas and the lean amine solution is at a lower temperature than the inlet gas.

Quench systems for sulfur recovery unit tail gas are the primary source of sour water in upstream applications. Hydrogenating tail gas units, such as Shell's SCOT system, are often used to improve the overall removal efficiency of SRUs. In these systems, any sulfur remaining in the tail gas is converted to H<sub>2</sub>S where it is subsequently removed in an amine plant and recycled back to the sulfur burner. Before the hydrogenated tail gas can be fed to the amine absorber, it must first be cooled, typically with a water quench system. This quench system produces a wastewater stream containing primarily H<sub>2</sub>S, but potentially NH<sub>3</sub> as well.

## Refining

There are more sources of sour water from refining than there are in gas processing applications. These sources include distillation, wash systems, water from knockouts and amine systems. The largest source of sour water, as indicated in Table 3, is from the steam stripping of the crude in the atmospheric and vacuum tower processing units. Fluidized catalytic crackers (FCC), hydrodesulphurization units (HDS) and hydrocrackers also generate a substantial amount of sour water. The byproduct water contains H<sub>2</sub>S, NH<sub>3</sub>, phenols and possibly HCN [8]. Note that, while the Claus process is one of the largest producers of sour water in gas processing, it accounts for less than 2% of that generated in a refinery.

**Table 3 : Process Wastewater at Petroleum Refineries [9]**

Process	Description	Flow Rate (gal/bbl)	Percent of Total
<b>Distillation</b>	H <sub>2</sub> S, NH <sub>3</sub> , solids, chlorides, mercaptans, phenol	26	44%
<b>Fluid catalytic cracking</b>	H <sub>2</sub> S, NH <sub>3</sub> , solids, chlorides, mercaptans, phenol	15	26%
<b>Catalytic Reforming</b>	H <sub>2</sub> S, NH <sub>3</sub> , solids, mercaptans	6	10%
<b>Alkylation</b>	Spent Caustic	2.6	4%
<b>Crude Desalting</b>	Salts, metals, H <sub>2</sub> S, NH <sub>3</sub> , and phenol	2.1	4%
<b>Visbreaking</b>	H <sub>2</sub> S, NH <sub>3</sub> , solids, and phenol	2	3%
<b>Hydrocracking</b>	H <sub>2</sub> S, NH <sub>3</sub> , some solids	2	3%
<b>Coking</b>	H <sub>2</sub> S, NH <sub>3</sub> , some solids	1	2%
<b>Isomerization</b>	H <sub>2</sub> S, NH <sub>3</sub> , spent caustic	1	2%
<b>Hydrotreating</b>	H <sub>2</sub> S, NH <sub>3</sub> , and phenol	1	2%
<b>Claus process</b>	H <sub>2</sub> S, NH <sub>3</sub>	<1	
<b>Other processes</b>	All of the above mentioned contaminants	<1	

## Section 2: Typical Contaminants

### Gas Processing

In gas processing, the main contaminant of concern in sour water is H<sub>2</sub>S. The wastewater from a tail gas cleanup unit quench loop- with no ammonia in the sulfur plant vapor effluent- contains, on average, 35 ppmw of hydrogen sulfide and 350 ppmw of carbon dioxide.

The contaminants for refinery streams may contain the acidic components hydrogen sulfide, hydrogen cyanide and phenol as well as the basic component ammonia. Table 4 shows a typical concentration of contaminants for both the unprocessed sour water and the liquid effluent leaving the bottom of the sour water stripper in refinery applications.

**Table 4 : Typical Sour Water Contaminants with Feed and Treated Water Concentration**

Contaminant	Feed [10]	Stripped Water [11]
H <sub>2</sub> S	300-12,000 ppm	<10 ppm (often <1 ppm)
NH <sub>3</sub>	100-8,000 ppm	<100 ppm (often < 30 ppm)
HCN	Various	Various
Phenol	Up to 200 ppm	Up to 200 ppm

### Section 3: Disposal Techniques for Treated Sour Water

Sour water must be processed, typically in a sour water stripper, before it is either used or disposed of in a variety of ways. Onshore, there are three common disposal techniques for treated water which include the common sewage stream, evaporation ponds, and reuse. Offshore, the most common disposal technique is discharge into the sea.

For refining locations, the treated water can be disposed of directly to the sewer provided that the impurities are below acceptable values, often 30ppm NH<sub>3</sub> and less than 1ppm H<sub>2</sub>S [10]. While municipal or other sewage systems may be used when available, many refineries contain onsite wastewater treatment facilities, including biotreatment ponds, where water is processed and discharged. Stripped water containing a large amount of phenol is often reused rather than disposed of. It is utilized in the crude desalter, as contacting with the crude oil allows for the removal of phenolic components back into the refining system.

### Section 4: Fundamentals of Sour Water Process Modeling

#### GPA Research

The GPA has made a significant commitment toward studying the sour water system. Table 5 lists the research reports, systems studied, and the year the study was completed. These works have increased the understanding and modeling capabilities for these complex systems. Furthermore, data from these reports-- along with the cited references in these reports-- have been used to develop not only the GPA sponsored GPSWAT model, but also other electrolytic models found in today's commercial simulation products such as ProMax.

Table 5 : Summary of GPA Sponsored Research for Sour Water Systems

Report	Systems Studied	Year
RR-41	H <sub>2</sub> S-H <sub>2</sub> O, N <sub>2</sub> -H <sub>2</sub> O, CO-H <sub>2</sub> O, H <sub>2</sub> -H <sub>2</sub> O	1980 [12]
RR-48	H <sub>2</sub> S-H <sub>2</sub> O, CO <sub>2</sub> -H <sub>2</sub> O, C1-H <sub>2</sub> O	1982 [13]
RR-52	NH <sub>3</sub> -CO <sub>2</sub> -H <sub>2</sub> S-CO-N <sub>2</sub> -C1-H <sub>2</sub> -H <sub>2</sub> O	1982 [14]
RR-65	NH <sub>3</sub> -H <sub>2</sub> S-H <sub>2</sub> O, NH <sub>3</sub> -CO <sub>2</sub> -H <sub>2</sub> O, NH <sub>3</sub> -H <sub>2</sub> S-CO <sub>2</sub> -H <sub>2</sub> O	1983 [15]
RR-78	C1SH-H <sub>2</sub> O, C <sub>2</sub> SH-H <sub>2</sub> O, CS <sub>2</sub> -H <sub>2</sub> O, COS-H <sub>2</sub> O	1984 [16]
RR-90	NH <sub>3</sub> -H <sub>2</sub> O	1985 [17]
RR-118	GPSWAT Sour Water Equilibria Model	1990 [18]

Table 6 compares the measured liquid compositions and pressures with the data reported in Research Report 52. The temperature ranges from 38 °C to 149 °C and the pressures from about 1.2 to 9 bara. The calculations were performed by setting the temperature and the vapor composition, and then solving for the dew point pressure and the liquid phase composition. In addition to this particular comparison, BR&E has done extensive comparisons with other sour water equilibrium data sources.

**Table 6 : Comparison of the Electrolytic ELR Model to Research Report 52**

T (°C)	P (bara)		Composition mol %	Vapor	Liquid	Liquid
	measured	ProMax		measured	measured	ProMax
<b>38</b>	2.30	2.73	NH <sub>3</sub>	0.85	2.11	3.17
			CO <sub>2</sub>	0.065	0.27	0.3
			H <sub>2</sub> S	0.47	0.53	0.8
			H <sub>2</sub> O	2.3	97.09	95.72
			CO <sub>2</sub>	25.99	-	0.00096
			N <sub>2</sub>	9.99	-	0.00026
			CH <sub>4</sub>	12.96	-	0.00067
			H <sub>2</sub>	47.35	-	0.0016
<b>93</b>	1.15	1.17	NH <sub>3</sub>	13.25	2.06	2.31
			CO <sub>2</sub>	8.8	0.26	0.17
			H <sub>2</sub> S	11.85	0.51	0.58
			H <sub>2</sub> O	66.1	97.17	96.94
<b>149</b>	9.72	10.0	NH <sub>3</sub>	8.33	2.12	2.63
			CO <sub>2</sub>	30.87	0.29	0.22
			H <sub>2</sub> S	14.44	0.53	0.68
			H <sub>2</sub> O	46.36	97.06	96.47
<b>93</b>	1.70	1.83	NH <sub>3</sub>	6.09	2	2.38
			CO <sub>2</sub>	33.99	0.57	0.5
			H <sub>2</sub> S	17.45	0.51	0.69
			H <sub>2</sub> O	42.47	96.92	96.43
<b>149</b>	8.97	8.83	NH <sub>3</sub>	6.81	2	1.91
			CO <sub>2</sub>	27.14	0.24	0.2
			H <sub>2</sub> S	13.78	0.49	0.53
			H <sub>2</sub> O	52.27	97.27	97.36

### H<sub>2</sub>S Only Cases

For systems which contain only a weak acid or a weak base, such as the binary system H<sub>2</sub>S-H<sub>2</sub>O or the binary system NH<sub>3</sub>-H<sub>2</sub>O, molecular models are sufficiently descriptive to model the system behavior. Examples of molecular models would be the cubic equations Peng-Robinson, Soave-

Redlich-Kwong, as well as any activity coefficient models that only account for molecular species. This acid only case is a special case and care must be taken if modeling a sour water system. These equations are not capable of describing the behavior when both an acid and a base are present. An electrolytic model is needed to account for the ionic interactions of the dissociated species in acid-base systems and can be used for acid only systems as well.

Figure 1 shows the Henry's constants for common sour water constituents in H<sub>2</sub>O. The data for HCN-water systems were obtained from Edwards et al. 1978 [19] and Gmehling et al 1998 [20]. The phenol-water data were obtained from Langes Handbook of Chemistry (1978) [21]. All other data were obtained from GPA Research Reports. Note that Phenol has a Henry's constant which is about four orders of magnitude lower than H<sub>2</sub>S or CO<sub>2</sub>. This suggests that Phenol will exit from the sour water stripper in the liquid effluent. Also note that the HCN has a Henry's constant about two orders of magnitude lower than H<sub>2</sub>S or CO<sub>2</sub>. This suggests that the HCN will tend to leave in the liquid effluent as well.

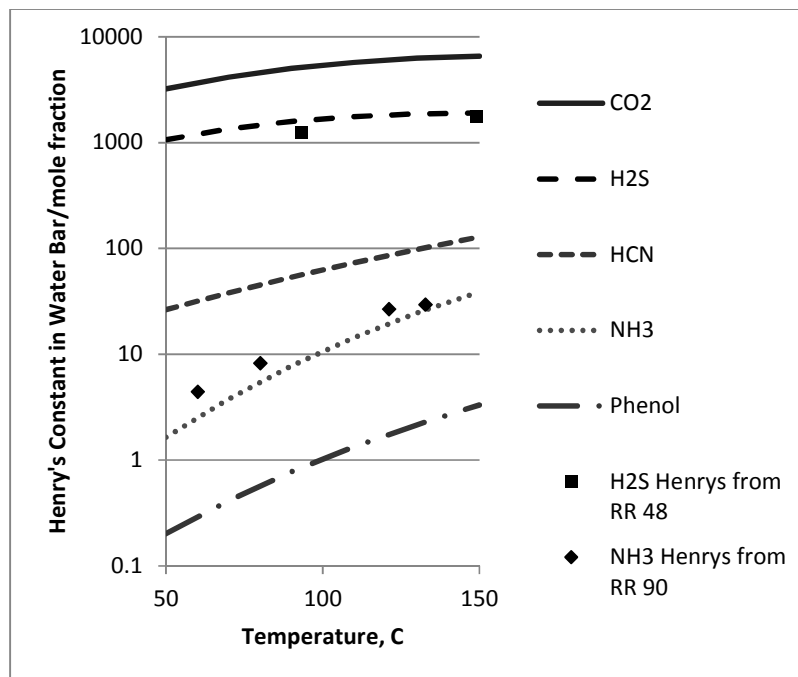


Figure 1 : Henry's Constants for Various Contaminants as Predicted using the Peng-Robinson Equation of State

## Ammonia Containing Cases

Figure 2 shows the effect of ammonia on the Henry's constant of  $H_2S$  at various temperatures. As can be seen, an increase in the  $NH_3$  concentration can have a major impact on the vapor pressure of  $H_2S$ , tying up the acidic component in the liquid phase. It is this effect which cannot be accounted for using a cubic equation of state and is why an electrolytic package is required whenever acid and bases are both present in the liquid. Other acid-base reactions must also be accounted for, such as the weak acid HCN, an acidic component that has a relatively low volatility, making ammonia more difficult to strip into the vapor phase.

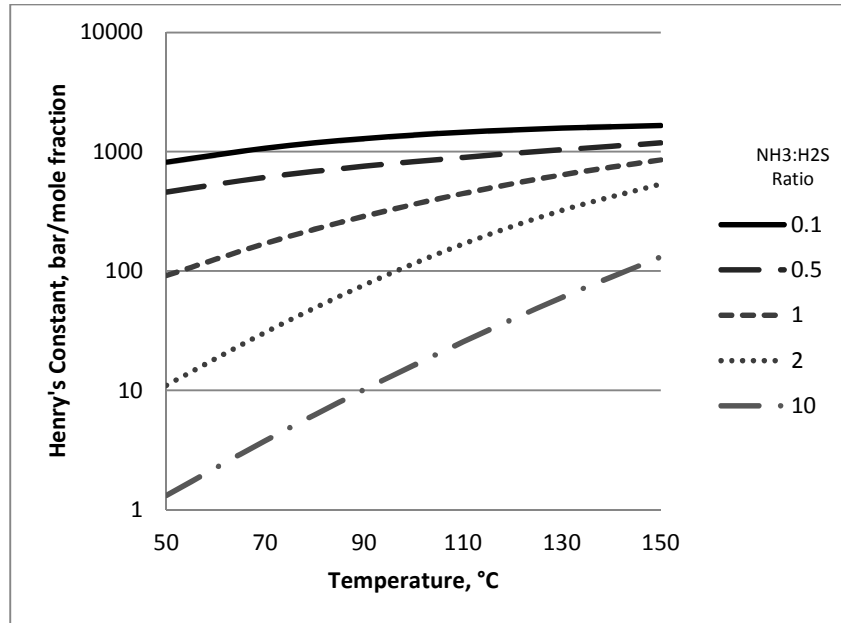


Figure 2 : Henry's Constants for 0.01%  $H_2S$  at various  $NH_3$  ratios using the Electrolytic ELR Model

## Modeling Basics

### Ideal Stage Method

Traditionally, sour water stripper calculations have been performed using ideal stages. Ideal stage calculations provide a fast and accurate means to quantify the trade-off between number of trays and stripping steam. Various simulations are performed to study the total number of ideal stages required to make specification, and, once the number of ideal stages has been determined, they are translated into a number of real trays or length of packed bed using efficiencies or HETPs. Overall tray efficiencies have been reported as ranging from 30 to 50% by Kohl [23] and 40% by Pilling [24]. Kohl also reports packed tower HETPs averaging 0.8 to 1.2 m.

For sizing the column, capacity should be derated for foaming. A system factor of 0.6-0.7 is recommended [23].

### Mass Transfer Model

Mass transfer models use rates of mass and heat transfer between the phases in the column. The mass and heat transfer coefficients and interfacial area are based on vapor and liquid diffusivities, viscosities, densities, heat capacities, and thermal conductivities. To estimate mass transfer



coefficients, detailed information about the column internals is required. This information includes column diameter, weir height and fraction active area for trays, and surface area per unit volume and void fraction for packing. Several different mass transfer coefficient correlations are available for both trays and packing and the predicted column performance may vary depending on the correlation that is selected.

## Section 5: Design Considerations.

In evaluating conventional and current sour water stripper designs, a literature search was performed but turned up limited sources. One well known source is provided by the American Petroleum Institute [26], but this survey, performed over 30 years ago, does not reflect the state-of-the-art and current operating practices for sour water strippers. A more recent reference which better reflects current designs was presented by al-Dhafiri and Reddy in 2010 [22]. However, this work was more concerned with corrosion than operating parameters and contains some discrepancies in the measured data. It is unfortunate that more current design data is not available in the public literature, but with these limitations, the data presented by al-Dhafiri was selected as a base case for example purposes in this study.

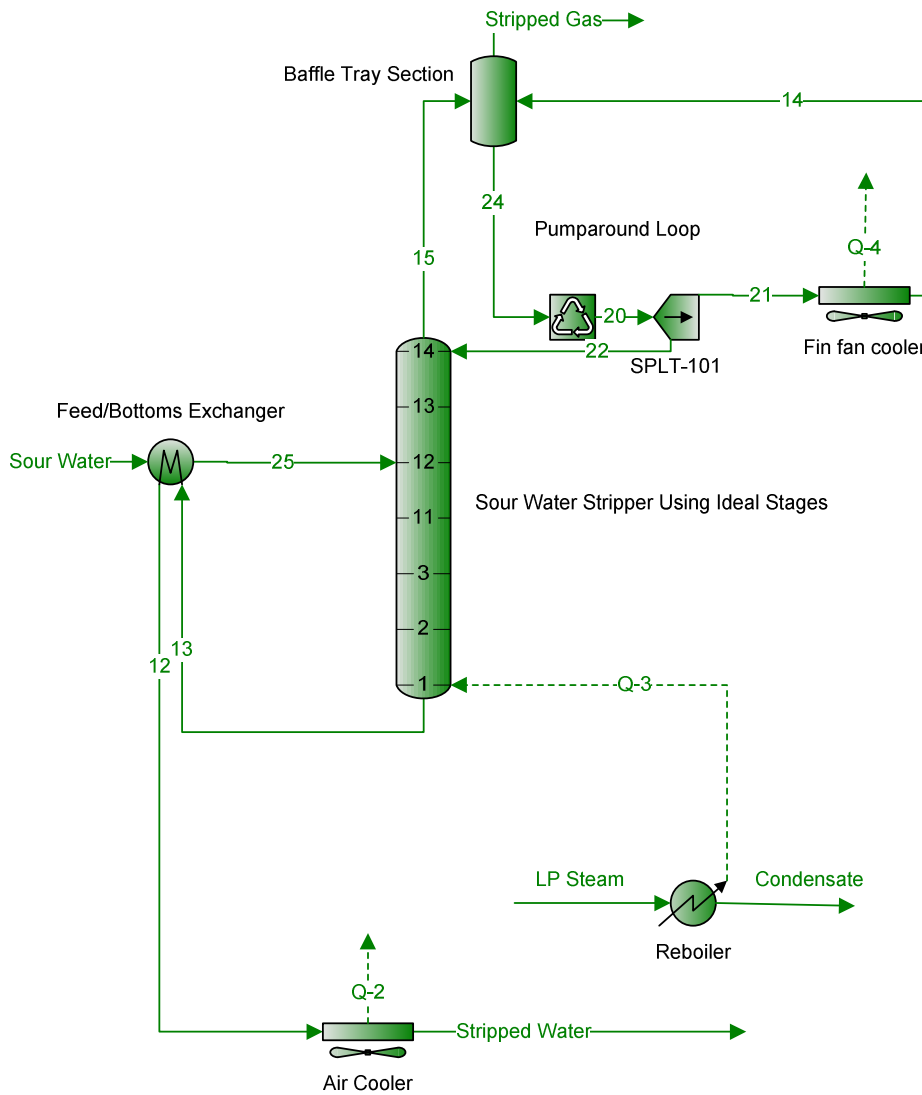
Typical sour water stripper operating conditions are given in Table 7. The sour water feed is warmed in a cross exchanger with the sour water stripper bottoms. The overhead temperature is kept above 80 °C to avoid the desublimation of ammonium bisulfide salts [22].

Table 7 : Typical Sour Water Stripper Operating Conditions

Feed	Overhead	Bottoms	Pressure	Steam Rate
82-99C	>80C	100-150C	110-450 kPa	60-300 kg steam/m <sup>3</sup> feed

### Conventional Design

A sour water stripper commissioned in 1987 is described in the paper by Al-Dhafiri and Reddy (2010). Sour water from a FCC unit is de-oiled and heated in a cross exchanger with the column bottoms before entering the stripper. The stripping section consists of 29 sieve trays along with 5 additional trays above the feed. A baffle tray section is at the top of the column with a pump around reflux loop. The sour water stripper was simulated initially using the ideal stage approach. Figure 3 shows a drawing of the configuration. The pumparound reflux loop will provide very little separation and is modeled as a single ideal stage. Al-Dhafiri gives the steam rate but does not indicate the type of reboiler used. Therefore the column was set up using a duty stream instead of a more detailed heat exchanger.



**Figure 3 : Typical Sour Water Stripper Configuration with Reboiler and Overhead Pumparound Loop**

In Table 8, the measured stripped water composition is compared to that predicted using an ideal stage calculation in ProMax [27]. The ideal stage model predicts 22ppm and <1ppm ammonia and H<sub>2</sub>S, respectively, while the plant data shows 21ppm and 7ppm. Notice little HCN and phenol are removed in the stripper.

**Table 8 : Comparison of Model Predictions to Plant Data**

	Reported Values		Ideal Stage Model				Mass Transfer
	Sour Feed	Stripped Water	Base Case	Kettle Reboiler	Live Steam	Partial Condenser	Base Case
<b>NH<sub>3</sub> (ppmw)</b>	2320	22	21	17	15	21	12-20
<b>H<sub>2</sub>S (ppmw)</b>	2700	7	<1	<1	<1	<1	<1
<b>HCN (ppmw)</b>	17	17	17	17	14	17	17
<b>Phenol (ppmw)</b>	300	-	298	298	250	298	296
<b>Rate (m<sup>3</sup>/h)</b>	22.7	-	22.5	22.5	26.8	22.5	22.5
<b>Cond. Duty (MW)</b>		-	1.99	1.99	2.09	1.99	1.99
<b>LP Steam (kg/h)</b>		4320	4320	4320	4320	4320	4320

Sour water strippers can be designed to use various types of heating including kettle reboiler, thermosiphon reboiler, live steam injection or a combination of these. For comparison, the kettle reboiler and live steam options were simulated with the results shown in Table 8. The ideal stage with kettle reboiler model shows an improved stripping of ammonia due to the additional ideal stage provided by the reboiler. Live steam injection shows even more improved stripping, but this is at the expense of added condenser duty and a 19% increase in the stripped water rate.

Some of the earliest sour water strippers were non-refluxed. However, sulfur recovery units downstream of the stripper will have their performance adversely affected by excessive water in the feed. So to reduce the water content of the acid gas stream, modern sour water strippers generally use some method of generating reflux.

To combat corrosion and fouling many modern sour water strippers use a pump around loop for generating this reflux, although some sour water strippers have also been built using a conventional partial condenser design. Shown in Table 8 are the results for both a pump around loop condenser and a conventional partial condenser for the example case. With no other change to the column, the total required duty to achieve a target overhead temperature is the same between the two systems. Likewise, the stripped water composition is identical. This is because the same amount of heat must be removed to achieve a set overhead vapor temperature, regardless of the method used. In a conventional condenser this heat is removed primarily as heat of condensation and in the pump around loop this heat is removed as sensible heat. Although the duty is the same for each of the two systems, because the pumparound system is in liquid only service and the partial condenser system is in condensing service, the area of the cooler required for the pumparound system is considerably larger.

The sour water stripper was also simulated using a mass transfer model in ProMax [27]. In this calculation the actual number of trays is used and the hardware is described in more detail by specifying the column diameter, weir height, and other tray details. Three different mass transfer coefficient correlations were used in the investigation. The mass transfer results given in Table 8 show the stripped water contains 12-20ppm NH<sub>3</sub> and <1ppm H<sub>2</sub>S. The mass transfer results given in Table 8 are practically identical to the ideal stage model. Temperatures and composition profiles from one of the mass transfer calculations are shown in Figure 4 and Figure 5. The decrease in liquid temperature at feed stage 29 is due to the feed being slightly subcooled. The ammonia and H<sub>2</sub>S concentrations in the water continually decrease moving down the tower while the phenol is practically constant and the HCN only changes a little.

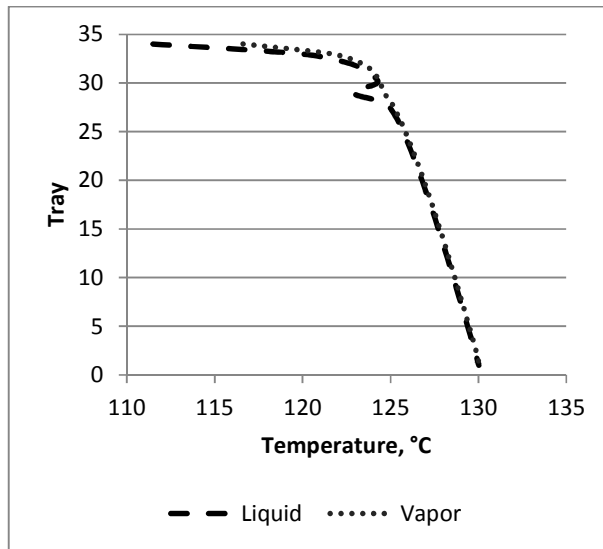


Figure 4 : Stripper Column Profile, Temperature

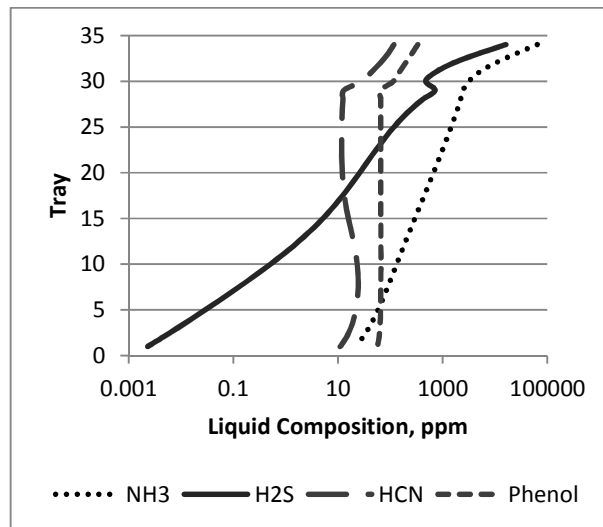


Figure 5 : Stripper Column Profile, Composition in Liquid Phase

The amount of steam used has a major effect on the composition of the stripped water. Figure 6 illustrates the effect of varying the steam rate on the stripped water composition. The  $H_2S$  concentration decreases rapidly as the steam rate is increased.  $NH_3$  concentration also initially decreases rapidly until it starts being influenced by acid-base chemistry of  $NH_3$  and  $HCN$ .  $HCN$  concentration is initially insensitive to steam rate and remains constant. However, once the  $NH_3$  concentration becomes sufficiently low, both  $NH_3$  and  $HCN$  can be stripped. Phenol ionizes in the water and significant removal by stripping is difficult.

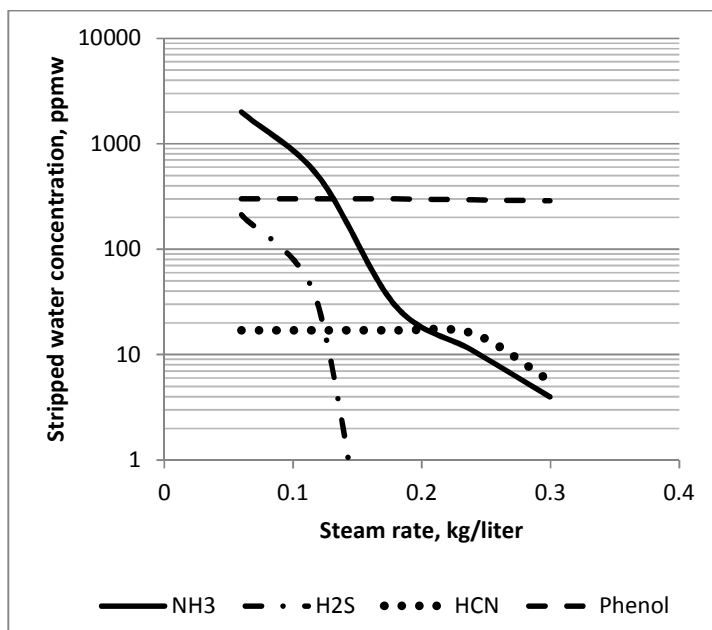


Figure 6 : Effect of steam rate on degree of stripping

### Double Column Design

With conventional sour water strippers in refining operation, an acid gas containing both H<sub>2</sub>S and NH<sub>3</sub> is produced. An alternative is to use a double column approach as shown in Figure 7 which produces separate NH<sub>3</sub> and H<sub>2</sub>S product streams. Chevron's WWT [23] process is a popular example of this approach. The H<sub>2</sub>S producing column typically operates at an elevated pressure (7 barg) and produces a stream containing <100 ppmw ammonia. The ammonia column typically operates around 3.5 barg and with additional scrubbing can produce an ammonia stream with <5 ppmw H<sub>2</sub>S. Table 9 compares the conventional sour water stripper to the double column approach.

The advantage of the double column design is the separation of H<sub>2</sub>S and NH<sub>3</sub> into different product streams. The ammonia stream can be combusted without producing significant SO<sub>2</sub>, or it can be purified and sold as feedstock. Likewise the purified H<sub>2</sub>S can be directly used as a feedstock for a sulfuric acid plant. Besides beneficial uses, diverting NH<sub>3</sub> away from the SRU can improve that unit's performance. NH<sub>3</sub> can cause operating problems such as catalyst deactivation and equipment plugging in the SRU. In addition, a higher flame temperature is required to fully destroy NH<sub>3</sub>, leading to higher COS and CS<sub>2</sub> formation and subsequently lower sulfur recoveries. The size of the SRU can be reduced or the throughput of an existing unit can be increased since the extra air required to burn the ammonia, as well as the ammonia itself, is eliminated from the feed [28].

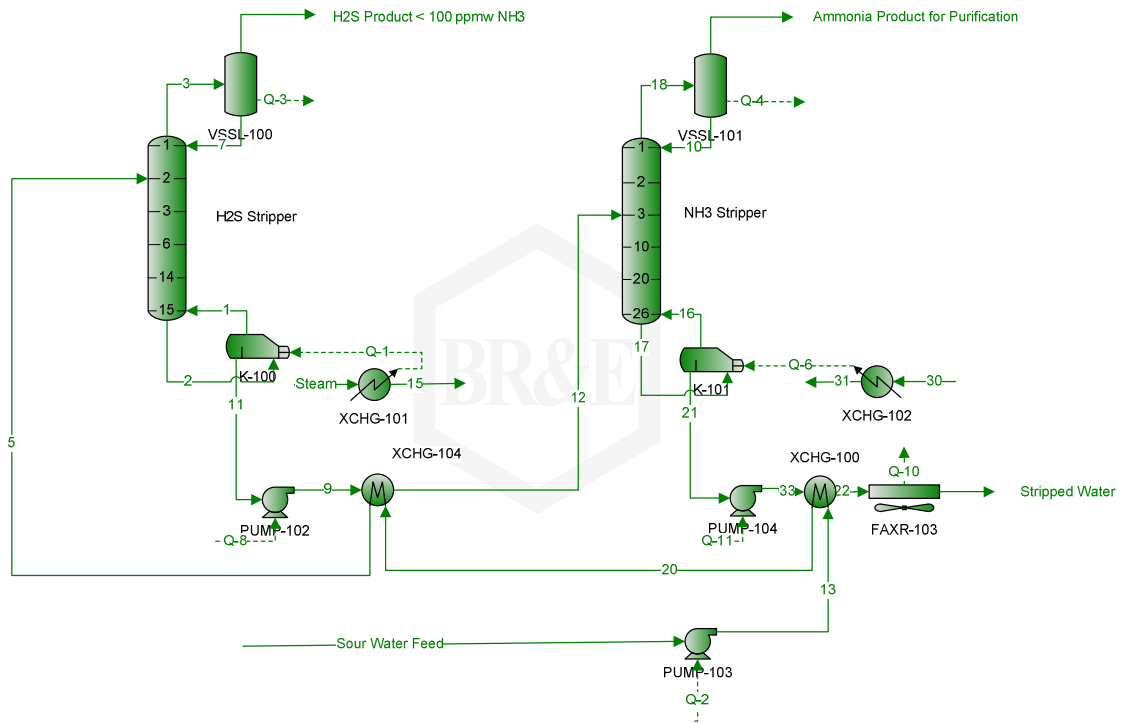


Figure 7 : PFD of a Double Column System

Table 9 : Comparison of a Conventional Single Column Stripper to a Two Column System

Stripped water	Conventional Stripper	Double Column System
NH <sub>3</sub> (ppmw)	21	44
H <sub>2</sub> S (ppmw)	<1	<1
HCN (ppmw)	17	17
Phenol (ppmw)	298	286
Rate (m <sup>3</sup> /h)	22.5	22
Utilities		
Cond. Duty (MW)	2.0	1.0
Reboiler Duty (MW)	2.5	3.1

### Ionic Considerations

The sour water system with hydrogen sulfide and ammonia consists of a weak base and a weak acid. Other naturally occurring acid components in sour water systems include HCN and Phenol. Ammonia is the only normally occurring base. Addition of strong acid or strong base is used to balance the pH of the exiting effluent and, in addition, the choice of using either a strong base or a strong acid depends on the constituents that are desired to be sent overhead. The addition of strong acid results in the liberation of the weak volatile acids of H<sub>2</sub>S and HCN (phenol is not considered a volatile acid) and the corresponding holding of ammonia in the liquid phase as a salt. The addition of strong base will result in the liberation of ammonia to the vapor phase and the corresponding holding of the acidic compounds, H<sub>2</sub>S, HCN, and Phenol in the liquid phase. When used, a strong base is typically injected towards the bottom of the column since much of the H<sub>2</sub>S is stripped higher up in the column than ammonia. Thus, injecting strong base towards the bottom will result in less H<sub>2</sub>S in the column bottoms while still enhancing the stripping of NH<sub>3</sub>.

Other minor contaminants are phenol and hydrogen cyanide. As phenol is not considered a volatile component, columns should be designed with the expectation that it will remain in the liquid phase. The hydrogen cyanide is a volatile acid, but it is also a stronger acid than hydrogen sulfide, forming ammonium salts and tending to exit in the liquid effluent. To achieve desired ammonia concentrations in the treated water, the presence of HCN and these ammonium salts may require an increase in the reboiler duty.

The amount of addition of the strong acid or strong base will depend on the flow rate of the acids or ammonia in the stream, as well as the objectives of this acid/base addition.

## **Section 6: Conclusions**

Sour water comes from a variety of sources in both upstream and downstream processing. Depending on those sources, the water can be divided into two basic categories: sour water with just acidic components or sour water with both basic and acidic components. When the sour water contains both acids and bases, standard equations of state are insufficient and a more sophisticated model, which describes the dissociations and ionic reactions, is required. Fortunately, the GPA has made the effort to obtain extensive sets of data with sour water to allow for adequate model development with predictive capabilities.

Sour water strippers can be designed using an ideal stage approach or a mass transfer approach. The ideal stage approach requires the use of overall tray efficiencies which range from about 30-50 %. The mass transfer model requires a complete description of column internals and will predict differences between the vapor and liquid temperatures.

Sour water strippers can be configured in a variety of ways, including various types of condensing loops, reboiler systems, or other stripping methods. There was little difference found in the predicted purity of the stripped water based on whether a condenser or pump around was used. When live steam was used in lieu of a reboiler, there was some enhancement of stripping, but at the expense of additional contaminated liquid effluent. Advanced processes, such as the double column process, can be used to produce highly pure hydrogen sulfide and ammonia streams instead of leaving both contaminants as a mixture to be fed to sulfur recovery units.

Along with varying the equipment used in design, strong acids or bases to the column can be used to effect column performance. The addition of strong base has the effect of liberating the ammonia and sending it overhead while forcing the acids to exit with the liquid effluent. The addition of strong acid will liberate the hydrogen sulfide, hydrogen cyanide and carbon dioxide while keeping the ammonia as a salt in the liquid effluent. Phenol is a weak acid with fairly low vapor pressure and, in almost all cases, will leave the stripper in the liquid bottoms.

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