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Revision Memo

- 12/99** Highlights of this revision are:
1. Updated Manuals and other references.
 2. Included discussion on benzene NESHAP strippers and other aqueous strippers.
 3. Included discussion of acid and EDTA chemical cleaning.
 4. Updated **Tables 1, 2, 4 and 5**.
 5. Updated **Figures 1 and 7-18**.



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SCOPE

This section gives guidelines and considerations for the design of facilities to remove dissolved hydrogen sulfide and ammonia from water by reboiling or steam stripping. It provides the background, definitions and philosophy of the application of sour water stripping in modern petroleum refineries / chemical plants.

- ✦ Several sour water stripper types are described, anticipating application to a wide variety of situations which may be encountered based on refinery size, local economics, local emphasis on energy conservation and environmental concerns. The types covered in this section include the single tower stripper (refluxed and non-refluxed), the two-tower stripper (with and without NH_3 recovery), the four-tower stripper with H_2S and NH_3 recovery, NESHAP strippers and other aqueous strippers.
- ✦ This section treats only steam strippers. While there are several configurations of sour water stripping installations, this section treats only the Single Tower Non-Refluxed and the Single Tower Refluxed or Conventional Sour Water Stripper types. The other configurations are described for informational purposes, and for further information on their implementation, the Fractionation / Thermodynamics Section of ER&E / EEPPE / GRPTD should be contacted.

A typical installation is described and design variables are discussed as well as process, equipment and materials considerations.

The process design method is based on Exxon's Computer Program "CHEMDIST" (Program # 2525) to determine the combinations of the number of stages and the stripping steam rate required to reduce the H_2S and NH_3 contents to appropriate levels. A suggested design procedure or approach is presented. A simplified estimation procedure is also given to provide guidance in selecting the initial values of the operating variables. Economic considerations determine the optimum combination.

The tower design itself is carried out according to **Design Practices, Section III, Fractionating Towers**. Specific considerations for sour water strippers are contained in **Section III**. The feed surge drum is designed according to **Design Practices, Section V, Drums**.

REFERENCES

DESIGN PRACTICES

- [Section III](#) Fractionating Tower
- [Section V](#) Drums
- [Section XII](#) Instrumentation
- [Section XV](#) Safety in Plant Design
- [Section XVII](#) Toxics and Industrial Hygiene Engineering Controls

ENVIRONMENTAL DESIGN PRACTICES

- [Section XIX-B](#) Water Reuse

COMPANY MANUALS / GUIDES

- ✦ Sour Water Stripper Guide (to be released 4Q'00)
- Refinery Construction Materials Manual, ER&E Report No. EETD028, December, 1996.
- Chemical Construction Materials Manual, ER&E Report No. CED 009, April, 1999.
- CHEMDIST User's Manual, Exxon Engineering Manual EETD038, November, 1986
- ✦ Exxon Guide to PRO II (TPFLSH), Exxon Engineering Manual CPEE078

OTHER REFERENCES

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2. Melin, G. A., *Improved Sour Water Stripping Processes*, ER&E Report No. EE.8E.76.
3. Melin, G. A., *Optimum Design of Sour Water Strippers*, ER&E Report No. EE.42E.74.
4. Springer, R. D., *Three-Phase Flash Calculations (TPFLSH) Computer Program 3677 (Revised)*, ER&E Report No. EE.51E.82.
5. Tsonopoulos, C., *Handling Equipment Plugging Problems Due to Deposition of Ammonium Salts*, ER&E Report No. EE.5E.78.
6. Yeich, W.G., *Preventing Fires and Explosions Caused by Pyrophoric Material*, ER&E Report No. EE.84E.92.
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BACKGROUND

Sour water, in the context of this section, is defined as process water from refinery / chemical plant units containing H_2S or H_2S and NH_3 . Sour water compositions may range from 30 wppm (mg/L) H_2S and 50 wppm (mg/L) NH_3 , for a typical vacuum pipestill overhead drum water, to 75,000 wppm (mg/L) H_2S and 38,000 wppm (mg/L) NH_3 for a typical GOFINING Unit sour water. Typical and ranges of H_2S and NH_3 concentrations for refinery sources are presented in **Table 1**. Currently, the most universally applied commercial technique used to remove the H_2S and NH_3 from the water is a reboiled or steam stripped sour water stripper.

FUNCTION AND DUTY OF SOUR WATER STRIPPERS

- ◆ To meet current environmental regulations / considerations, it is typically necessary to reduce the H_2S content of sour water to 5 wppm (mg/L) or less and the NH_3 content to 50 wppm (mg/L) or less prior to discharge into water streams outside of the refinery / chemical plant fence line. However, if further processing is required in wastewater treatment facilities such as biological oxidation units, the stripped sour water H_2S and NH_3 concentrations will depend on the wastewater treatment facility feed requirements (**Section XIX-A5, Biological Treatment of Wastewater**). Sour water strippers remove the dissolved H_2S and NH_3 from the water as well as other dissolved compounds such as CO_2 , mercaptans, HCN , etc. These dissolved materials cannot be removed by settling or filtration. Even in situations where the sour water is diluted several fold by other wastewaters, the required discharge water quality is not typically met and stripping of the sour water is required.

SOURCES, QUANTITIES, AND CHARACTERISTICS OF SOUR WATER

Sources and Quantities

- ◆ Sour water is derived from many sources within the refinery / chemical plant. **Table 1** gives typical refinery sour water sources with typical water rates and ranges of primary contaminants (sulfides, ammonia, phenols, cyanides) for which some data has been gathered. Other contaminants (chlorides, thiocyanates, mercaptans, thiosulfates, sulfates, and carbonates) are of interest due to their possible detrimental effect on the stripping of the H_2S and NH_3 . The sour water composition, and hence the sour water stripper design and operating parameters, is highly influenced by the crude being processed, the severity of conversion processes and other factors. Therefore, as indicated in the **PROCESS DESIGN CONSIDERATIONS** Section, a complete analysis of the sour water stripper feed is recommended to identify all possible contaminants and their composition (see **PROVISION FOR SAMPLING** Section and **Table 5**).

Characteristics

Sour water strippers are typically designed for a feed concentration in the range of 500 to 15,000 wppm (mg/L) each of NH_3 and H_2S . The molar ratio of NH_3 to H_2S can range between 0.75 and 2 but averages mainly between 0.9 and 1.2; hence, an average of 1.0 is a good first approximation when complete information is lacking. The pH is typically between 7 and 9.3.

- ◆ Desalter effluent water, which may contain somewhat more than 50 wppm (mg/L) H_2S / NH_3 , and spent caustics, which may contain significant levels of sulfides, are excluded from the definition of sour water in the context of this section. Due to their high concentration of dissolved solids, separate treatment of these sources has been found to be economical if reuse of the stripped sour water is being considered. Even if stripped sour water reuse is not being considered, separate stripping of the desalter water should be considered due to its relatively low H_2S / NH_3 content relative to 50 wppm (mg/L), its high volume and its contribution to stripper operating problems, namely tower plugging, when processed with sour water. Desalter water is typically sent directly to the Wastewater Treatment Plant (WWTP) unless benzene must be stripped from it. In that case, a fuel gas stripper is recommended to avoid plugging concerns. Control of pH may become necessary to prevent the precipitation of salts, and thus plugging, at higher pHs. For the relatively small spent caustic stream, a separate neutralization and stripping facility is recommended with special metallurgy to avoid having to upgrade the metallurgy of the larger stripper as well as avoid stripping problems associated with the pH of the neutralized caustic.

SOUR WATER STRIPPER TYPES AND APPLICATIONS

There are several different types of sour water strippers. They all operate by passing the sour water downward through a multistage tower while an upward flow of stripping medium removes the H_2S and NH_3 . In addition to the types of internals, i.e., trays or packing, they differ in the stripping medium, tower configuration and the number of towers.

- ◆ **Table 2** is a decision diagram for selecting the stripper type. The stripper type depends on whether or not the off-gas is sent to a sulfur plant, whether or not sulfur plant savings justify H_2S/NH_3 separation, whether or not some of the H_2S can be incinerated, whether or not the investment can be justified for aqueous NH_3 collection, whether or not there is a market for ammonium acid salts, whether or not sulfidic caustic can be regenerated, whether or not it is a grass roots design, whether or not sparing service is necessary and whether or not acid addition is necessary to improve H_2S removal. **Table 3** summarizes the advantages and disadvantages of the various types. Only the typical practice types are described here, and only the single tower non-refluxed and the conventional single tower refluxed strippers are covered in detail in this section.

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SOUR WATER STRIPPER TYPES AND APPLICATIONS (Cont)

STRIPPING MEDIUM

As previously mentioned, this section covers only steam as the stripping medium. Flue gas, fuel gas, natural gas, etc. have also been used as stripping mediums. With the exception of their use in desalter water strippers, these other stripping mediums do not have widespread use within Exxon, primarily because they suffer from the following disadvantages:

- Flue gas introduces CO_2 into the system that can react to form carbonates that can plug the tower and/or reboiler. At high concentrations, CO_2 reacts with NH_3 to form carbonates.
- Flue gas is usually available at low pressure and must be compressed before use as a stripping gas.
- Fuel gas stripping contaminates the fuel gas system with H_2S , NH_3 and water vapor leading to corrosion problems.
- Fuel gas stripping is typically used in conjunction with incineration. The contaminated fuel gas would typically be burned in a furnace. Both of these lead to increased air emissions of H_2S or SO_2 .

STRIPPER TYPES

The single tower refluxed or conventional configuration is the most typically used configuration. It is thus the subject of this section. The other types described here are for informational purposes.

The discussion of the operation and design parameters is given in the subsequent sections: **DESIGN VARIABLES**, **PROCESS DESIGN CONSIDERATIONS** and **EQUIPMENT DESIGN CONSIDERATIONS**.

Single Tower Non-Refluxed (Figure 1)

Before the advent of modern environmental control regulations, it was necessary to strip most of the H_2S from the sour water such that when mixed with the other wastewaters, the odor around the API separator was acceptable. Hence, this configuration was named a deodorizer. With somewhat more sophistication than the earliest versions, the deodorizer still has application where only the H_2S in the wastewater is of concern or when the off-gas can be incinerated. This type of stripper is referred to as a non-refluxed stripper and is illustrated in **Figure 1**. It is the only stripper type where fuel gas, flue gas or natural gas have been used as the stripping medium in an Exxon installation.

Single Tower Refluxed or Conventional (Figure 2)

This is the most widely applied type of sour water stripper. It is illustrated in **Figure 2**. It is applied instead of the non-refluxed type when the H_2S in the off-gas must be recovered in the Sulfur plant, as is the typical case today, and when H_2S / NH_3 separation is not economically justified.

The main feature of this type is the overhead condensing system that enables economical recovery of the H_2S in the Sulfur Plant. By cooling the off-gas from 250°F (120°C) to about 180°F (80°C), there is a significant reduction in the volume of water vapor going to the Sulfur Plant. The Sulfur Plant savings justify the expensive overhead system and additional stripper operating costs to handle the returned condensate (reflux) which is rich in H_2S and NH_3 .

- A variation of this basic refluxed stripper is the addition of a rectification section at the top of the tower to strip the rich reflux before it combines with the typically more dilute stripper feed. This feature generally reduces the stripping steam requirement by approximately 10% compared to the conventional type shown in **Figure 2**. Note that as the feed becomes more concentrated, the benefits of a rectification section become less advantageous.

Two-Tower Without NH_3 Recovery (Figure 3)

The two-tower stripper is used when it is desired to produce a relatively pure H_2S stream while contamination of the ammonia stream with H_2S is acceptable. It is illustrated in **Figure 3**. The design of the first tower in the sequence, or the H_2S stripper, is based on the principles of high pressure, 60 to 80 psig (4.1 to 5.5 barg) and a cold feed bypass to separate NH_3 from the H_2S off-gas. In the second tower, the NH_3 stripper, the NH_3 is stripped along with the small residual amounts of H_2S . The combination of the relatively high operating pressure and cold feed bypass at the top of the first tower limits the water vapor rate in the tower overhead, which typically goes to a Sulfur Plant, at a rate comparable to that from a conventional refluxed stripper.

The advantage of this type of stripper relative to the conventional refluxed stripper is the elimination of the overhead condensing system. The overhead condenser is expensive and has significant operating problems due to corrosion and plugging. This is in addition to the benefits for reducing the inerts (ammonia and water) load on the Sulfur Plant.

Compared to the conventional refluxed tower, this configuration requires a means of disposal for the ammonia off-gas, typically an incinerator, an additional tower and approximately 15% more stripping steam.

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SOUR WATER STRIPPER TYPES AND APPLICATIONS (Cont)

Two-Tower With NH_3 Recovery Using Chemicals (Figure 4)

H_2S and NH_3 can be completely separated in a two-tower sequence as shown in Figure 4. Acid is added to the first tower thereby tying up the NH_3 so that only the H_2S is stripped. This yields an essentially pure H_2S overhead vapor product except for its water content. Caustic is then added to the feed to the second tower such that the NH_3 can be stripped producing an essentially pure NH_3 overhead vapor product except for its water content.

This scheme has not found widespread use within Exxon due to the costs associated with the acid and caustic consumption as well as the increased dissolved solids content of the stripped water. The increased solids content of the stripped water limits its reuse within the refinery / chemical plant and adds an additional dissolved solids component to discharge wastewater.

Four-Tower with H_2S and NH_3 Recovery (Figure 5)

The four-tower stripping sequence is used when there is sufficient NH_3 present in the feed to justify the additional investment and operating costs associated with this sequence. This is essentially the two tower without ammonia recovery sequence with the addition of an overhead condenser to the NH_3 stripper and two absorber towers. The condenser on the NH_3 tower reduces the water content of the overhead vapor thereby improving the absorber performance. The H_2S absorber scrubs the H_2S from the overhead vapor using aqueous NH_3 . If the NH_3 product has to be completely free of H_2S , a caustic wash tower is used. The "pure" NH_3 is absorbed in water in the NH_3 absorber.

This sequence requires on the order of 3–5 lbs steam/gallon (360–600 kg steam/ m^3) of sour water feed, significantly higher than the conventional tower.

► NESHAP Strippers

Typical sour waters from the refinery / chemical plant contain H_2S and NH_3 and are treated in sour water strippers (SWS) using steam to remove the contaminants prior to sending the SWS bottoms to downstream wastewater treatment facilities. However, some wastewaters containing benzene also contain NH_3 and H_2S , and they need to be treated in strippers designed to meet the stripped water benzene specification. Benzene removal is mandated by the National Environmental Standards for Hazardous Air Pollutants (NESHAP) in the USA, and hence, they are referred to as NESHAP strippers.

The NESHAP strippers are significantly different from sour water strippers in their H_2S and NH_3 contents. Typically, the feeds are relatively low in H_2S and NH_3 so that the overhead does not have to be routed to a sulfur plant. Sour water stripper overheads need to be routed to the sulfur plant. Sour water strippers will remove benzene; however, the presence of benzene, above a certain level, will cause catalyst deactivation in Claus plants. Therefore, streams with high concentrations of benzene are not handled in the sour water system, but rather in the separate NESHAP system in the USA because of NESHAP regulations. At other locations and in the USA prior to NESHAP regulations, streams with high concentrations of benzene (low $\text{H}_2\text{S}/\text{NH}_3$) are and were being typically sent directly to wastewater treatment plants.

Most of the wastewaters from the refinery / chemical plant that contain benzene also contain varying concentrations of different soluble salts. For example, most refinery wastewaters (~ 80%) treated in NESHAP strippers are desalter washwaters. These washwaters contain large concentrations of dissolved salts in addition to the benzene. To strip the benzene from these waters, care must be taken to operate the stripper so that the benzene is removed but the salts remain dissolved. In these strippers, steam is not the preferred stripping medium since the solubilities of the salts are inversely proportional to temperature and are pH dependent, which could create major plugging problems. Depending on the salt contents of the wastewater, the preferred NESHAP stripping mediums are (1) fuel gas / natural gas, (2) vacuum steam stripping and then (3) steam.

Exxon operates five such NESHAP strippers in the USA. Equipment information and design / operating conditions are listed for these strippers in Table 4. The BRRF NESHAP stripper uses fuel gas as its stripping medium. It also receives desalter washwater, but because the operation is essentially at ambient conditions, it has not encountered salt deposition problems. The Baton Rouge Chemicals area has three NESHAP strippers. The BRCP WILA Stripper is based on a patented process from Dow Chemical Co. and utilizes vacuum to strip the benzene. Another NESHAP stripper, Basic Chemicals OLA-2X SWS, removes large quantities of benzene using steam as the stripping medium since its wastewater does not contain large amounts of salts as does desalter washwater. The BR Chemicals Polymers E-1000 ET-01 Tower also strips benzene with steam. These last two strippers do not receive wastewater containing significant concentrations of dissolved salts and, therefore, have never had salt deposition problems using steam as their stripping medium. The BTRF NESHAP stripper uses steam as its stripping medium but, because the BTRF stripper receives relatively large amounts of desalter water, salt deposition problems have occurred. The BTRF steam stripper temperatures are higher than desalter water treating temperatures, and it operates at higher pH conditions.

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SOUR WATER STRIPPER TYPES AND APPLICATIONS (Cont)

Other Aqueous Strippers

Exxon operates other aqueous strippers that are designed, not as sour water or benzene strippers, but as parts of product recovery processes. These are typically strippers that separate hydrocarbons from water, returning the hydrocarbons to their processing units and sending the water to further processing. These strippers have other design considerations based on specific process design parameters / requirements. For further information, the Fractionation / Thermodynamics Section of ER&E / EEPPE / GRPTD should be contacted.

DESCRIPTION OF A TYPICAL SINGLE TOWER REFLUXED INSTALLATION

Figure 6 presents a typical design of a refluxed stripper installation. The typical values are shown for various operating parameters, and a typical heat integration scheme is illustrated.

A sour water stripper is a fractionating tower whose primary purpose is to remove hydrogen sulfide and ammonia from water by stripping. It also partially removes the following: mercaptans, aromatics, other dissolved hydrocarbons, and phenols. Normally, these towers are refluxed to reduce the quantity of water in the off-gas, thus reducing the size and cost of downstream processing units such as sulfur plants. If a downstream process will not be affected, the sour water stripper need not be refluxed. Sour water strippers have been located in both the processing area and the wastewater treating area.

In a "typical" sour water stripping facility, the stream flow is typically as follows: the feed sour water is preheated by heat exchange and fed to the top of the tower. The feed preheat typically consists of a feed / bottoms exchanger. Whether there is feed / overhead integration depends on the individual situation. Steam, either as open steam injection or as the heat source in a reboiler, is introduced to the bottom of the tower. As the sour water descends, the H_2S and NH_3 are stripped.

The overhead condenser reduces the water content of the off-gas, which is of particular importance when off-gas is sent to a sulfur recovery plant. The condensed overhead refluxes to the tower.

Steam stripper operating conditions for refinery / chemical plant sour water strippers typically fall within the following ranges:

OPERATING CONDITION	RANGE	TYPICAL VALUES
Tower Top Pressure, psig (barg)	1 to 50 (0.1 to 3.5)	20 to 25 (1.4 to 1.7)
Tower Bottom Temperature, °F (°C)	100 to 300 (40 to 150)	260 to 270 (127 to 132)
Total Steam Rate, pounds steam/gallon feed (kg steam/m ³ feed)	0.5 to 4.0 (60 to 480)	1.2 to 1.4 (145 to 170)

Specific values for several designs and operating towers are given in **Table 4**.

DESIGN VARIABLES

The required bottoms purity in a sour water stripping system can be achieved by various process and equipment designs. Off-gas disposition, NH_3 recovery and economics determine the route selected. As mentioned previously, this section cover only the conventional sour water stripper configuration.

The key design variables are:

- Effect of pH.
- Number of towers.
- Stripping steam rate / Number of theoretical stages.
- Operating pressure.
- Distillate drum temperature.
- Feed composition.
- Feed preheat.

The major parameters influencing stripper performance in terms of utility consumption, i.e., steam to feed ratio, are the number of theoretical trays and the operating pressure. Parameters, which have a less important effect, are the feed temperature, distillate drum temperature and feed NH_3 or H_2S concentration. The use of a rectification section in a refluxed stripper can reduce the steam requirements by 5-10%, and this is discussed in the **PROCESS DESIGN CONSIDERATIONS** section. pH can have a profound effect on the ability to strip either the H_2S or NH_3 as opposed to affecting the utilities as discussed below.

- The influence of each of these key design variables is discussed below.

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DESIGN VARIABLES (Cont)

EFFECT OF pH

Adjustment of the pH downward, by the addition of acid, facilitates the removal of H_2S while hindering the removal of NH_3 . Acidification reduces the steam consumption if it is desired to remove only H_2S , while it increases the steam consumption if it is also desired to remove NH_3 . If the pH is too low, the NH_3 will exist only in the form of NH_4^+ and will not be strippable, no matter how high the steam rate used. Therefore, acidification should be considered only when one or more of the following situations apply:

- The sour water contains no ammonia or a negligible quantity of ammonia.
- The stripping is followed by alkalization (caustic addition) and restripping for NH_3 removal.
- Stripped water reuse possibilities will not be affected by the resulting increase in salt concentration.

Adjustment of the pH upward, by the addition of caustic, facilitates the removal of NH_3 while hindering the removal of H_2S . Raising the pH typically reduces the steam consumption; however, care must be taken not to raise the pH to the point where H_2S stripping is hindered such that the stripped water H_2S specification is not met.

To take full advantage of the benefits of pH adjustment when both NH_3 and H_2S are to be stripped, two towers are generally required. This facility is discussed in the preceding section on **STRIPPER TYPES – Two-Tower with NH_3 Recovery Using Chemicals**.

- ◆ When carefully implemented and operated, some pH adjustment may be advantageous when simultaneously stripping NH_3 and H_2S as is done in a conventional sour water stripping facility, but only to keep the pH in the desirable range for co-stripping. One variation of this, which is the implementation of choice, is to inject caustic into the bottom section of the tower after the H_2S has been stripped to its desired value to facilitate stripping of the NH_3 .
- ◆ pH calculations for sour water, including those containing inorganic ions in addition to H_2S and NH_3 , are done using the TPFLSH (Program Number 3677) computer program, the TPFLSH option in PRO II or the OLI Environmental Simulation Program (contact the ER&E Water Chemistry / Modeling specialists).

NUMBER OF TOWERS

As can be seen in **Figure 2** for a conventional refluxed stripper, stripping is nominally accomplished in a single tower. If feed segregation is required, then parallel towers would be used to process the individual segregated feeds. If some degree of chemical separation of the H_2S and NH_3 is required, then more than one tower would be required as shown in **Figures 3 - 5**.

STRIPPING STEAM RATE / NUMBER OF THEORETICAL TRAYS

The stripping steam rate and the number of theoretical trays are the most significant determinants of the stripped water quality. Increasing either one results in more complete stripping. The tradeoff between stripping steam and theoretical trays is based on economics. Typical designs have consisted of 20 theoretical trays.

Figure 7 gives the expected stripped water NH_3 concentration for a single tower non-refluxed stripper versus stripping steam to feed ratio with the number of theoretical trays as a parameter. **Figure 8** presents the same information for a single tower refluxed stripper with only stripping trays, and **Figure 9** is for a single tower refluxed stripper containing 2 theoretical rectification trays in addition to the stripping trays. The corrections to the stripping steam rate for other operating parameters are discussed below.

Calculation of the actual stripping steam rate, taking into account all the operating parameters as well as composition of the feed including all impurities and salts, is done using Exxon's CHEMDIST (Program Number 2525) plate-to-plate calculation program.

OPERATING OVERHEAD (DISTILLATE DRUM) PRESSURE

The overhead (distillate drum) pressure affects the vapor / liquid equilibrium of the H_2S and NH_3 throughout the tower, the reflux rate, and the reflux composition. The lower the operating pressure of the tower, the easier it is to strip the H_2S and NH_3 from the water. Therefore, the tower pressure is set at a level to provide enough pressure to get the off-gas to its destination, typically the pressure at sulfur plant plus the pressure drop across the tower pressure control valve. Typical tower pressures have been in the range of 20–25 psig (1.4–1.7 barg).

Figure 10 gives the correction to the stripping steam / feed ratio for non-refluxed strippers, and the correction would be applied to the value obtained from **Figure 7** to correct for different operating pressures. For refluxed strippers, the correction is given in **Figure 11**, and the correction would be applied to the value obtained from **Figures 8 or 9** as appropriate.

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DISTILLATE DRUM TEMPERATURE

The distillate drum temperature is typically set in the range of 180 – 195°F (82 – 91°C). The lower the distillate drum temperature, the greater the stripping steam requirement, and the reflux becomes richer in H₂S and NH₃. The higher the temperature, the more water vapor exits with the off-gas, which affects the downstream equipment. In the case where the downstream processing is a sulfur plant, the additional water decreases its capacity and increases the load on the tail gas cleanup due to its diluent effect. The minimum temperature is set by plugging considerations, i.e., the deposition of solid NH₄HS. **Figure 12** gives the dissociation constant for NH₄HS and defines the region where solid deposition can occur.

A distillate drum temperature of 180°F (82°C) is the current minimum recommended to avoid plugging by ammonium hydrosulfide and still minimize the water content of the off-gas.

Figure 13 gives the correction to the stripping steam / feed ratio for refluxed strippers to correct for different distillate drum temperatures. The correction would be applied to **Figures 8** or **9** as appropriate.

FEED COMPOSITION

The stripping steam requirement, in addition to being affected by those contaminants other than H₂S and NH₃ that effect the pH and hinder the H₂S or NH₃ stripping, is effected by the NH₃ composition of the feed. The higher the NH₃ content, the greater the stripping steam requirement. **Figure 14** gives the correction to be applied for non-refluxed strippers to correct for different feed compositions. **Figure 15** gives the correction for refluxed strippers. The steam requirement is essentially independent of the ratio of H₂S to NH₃.

FEED PREHEAT

- ♦ The feed preheat or the tower feed temperature determines how much steam is condensed to heat the feed up to its bubble point at the tower conditions. The greater the feed preheat, the lower the stripping steam requirement to achieve the desired stripped water H₂S and NH₃ targets. The effect of feed preheat is rather small for towers containing only stripping trays; however, the impact is greater for towers containing rectification trays. It is common practice to preheat the feed with the tower bottoms. This serves both to minimize steam requirements and cool the bottoms. The degree of feed preheat is an economic tradeoff between incremental preheat exchanger area and the reduction in stripping steam requirement. This economic evaluation has typically yielded a feed temperature 40°F (22°C) less than the stripper bottoms temperature.

Figure 16 gives the correction to the stripping steam / feed ratio for non-refluxed strippers to correct for different levels of feed preheat. **Figure 17** gives the correction for refluxed strippers.

PROCESS DESIGN CONSIDERATIONS

REUSE OPPORTUNITIES

In general, stripped water has low total dissolved solids (TDS), low metals content, and low suspended solids. Hence, it is a good candidate for water reuse when pH adjustment is not carried out in the stripping process. The pH of a typical stripped sour water ranges from 8 to 10. If the stripped water were to be neutralized, it requires addition of acids, such as sulfuric or hydrochloric acid, that in turn would increase the ion contents, or total dissolved solids.

- ♦ Exxon affiliates are already reusing stripped sour water (SSW) in various process units. The most common form of reuse is the crude desalters. But recently, other more dynamic reuses, such as SSW reuse as make up to the cooling tower, are being investigated. Potential uses for this water include:

- Crude oil desalter washwater.
- Cooling tower make-up.
- Steam generation.
- HYDROFINING unit treat gas scrubber washwater.
- HYDROFINING unit recycle gas scrubber washwater.
- GOFINING unit recycle gas absorber.
- HYDROCRACKING unit recycle gas scrubber.
- Debutanizer overhead gas scrubber.
- Flare seal drum seal water.

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- Makeup for caustic wash systems.
 - Catalytic cracking unit flue gas cooling.
 - Incinerator flue gas quench.
 - Coker Quench Water.
- ◆ Before implementing these potential reuse option(s), water chemistry analysis, computer modeling, and/or lab / field tests may be necessary to determine the water compatibility to the process unit(s). In addition, controls to avoid corrosion may be warranted. The user should consult Exxon Environmental Water and Wastewater specialists prior to water reuse implementation. Brief discussions of two major reuse potentials are described below. For detailed water reuse applications and limitation, refer to [Section XIX-B, Water Reuse](#).

SSW to Desalter

There are several important issues associated with this reuse option. The first relates to desalter performance: washwaters that have a tendency to form desalter emulsions (typically by raising the pH of the desalter brine to above about 8.5, or via the precipitation of solids) must be avoided. Secondly, as corrosive ammonium salts may deposit out in the pipestill overheads, it is important that the washwater not introduce unacceptable levels of ammonia into the crude. Additionally, the desalter effluent brine should not contain high levels of hydrogen sulfide as these could adversely impact wastewater treatment plant performance.

To minimize the transfer of ammonia from the washwater into the crude, controlling the pH of the desalter brine to 7 by acid addition to the washwater is recommended. This reduces the potential for deposition of ammonium chloride salts in the pipestill overhead, and allows washwater with very high ammonia content to be used. With lower pH, the emulsion problem will be reduced as well. However, pH adjustment by acid addition, such as sulfuric acid, may exceed $\text{Ca}(\text{SO}_4)$ saturation pH, thus producing undesirable precipitation.

SSW Reuse as Makeup to the Cooling Tower

Reuse of SSW to the cooling tower has not been a common alternative because of corrosion and biofouling concerns. Biofouling is caused by high BOD and ammonia, and corrosion problems are caused by high ammonia and hydrogen sulfide contents. However, by careful monitoring of BOD, ammonia and hydrogen sulfide in stripped sour water, the potential to reuse it as makeup to the cooling tower is optimistic.

- ◆ As part of ER&E's R&D study, the feasibility of reusing stripped sour water as partial makeup to the cooling tower was investigated at the Antwerp Refinery. Using a state-of-the-art program called the OLI Environmental Simulation Program (ESP), a modeling of the cooling tower predicted that this reuse option was very possible at Antwerp. The ESP model is unique in that it predicts the formation of solids (scaling) or evolution of gases in addition to water chemistry when blending or splitting water streams.
- ◆ The guidelines for the maximum allowable levels in the cooling tower basin (blowdown) are provided in [Table 3, Cooling Tower Basin Water Quality Limits](#), in [Section XIX-B, Water Reuse](#). These levels are guidelines; computer modeling using actual water analyses will determine the site specific limits.

FEED IMPURITIES

Wastewaters processed in sour water strippers are generally neither highly acidic nor highly alkaline and consist primarily of H_2S and NH_3 (frequently in the range of 1,000 and 4,000 ppm (mg/L) each). Sour water is produced in a number of refinery / chemical plant process units, primarily those that use steam for fractionation and stripping, or add water for fouling control.

- ◆ Feed impurities can affect the operation of sour water strippers, and affect downstream equipment. Sour water should be analyzed routinely for the consistency of the pH and the H_2S and NH_3 contents. Any inconsistency suggests that one or more other ions (basic or acidic) are present in solution. Such ions may "fix" H_2S or NH_3 , retarding their stripping, and perhaps preventing a specification from being reached in the stripped water. If the pH inconsistency is large (as when spent caustic is present in the sour water feed), consider a pH adjusting system. Sour water with a low pH (< 6) impedes NH_3 stripping, while sour water with a high pH (> 9) impedes H_2S stripping.
- ◆ Ions also have other effects. The ionic strength of the solution (affected by the presence of ions such as Cl^- , etc.) affects the vapor-liquid equilibrium of the system. At elevated temperatures in the stripping tower, ions may precipitate as salts and foul the tower. Computer models such as the OLI ESP can predict this if analyses of the ions in the sour water are available. These predictions should be done if wastewaters other than sour water from steam condensate are in the feed to the stripper.

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Some impurities do not significantly affect the pH of the water but are nevertheless important. Before designing a sour water stripper, therefore, determine not only the concentration of H_2S , NH_3 and strong ions (Cl^- , SO_4^{--} , Na^+ , Mg^{++} , Ca^{++} , etc.) in the feed, but also the concentration of:

- Oil
- Phenols
- Silica
- Carbonates / bicarbonates
- Mercaptans
- MEA / DEA
- Cyanides
- Thiocyanates
- Polysulfides

These can affect the process selection, tower sizing, and materials specifications.

Oil – Oil in the feed to a sour water stripper can create problems. Stripped oil ends up in the sulfur plant (when that is the disposition of the off-gas); unstripped oil can cause reboiler fouling and foaming in the tower and can also contaminate the stripped water. If the water is reused, the oil can create foaming problems downstream such as heat exchanger fouling. When feasible, before beginning a sour water stripper design, obtain laboratory analyses for soluble oil, entrained oil, settling times required, oil volatility and a rough identification of hydrocarbons present. Always provide feed settling facilities.

Process problems arise if large amounts of oil condense in the overhead system, and an effective means must be provided to remove oil from the system.

Phenols – The only adverse effects of phenol on stripping stem from its weak acid properties. CHEMDIST would predict no phenol removal at the usual sour water stripper operating conditions. Some phenol removal is predicted for non-refluxed strippers having a large overhead vapor product. Some field measurements show 20 to 30% phenols removed.

Silica – Silica has low solubility that may produce scale deposits caused by its reaction with magnesium salts. The precipitation, also known as the crude glass, may plug the stripper.

Carbonates / Bicarbonates – Carbonates are found in catalytic cracking unit sour water. When cations such as Mg^{++} and Ca^{++} are also present, $Mg(OH)_2$ and $CaCO_3$ are formed and may plug the stripper. Desalter brine should, therefore, be segregated from sour water that contains over 15 wppm (mg/L) total carbonates.

Mercaptans – Mercaptans in sour water are stripped to about the same degree as H_2S and have no known adverse effects.

MEA / DEA – Monoethanolamine / Diethanolamine in sour water stripper ends up in the stripped water. MEA / DEA does not affect NH_3 removal but may be converted to NH_3 during biological oxidation (bioX) treatment. Since MEA / DEA is a base, it hinders H_2S stripping at MEA / DEA concentrations greater than 1 weight percent.

♦ **Cyanides** – Cyanides are typically found in the sour water stripper from conversion units (e.g., fluid catalytic cracking units). Cyanides can cause hydrogen blistering and corrosion, and can upset a downstream bioX plant if the cyanide concentration in the bioX plant feed exceeds 15 wppm (mg/L) or varies to this level. Cyanides are only partially (30 to 40%) stripped. This may be because of their conversion to thiocyanates (see below) or to their forming metal complexes, neither of which is stripped. CHEMDIST, however, would predict almost complete removal of cyanides at sour water stripper conditions if the cyanides are assumed to be HCN. Sour water containing excessive cyanides should be considered for segregated treatment due to costly metallurgical requirements.

♦ **Thiocyanates** – When polysulfides are present along with cyanides, the bulk of the cyanides are usually in the form of thiocyanates, since they are converted to that form by the polysulfides. To achieve this conversion, polysulfides are often added to FCC unit and coker sour waters prior to routing these to a sour water stripper. These thiocyanates remain in the stripped water, but can be treated in nitrifying bioX units.

Polysulfides – Polysulfides may be formed in situ by the reaction of organic sulfides with air, and are also typically found in sour water from catalytic cracking units and coker units, where they are injected for corrosion control. An alternative injection point is directly into the sour water stripper to control corrosion of this unit, especially when cyanides are present. If polysulfides are present in high concentrations as a result of over-injection, NH_3 stripping will be retarded and plugging may also occur. Polysulfides will remain in the stripped water.

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STRIPPED WATER QUALITY

The required quality of the stripped water must be determined for each case. This required quality depends on subsequent treatment processes, local regulations and the amount the water is diluted. The required quality of stripped water must be given in the Design Basis Memorandum.

SERVICE FACTOR AND SPARING

The service factors of sour water strippers have usually been low. Problems have been due to both corrosion / erosion and plugging. If critical equipment has been spared, a 95% service factor can be achieved. Each design should be individually examined for the effect of a shutdown of the sour water stripping facilities, and appropriate safeguards should be provided.

Possible safeguards include:

- A complete spare unit.
- A spare overhead system if NH_3 and H_2S are both being stripped (the corrosion / erosion problems have typically been confined to the overhead system).
- Three 50% units.
- Two 50% units and bypassing selected streams to the sewer (if allowed) or holding up half the feed in tankage when one of the units is down.
- One unit with downtime accommodated by either bypassing (if allowed) or holdup provisions.
- A single isolatable reboiler spared with live steam.
- Two or three 50% feed drums.
- Spare reflux pumps.

The service factor can be improved by:

- Using more corrosion resistant materials.
- Limiting velocities to reduce corrosion / erosion.
- Minimizing air in the system.
- Eliminating washwaters containing magnesium or calcium salts.
- Providing live steam injection as a backup to the reboiler.
- Providing block valves for onstream cleaning of the reboiler.
- Providing separate electrical buses to each pump with individual cables.

AVOID PLUGGING

Plugging occurs in the tower, overhead system, and reboiler. Avoid plugging by designing for overhead temperatures of at least 180°F (82°C), maintaining sufficient temperature in lines containing H_2S and NH_3 gas (see **Figure 12**), excluding magnesium and calcium carbonates, excluding air, settling the feed, providing blowdown for the reboiler, and employing corrosion-resistant materials.

Provide a water-flushing connection on the overhead line upstream of the overhead condenser.

Materials, which can cause plugging, are discussed below.

Sulfur – Crystalline or colloidal sulfur can plug sour water stripping facilities, primarily when stripping waters from fluid conversion units. The sulfur can come from four sources: 1) decomposition of polysulfides, 2) oxidation of ammonium hydrosulfide, 3) oxidation of H_2S , and 4) reaction of SO_2 and H_2S . The first source has been verified as a source of serious plugging, and can be minimized by avoiding the addition of unnecessary polysulfides. The second and third sources are eliminated by excluding air from the system (although this is not always feasible). Little or nothing can be done about the fourth.

Iron Sulfide and/or Other Corrosion Products – Iron sulfide is the combined corrosion product from all upstream equipment and from the stripper itself. Iron sulfide formation can be reduced by the proper choice of materials for the sour water stripping installation, although this does not affect corrosion products from upstream equipment. Providing blowdown on the reboiler, and minimizing pipe lengths also helps to minimize problems. The iron sulfide may be pyrophoric, and care should be taken in exposing any potential iron sulfide to air. (Refer to **Section XV-A, Basic Principles** and **Reference 6.**)

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Ammonium Hydrosulfide – Ammonia and hydrogen sulfide in aqueous solution react to form ammonium hydrosulfide (NH_4HS) and diammonium sulfide $[(\text{NH}_4)_2\text{S}]$. $(\text{NH}_4)_2\text{S}$ is stable only up to 0°F (-25°C) in the absence of water, and is formed to only a negligible extent, so it is not a problem. Both of these materials are soluble, crystalline solids in the pure state. Ammonium hydrosulfide can deposit if the gas is cold enough and there is insufficient water to dissolve the solid. Deposition of NH_4HS can be avoided by maintaining condensate temperature at a minimum of 180°F (82°C) and the condenser tube metal temperature above 150°F (66°C). See the discussion of distillate drum temperature under **DESIGN VARIABLES**. If an air-cooled condenser is used, specify a provision for tempering the air, such as an air recirculating or a steam preheater coil. If a shell-and-tube condenser is used, temper the cooling water.

Quantitative information on ammonium hydrosulfide deposition is given in **Figure 12**. Do the following to avoid ammonium hydrosulfide plugging:

1. Maintain all gas streams containing H_2S and NH_3 at a temperature at least 25°F (14°C) higher than the deposition temperature indicated by **Figure 12** for the partial pressure of these two materials; and never less than 120 to 130°F (50 to 55°C), regardless of partial pressures. This will nominally require steam tracing of $\text{H}_2\text{S}/\text{NH}_3$ off-gas lines, flare lines, and pressure relief valve / device discharge lines.
2. Provide a steam-out connection with a check valve at each of the following locations:
 - a. Downstream of the control valve on the $\text{H}_2\text{S}/\text{NH}_3$ off-gas line.
 - b. On $\text{H}_2\text{S}/\text{NH}_3$ flare lines.
 - c. On the discharge lines from safety valves discharging H_2S and NH_3 .
3. Steam trace instruments and instrument leads on the distillate drum.

Carbonates – Plugging by carbonates in the strippers has also been a problem in some plants. Carbonates have formed by mixing catalytic cracking unit and/or coker sour water having CO_2 present, with process waters containing magnesium and calcium salts. Desalter and fresh waters typically contain these salts. Sour waters can be analyzed for magnesium, calcium, and hardness in a manner similar to that used for boiler feedwater treating.

Totally exclude desalter water from strippers handling catalytic cracking unit or coker waters, and minimize the amount of fresh water in the stripper feed by substituting stripped sour water, sour water from other processes, or boiler feed water in the fresh water consuming process. Using these waters also helps to exclude air.

It is also possible for an ammonium carbonate compound to cause plugging. Both ammonia and carbonate are normally present in catalytic cracking unit and coker sour waters. If plugging by an ammonium carbonate compound is anticipated, reduce the amount of carbonate, if possible, or provide the necessary chemical cleaning connections for the bottom of the tower and the reboiler.

- Chemical cleaning of sour water strippers to remove deposits has been used more recently. Acid (HCl) has been used to clean deposits from stripper towers when the units are down. EDTA (ethylene diamine tetraacetic acid) has been used to clean sour water strippers either online or offline. **Any application should be discussed with ER&E specialists so that all pertinent parameters such as operating conditions, water composition, required chelating agents / concentrations, etc., are considered.** If possible, the deposits should be analyzed to determine whether acid or EDTA will dissolve them. Cleaning with either acid or EDTA must be carefully controlled because the removal of the deposits can result in corrosion, metal loss or the ultimate plugging of the tower, downstream lines and equipment. Additional information regarding chemical cleaning can be obtained by consulting the ER&E Chemical and Mechanical Cleaning Manual.

Magnesium-Ammonia Complex – A complex of magnesium, chloride, and ammonia is another potential plugging agent. Segregate streams containing magnesium from sour water streams rich in ammonia.

SELECTING THE OVERHEAD SYSTEM

The overhead system has been one of the main problem areas. Problems have been from erosion / corrosion and plugging. A non-refluxed stripper (non-condensing or no overhead condenser) has relatively few corrosion problems, therefore requiring a minimum of alloy construction. Unfortunately, because of air pollution considerations and the economic incentive for recovering the sulfur, non-refluxed strippers have found few applications.

There are three basic types of condensing systems: an external overhead condenser; direct contact or self-refluxing using a portion of the cold tower feed; and a top pumparound.

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External Overhead Condenser

An overhead condenser, either shell and tube or air fin, is the preferred choice. An appropriate combination of materials of construction and maximum fluid velocities must be selected to minimize corrosion and erosion. Another key consideration in the selection of the type of condenser is the need to control the distillate drum temperature. If the distillate drum temperature is not stable, there can be wide variations in the wet off-gas rate going to the sulfur plant as well as poor tower stripping performance. The following variations have been used in designs: all air fin condensing; partial air fin condensing with trim tempered cooling water; shell and tube condensing with tempered cooling water; and shell and tube condensing with "cold" feed.

Direct Contact (Self-Reflexing with Tower Feed)

A direct contact condenser employing trays or a packed section can be used in those rare situations where plugging will not be a problem and ammonia removal is not required. In a self-refluxed design, some of the feed goes to the top of the condensing section. Provision must be made to heat this stream, typically to 150°F (66°C), to avoid NH₄HS plugging in the tower.

The direct contact condenser constitutes heat transfer stages within the tower, and the number of stages or height of packing is determined from heat transfer considerations.

A direct contact condenser is not to be used where ammonia removal is required. The heat transfer section acts as an ammonia absorber impeding the stripping of ammonia.

Top Pumparound

A pumparound system at the top of the tower combines the undesirable features of both the overhead condenser and the direct contact systems described above. It requires a cooler and a pump which are both prone to plugging. This system has not been used.

REFLUX

A separate reflux drum should be provided and the reflux returned to the top tray of the tower. Where the H₂S and NH₃ concentrations are substantial, as in almost all refinery / chemical plant sour water strippers, the reflux should not be returned to the feed drum. This would raise the H₂S and NH₃ concentration, and possibly require more costly materials in the feed circuit and increase the size of the feed drum and pumps.

HEATING AND COOLING (SEE ALSO "DESCRIPTION OF A TYPICAL INSTALLATION")

Feed-effluent heat exchange raises the feed temperature to 180 – 215°F (82 – 102°C) thereby reducing the steam requirements while simultaneously cooling the tower bottoms. Preheating the feed will release some of the dissolved gases; therefore, the line

from the feed preheaters to the tower should be laid out and sized to avoid slugging. The effluent is normally further cooled in a trim cooler as dictated by its final disposition.

- Too low a feed temperature promotes plugging. A feed temperature of 195°F (91°C) is the lowest that has been demonstrated in actual operations. A lower temperature would reduce the size of the preheat exchanger and overhead condenser but increase the steam requirements. As previously mentioned, the degree of feed preheat is based on economics, but due to plugging concerns, 195°F (91°C) should be considered the minimum feed temperature.

RECTIFICATION TRAYS

The utilization of a rectification section in a sour water stripper can reduce the steam requirements. The reason for the improvement is that the reflux has a higher concentration of NH₃ and H₂S than the feed and will therefore affect the concentration profile in the tower, i.e., force these compounds lower down the tower. With rectification stages, a large fraction of the NH₃ and H₂S introduced with the reflux is stripped from the tower internal liquid prior to reaching the feed stage.

Figure 18 shows the predicted steam savings in a tower having two theoretical rectifying trays as compared with a tower having the same number of total theoretical trays but as all stripping trays. Note that as the feed concentration of NH₃ approaches the NH₃ reflux concentration, the benefit of rectifying stages decreases. This figure, in combination with the **Figures 10 – 11** and **13 – 17**, giving the incremental steam consumption changes for other conditions for towers with and without rectification stages, can be used to determine the benefits for the actual proposed operating conditions.

Studies have shown that two theoretical rectification trays are optimal.