The seven deadly sins of sour water stripping

Sour water systems should be designed to minimise operating problems, maximise on-line factor and optimise the quality of the feed gas to the sulphur recovery unit. **D. Engel, P. le Grange, M. Sheilan** and **B. Spooner** of Sulphur Experts describe the process of sour water stripping and focus on the most common mistakes (the seven deadly sins) made in operating and designing these units.

Sour water stripping is the first step in the treatment of 'process' wastewater in many industrial operations, particularly in refineries. Water streams from a number of process units throughout a refinery complex are typically sent to the sour water stripper (SWS), which is designed to remove hydrogen sulphide (H_2S) and ammonia (NH_3) from the process water. There are several variations in the designs of sour water strippers, all playing upon the same theme of using heat to break the bonded ions in the NH_4SH salt contaminant in the wastewater. This liberates gaseous ammonia and hydrogen sulphide in a produced sour water acid gas (SWAG). In some designs the NH_3 and H_2S are separated in separate columns and sent to individual destinations, but in the majority of SWS applications the effluent acid gas from a sour water stripper overhead is processed in a sulphur plant.

As oil and gas processing facilities deal with increasing sulphur content in their feedstock in combination with enhanced environmental pressures to remove sulphur from finished hydrocarbon products, the volume of "sour" water containing H_2S, ammonia and other contaminants is increasing. Additionally, the concentration of contaminants is increasing and exerting higher demands for sour water processing capacity. Simultaneously, more stringent environmental legislation and tougher fines for non-compliance have led to increased focus on the availability and reliability of sour water treating units.

A correctly designed, properly operated and well maintained sour water stripper (SWS) unit is critical to these operations. If the SWS unit is ever out of service, the facility must often run at reduced through-put or even temporarily shut down. As a result, sour water must be stored in a holding tank until processing is re-established and must often use tank capacity not designated for water storage. Quite often sour water composition is unknown (especially the contaminants other than H_2S and NH_3), which can make correctly setting operating conditions quite difficult. In other situations, SWS units with fluctuating hydrocarbons in the feed create problems for the downstream sulphur recovery unit. In these cases the acid gas is sent to a furnace or flare system for incineration, resulting in significant SOx and NOx emissions. Finally, some units do not make product specification treated water and therefore a proper understanding of the fundamentals of the process can help the operator come to a rapid and effective optimisation of the unit.

Sour water stripping process chemistry

The purpose of a sour water stripper is to remove components that are toxic or cause undesired odour. The most important ones are H_2S and NH_3 but other components like CO_2, HCN, mercaptans, phenols, hydrocarbons and solids are removed to varying degrees.

The SWS process entails contacting the sour water flowing down a stripper column with steam flowing up the tower. When sour water enters the stripper it is heated, causing the ionically-bonded ammonium sulphate salt (NH_4SH), which is in the aqueous phase and has no vapour pressure, to decompose into H_2S and NH_3. H_2S and NH_3 have a vapour pressure and thus can be stripped into the vapour phase and separated into a different process stream. Any other volatile species in the sour water such as carbon dioxide, hydrogen cyanide, mercaptans and 'light' hydrocarbons are also stripped.

$$H_2S + NH_3 \rightleftharpoons NH_4SH \rightleftharpoons NH_4^+ + HS^-$$
$$\longleftarrow \quad temperature \quad \longleftarrow$$
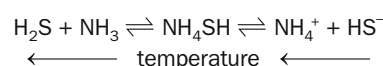
There are many process wastewater sources in a refinery, all of which have different contaminant compositions, flow rates and pressures. In addition, some sources may be continuous while others are intermittent. As a result, without proper upstream equilibration, design, and operation, the chemical composition and flow of water to the SWS may vary significantly. This can result in frequent and severe operational upsets both for the stripper and the downstream sulphur plant, the destination for the gases stripped from the water.

The most common process feed water sources are from: atmospheric crude columns, vacuum crude towers, steam crackers, fluid catalytic crackers (FCC), hydrodesulphurisation (HDS) units, hydrocracking (HCU) units, atmospheric desulphurisation (ARDS) units, coker units, amine reflux purges and TGTU quench towers. H_2S and NH_3 concentrations are the highest in water from the HDS, HCU, ARDS, and FCC units. Any water stream containing 10ppm or more of H_2S requires treatment before leaving site limits.

Meeting specification on NH_3 and H_2S in the treated water is extremely important as subsequent steps in wastewater treatment usually involve biological treatment which cannot operate under high hydrogen sulphide levels.

Sour water process description

The process can be viewed in and summarised as follows:

Fig 1: Generalised sour water process scheme for a pumparound SWS
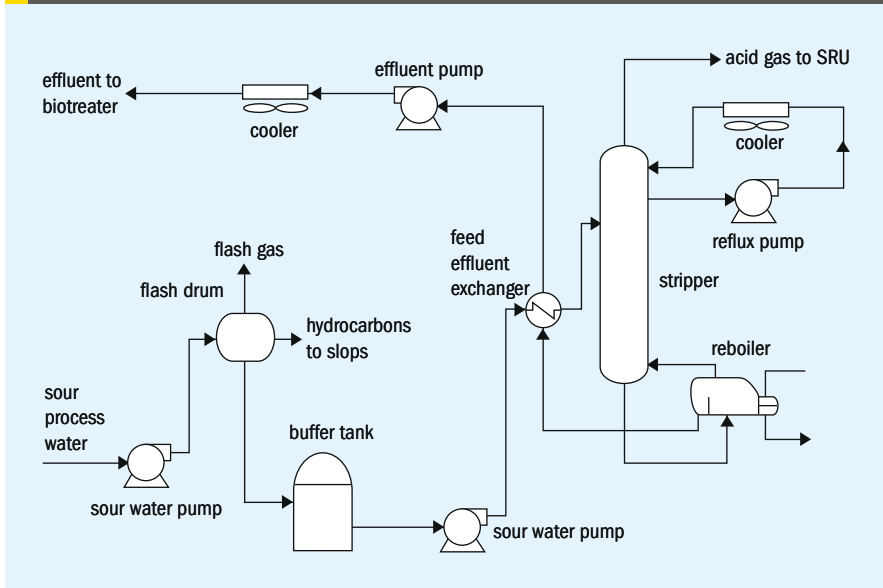
Various sour water streams are collected from throughout the refinery and sent to the flash drum. The flash drum removes entrained and dissolved gases by allowing the water to de-pressurise and settle.

The degassed water flows to a holding, or settling tank (buffer tank). In this tank there may be further degassing as well as the separation of some liquid hydrocarbons that float to the surface of the water. If the residence time is long enough, the composition of the water stabilises and allows for a consistent flow and composition of water to the stripper.

If any filters are present in the process loop, they may be present upstream or downstream of the settling tank.

The water exiting the settling tank is heated in an exchanger (feed/effluent exchanger) by hot, stripped water exiting the stripper.

The heated sour water enters near the top of the stripper tower where it flows downwards and is stripped of H_2S, NH_3, 'light' hydrocarbons and other volatile species, by the steam rising from the bottom. Steam is produced in a reboiler or introduced into the column directly as live steam.

The overhead of the stripper may consist of a pump-around cooling section which cools the stream to a minimum of 85°C. Alternatively, a reflux system is used for the same purpose. These systems recover a portion of the water in the overhead stream, decreasing the amount being sent to the SRU.

The stripped water is cooled in the feed/effluent exchanger, then pumped to various areas for further use or processing (crude desalter, tail gas unit quench tower, biological treatment, etc.).

Sour water sources

In a refinery setting or any plant in general, sour water can be generated in many locations. Water for process applications is used in many ways such as: quench water, steam, wash water and is also generated by the various distillation fractions where water is co-distilled with certain hydrocarbons. Figures 2 and 3 show the diversity of a number of sour waters originating from various units and Fig. 3 provides an indication of the quality of the treated water in relation to the feed quality.

Primary sour water sources include:
- Amine system reflux water purges. TGTU quench water.
- Atmospheric and vacuum crude towers: water is produced by condensation of steam in overhead streams. Vacuum towers may also contribute sour water from ejectors and barometric condensers.
- Thermal and catalytic cracking units: sour water originates from wash water injection, stripping and aeration.
- Hydrotreater and hydrocracker wash water from high and low pressure separators.
- Cokers, delayed and fluid type plants. Water is produced from decoking and quench water.
- Flare seals and knock out drums.
- Hot condensates from throughout the refinery which may have had contact with hydrocarbons (often the concentration of contaminants in these streams is low).
- Any refinery water draw boot: each contains a different sour water composition and flow, depending on crude type and the severity of the process. Manual level controls can also affect the hydrocarbon content of the water especially if they are accidently left open for too long.

According to a previous study by the American Petroleum Institute[2] covering process water consumption estimates, the summary level quantities of water used in refineries were as presented in Table 1.

Seven deadly sins of sour water stripping

Over the years, multiple problems and deficiencies have been uncovered. These have been compiled in the form of a list of the seven most deadly sins of sour water stripping:
1. incorrectly designing the sour water stripper column;
2. incorrectly controlling the overhead and acid gas temperatures;
3. poorly managing the sour water;
4. poorly operating or designing the flash vessel and feed stabilisation tank;

Table 1: Refinery conversion unit process water estimates[2]

Refinery conversion unit	Estimated process water use US Gal/1000 bbl	Water use, US gpm per 100,000 BPSD crude
Distillate hydrotreater	1,500	31
Cat Feed hydrotreater	2,400	66
Vacuum unit	2,000	69
Crude unit	1,400	97
Coker	8,000	112
FCCU	4,500	125
Total		**500**

5. inadequate removal of solids and liquid hydrocarbons;
6. lack of a detailed sour water analysis;
7. neglecting the sour water stripper metallurgy.

No. 1: Incorrectly designing the sour water stripper column

In designing a sour water stripper tower, there are several options available depending on the treated water specification of the particular plant. The downstream destination of the water determines the allowable amount of H_2S and NH_3. The typical design basis can be described as follows:

Feed
$[H_2S] \approx 500 - 24,000$ ppm
$[NH_3] \approx 250 - 12,000$ ppm

Product
$[H_2S] \approx 1 - 25$ ppm
$[NH_3] \approx 10 - 50$ ppm

Generally, the options for design relate to a trade-off between the number of trays or height of packing and the quantity of steam required for stripping the contaminants from the process feed water. That is, the more contact stages available in the tower, the less steam required for stripping. Also, since ammonia is less volatile than hydrogen sulphide (therefore, harder to strip) it is usually the component that sets the quantity of contact stages. In general, the more the ammonia content in the feed stream, the more contact stages required or the higher the steam rates for stripping.

There are also options related to the regeneration medium; stripping steam generated within a reboiler or live stream injection directly into the base of the tower. If a reboiler is used, there is an option to go with a kettle-type or thermosyphon, or one of these reboiler types in combination with the option of incremental live steam injection. If live steam is used, it must be understood that this will increase the treated water content by 10-15%, which could increase treatment costs, which are normally linked to volume.

Lieberman[3] has stated that it may be possible that the extra water generated in the live steam mode could reduce the make-up water requirements for processes such as de-salters and hydrotreater effluent washes. Since external water is required for make-up for the above mentioned units, the increased water produced by the live steam injection could off-set the fresh water make-up. The typical energy usage in the stripper is in the range of 15% steam on a mass basis to the pounds/kilograms of sour water; 1.3 – 1.5 lb steam per US gallon of sour water[1].

There are several options related to the type of reflux section in the top of the tower. Options to choose from include:
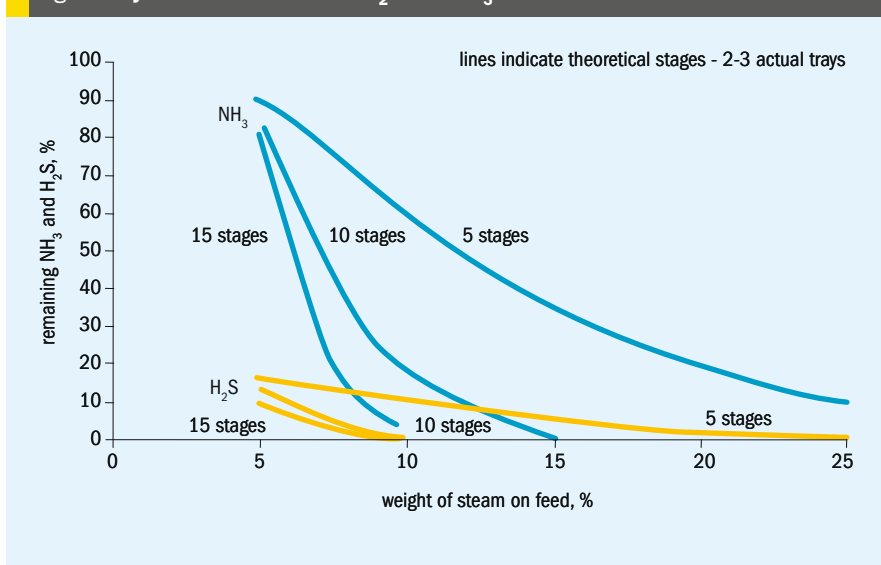
● no reflux at all (generating enough steam in the reboiler (or via live steam) to produce a stripper overhead temperature of around 88°C)[3];
● standard refluxed sour water stripper, with condenser/cooler, accumulator and pump;
● pumparound reflux, with externally cooled and pumped water system in a discreet top section of the tower.

The majority of the sour water strippers around the world use either the pumparound or refluxed condenser methods, with close to an even split between the two methods. Non-refluxed strippers are not favoured in modern industry as they can have excessive water content in the SWAG if overhead temperatures are not diligently monitored. Further they may experience significant capacity limitations in the event that feed temperature drops, because of exchanger fouling for instance. A feed temperature drop in a non-refluxed stripper needs to be compensated for via increased boil-up which in turn leads to higher vapour and liquid traffic below the feed tray with potentially lower flood points in the column as a result.

The pumparound process has potential for less corrosion than a refluxed system because it is liquid filled and not as prone to solid salt deposition; the relative concentration of ammonium salts is less in the pumparound as long as the temperature does not drop too low. The general target for the reflux temperature is >185°F (>85°C) to eliminate the potential for ammonium salt precipitation in the water loop and the associated piping to the SRU.

There are also options on the tower internals themselves. Historically, the towers have been trayed, with an option for sieve or valve trays. Anecdotal evidence seems to indicate that either sieve trays or grid trays will handle the inherently fouling service best. Valves can become stuck to the tray deck, which will promote plugging and flooding. In recent years, some operators/designers have tried using random

Fig 2: **Various process water streams feeding an SWS**

Fig 3: **Water quality in feed and effluent of an FCC (L), Coker (C) & HT (R) SWS**

Fig 4: **Tray and steam effect on H₂S and NH₃ removal**

packing. Random packing has much lower pressure drop, thus providing a higher tower capacity than a trayed vessel. Unfortunately, a packed bed requires exceptionally good liquid and vapour distribution within the tower and given the potential for fouling in sour water service, this option may prove to be troublesome. To be safe, Sulphur Experts recommends that packing (either random or structured) not be used in sour water service.

The core question becomes how many stripping trays or how high a packing height and how many reflux trays are required to properly strip the sour water. Figure 4 provides a graphical overview of the effect of theoretical stripping stages and weight of steam to feed on the treated water H_2S and NH_3 content. Tray efficiencies have been loosely regarded as being somewhere between 30-45%, so around three trays per theoretical stage. There are rate-based software simulators available that can accurately predict sour water performance on an actual tray-by-tray basis, allowing the design engineer to feel confident in accurately determining the tray-to-steam ratio that will most economically and efficiently treat the sour water.

The pH of the sour water plays a very significant role in the ability of the steam to strip the H_2S and NH_3. Because H_2S is a weak acid in solution, it remains dissociated under alkaline conditions and is difficult to strip from the water. If the pH is low (<5.5) it returns to its gaseous form much more readily and it is possible to remove almost all of the H_2S from the water. NH_3 is basic in nature, so it would require a

high pH of the water to return to its gaseous form. Full dissolution can be achieved if the pH is in excess of 10 and sufficient steam is introduced to the regenerator or stripper bottoms.

Theoretically, there would be two strippers, one operating with a low pH for maximum H_2S removal and another operating at high pH for maximum NH_3 removal. Because most refineries do not have that luxury, the single stripper may need to be modified to improve the potential for success of removing these disparate contaminants from the water. Because H_2S is easier to strip than NH_3, operations should err on the side of improving the NH_3 removal so the target pH of the sour water is slightly basic (around 7.5 to 8.5) to try to improve the removal of the less volatile ammonia fraction.

A possible modification would be the addition of a strong base such as caustic. Historically, the addition point has been recommended at some point lower in the tower to reduce the likelihood of "binding" the H_2S before it has had a chance to be stripped from the sour water. The ideal location of addition may even be in the sour water feed itself, but that is best decided upon with rigorous rate-based modelling for any particular application. Associated with the addition of the caustic is the need for an accurate means of measuring the water pH in both the sour water feed and effluent. Any excess addition of caustic can be detrimental and result in caustic deposition, binding of H_2S and poor stripped water performance in the de-salter as emulsion formation is

elevated. It is important that the lag time between dosing and pH measurement is minimised to avoid overdosing the unit.

Figure 5 provides a review of a particularly poorly designed sour water system.

There was no buffer tank after the flash drum, leaving no opportunity to moderate flow rate and composition. Lack of a buffer tank also means there is no place to store sour water in the event of a stripper outage.

With no feed/effluent exchanger, the feed temperature to the SWS is too cold, requiring an inordinately high amount of stripping steam.

Because there is no reboiler, this extra steam is all live steam injection, which increases the effluent water volume dramatically.

Finally, and most troubling, is the routing of the flash gas vapours (primarily hydrocarbons) to the SRU feed stream. The flash tank is present to remove hydrocarbons from the feed to the SWS because they will naturally end up in the SWS overhead stream feeding the SRU. But this design sends these removed hydrocarbons right back into the SRU feed. There is practically no reason to have the flash tank in this design. These hydrocarbons wreak havoc in the SRU as far as air demand in the reaction furnace, side reactions to unwanted species and major coking on the sulphur catalyst.
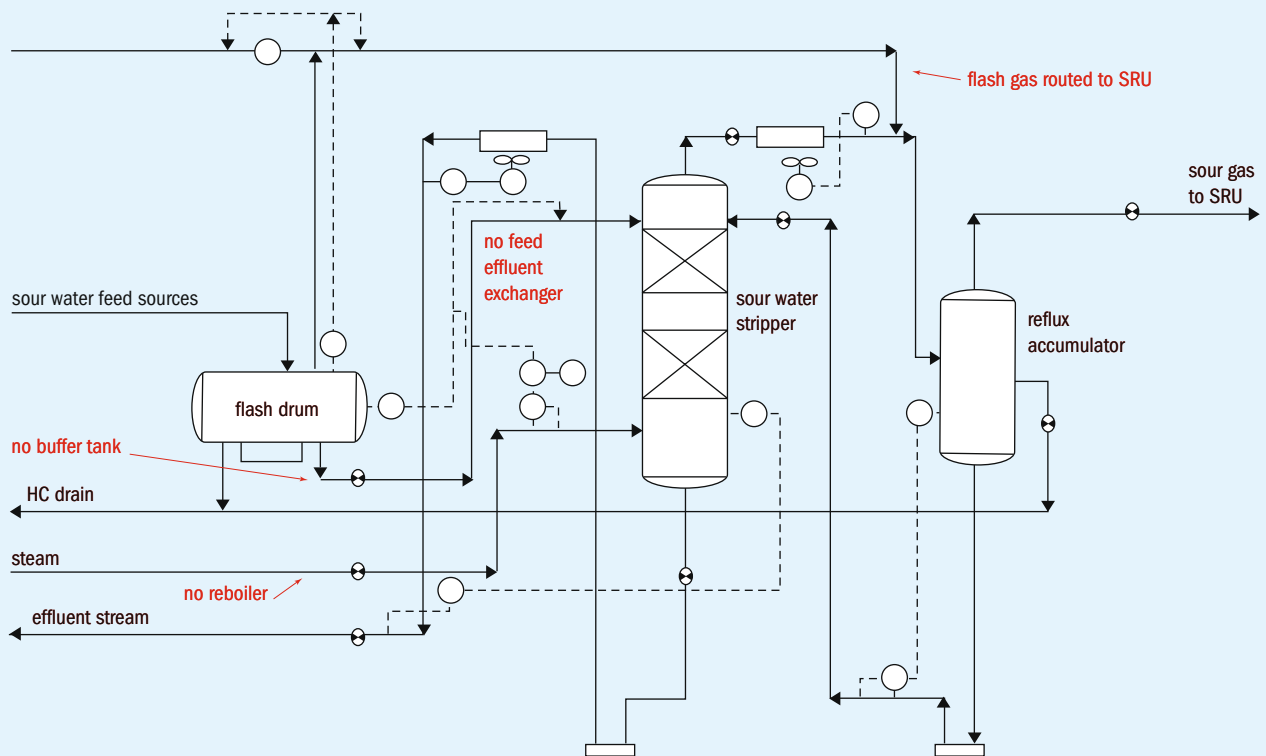
Major capital outlay was required to bring the unit up to 'best practices' guidelines (installed a buffer tank, a reboiler and a feed/effluent exchanger) and the flash gas was re-routed to a low pressure refinery absorber. Currently, the unit runs virtually trouble-free, steam consumption has been more than halved, SRU operations are smooth and sulphur quality is excellent.

No. 2: Incorrectly controlling the overhead and acid gas temperatures

Heat is the primary component in effective SWS operation. Heat is required for:

- raising the water temperature from the feed temperature to the boiling point (reboiler temperature); sensible heat load;
- providing the temperature for the reaction of the ionic salts back into pure components;
- providing the heat to transfer the pure components from the liquid to the vapour phase;
- providing a diluent environment by lowering the partial pressure of the stripped gases by providing excess steam vapour (produces the reflux flow).

Fig 5: **Improperly designed sour water system**

flash gas routed to SRU

sour gas to SRU

no feed effluent exchanger

sour water stripper

reflux accumulator

sour water feed sources

flash drum

no buffer tank

HC drain

steam

no reboiler

effluent stream

Without sufficient heat, the stripping of H_2S and NH_3 will not occur. In a well operated and designed sour water stripper there is always sufficient heat available in the column for the final stripping of H_2S and NH_3 to occur.

There are three temperature effects in the overhead system that the SWS operator should be aware of:

● ammonium salt sublimation;
● corrosion due to high salt content in the reflux water;
● high temperature polymerisation.

Ammonium salt sublimation

Ammonium carbonate and bicarbonate sublime in the temperature range of 55 to 75°C (130 to 167°F). When SWS overhead gas is cooled too much, salts precipitate and foul instruments, control valves and lines. This has been experienced on numerous sites throughout the industry, some typical examples of this are shown in Fig. 6. Sulphur Experts recommends a minimum temperature of 85°C to prevent fouling of the system due to salt deposition. Checking the instruments and overhead lines to the sulphur recovery unit (SRU) for cold spots should be done on a regu-

Fig 6: **Ammonium salt sublimation**

$NH_3 - CO_2$ plug in cold SWS AG line

lar basis. It is standard industry practice for these lines to be insulated and steam traced but steam jacketing is preferred.

Corrosion due to high salt content in the reflux water

Most metallurgy is not rated for the high salt contents (>35 wt-%) that can be found in reflux water if the temperature is not maintained (Fig. 6). As H_2S and NH_3 are more volatile than H_2O, operating the overhead system at a higher temperature will decrease the salt content in the reflux water. This, unfortunately, increases the water content of the SWAG gas to the

SRU which has an adverse effect on its operation. Salt content in the reflux system is SWS specific. With good test data a safe operational temperature can be set.

The pump shown in Fig. 7 is from the pumparound reflux of the first stage of a two stage stripper unit. The highly corroded stainless steel impeller was found only six months after the unit was commissioned along with multiple other leaks in the pumparound system. The pumparound was operating at 59°C. Simulation revealed that the ammonium salt content in the reflux was at 35 wt-%; subsequent

Fig 7: **Reflux pump corrosion due to elevated salt content**

lab analysis revealed 38 wt-% of NH_4HS in the pumparound.

After extensive simulation study the best solution (which was later implemented) was to take the pumparound out of service and utilise a water wash in the top of the column to keep the stripper top temperature at a reasonable level (~85°C).

High temperature polymerisation

Steam tracing/jacketing for winterisation or fouling prevention should not exceed 150°C as this increases polymerisation reactions which can result in fouling.

No. 3: Poorly managing the sour water

Poor water management is, unfortunately, quite prevalent in the industry. Broadly, this falls into four categories:
● cross contamination;
● dilution;
● segregation of phenolic water;
● bulk hydrocarbon ingress.

Cross contamination

Contamination of the SWS system with improper water streams needs to be avoided. There is no reason for cooling, fire or ballast water in a SWS system, as the Ca/Mg hardness in these streams will foul the reboiler and trays below the feed nozzle. Spent caustic or waste from an alkylation unit should also not be sent to a SWS, as these streams contain strong bases or acids which will bind H_2S or NH_3, resulting in off specification stripped water. It is critical that only "process" water streams be routed to the SWS. Note that spent caustic could potentially be used for caustic dosing, however the caustic strength must be quantified and dosing rates or PH controller tuning should be adjusted accordingly.

Dilution

Dilution has the following negative impacts:
● causes poor energy efficiency in the SWS due to unnecessary processing of inappropriate waters
● increases the cost of downstream treatment and disposal due to greater treated water volumes
● uses SWS capacity unnecessarily, which may affect plant flexibility

Common sources of SWS water dilution include:
● direct steam injection: this traditional (low capital) design approach should not be used because it increases the effluent water quantity by 10 to 20%;
● routing uncontaminated or low contamination streams to SWS (streams feeding the stripper should be tested for H_2S, NH_3 and phenols);
● dumping of other (non-sour) water streams into the SWS system.

Segregation of phenolic water

Phenolic water primarily comes from refinery cracking units such as cokers or FCCs. It is important to understand that only a small fraction of phenols in water will be removed in a SWS. One African refinery was off-specification on phenols for several years as a result of not been cognisant of this. This is largely a result of the low phenol volatility. A good simulation study of this was published by Hatcher et al[14].

Most of the phenols can be removed in the crude desalter unit, which is downstream of the SWS. It is important to route all the phenolic effluent water to the desalter, as the phenols tend to partition into the oil phase, thus reducing their phenol content in the effluent stream. If possible it is also recommended to use a separate SWS for phenolic waters so that the non-phenolic water can stay segregated from the phenolic waters.

Bulk Hydrocarbon Ingress

The best solution to minimising hydrocarbons in sour water feeds is to ensure that the hydrocarbons are not in the water in the first place. This is carried out by a comprehensive and thorough evaluation of sour water generation points. It is important that all SWS feed streams are analysed, regardless of flow rate. An example of this is shown in Fig. 8, which shows a sample from a water stream which contributed less than 10% of the feed flow, but was responsible for over 90% of the hydrocarbon contamination.

Fig 8: **A low-flow sour water system with high hydrocarbon levels**
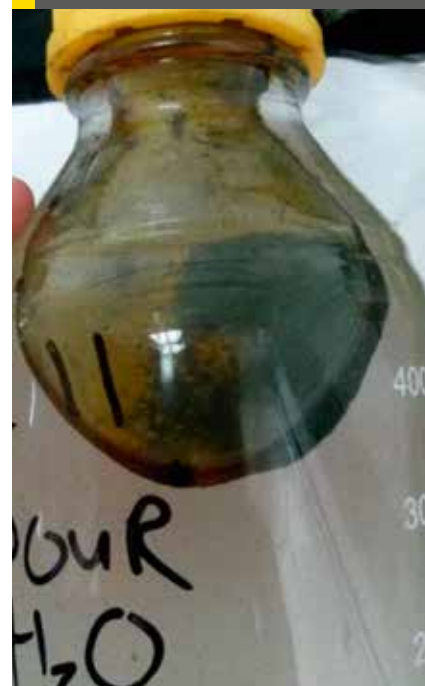
At the commissioning of a Middle Eastern refinery, there was a significant amount of bulk heavy diesel fraction hydrocarbon in the sour water. This led to fouling of the feed/effluent exchanger within three months of start-up and reduced performance on the stripper.

No. 4: Poorly operating or designing the flash vessel and feed stabilisation tank

Good flash vessel operation and design is vital. The flash vessel serves to remove the light hydrocarbons and the bulk of the heavier liquid hydrocarbons. Without a proper flash vessel the SWAG cannot be safely sent to an SRU.

Preventing hydrocarbons from entering the SWS will prevent hydrocarbon from entering the sulphur plant (SRU). There are several reasons why it is advantageous to minimise hydrocarbon in the SRU feed, the most important being:
● difficulties maintaining stable SWS (and consequently SRU) operation;
● decreased capacity;
● lower efficiencies;
● potential catalyst deactivation and sulphur quality issues due to soot formation in the downstream Claus reactors.

Hydrocarbons in the sour water feeding the stripper will also significantly increase the fouling of stripper internals. The "black shoe polish", which is found on sour water

stripper internals, typically contains heavy hydrocarbons at varying degrees.

The flash vessel is a three phase separator; its purpose is to separate water, oil and gas. This is achieved through pressure drop and residence time; the greater the pressure drop or greater the residence time, the better the separation of the three phases. Flash vessel operation is therefore at its peak when the pressure in the vessel is as low as possible and residence time maximised. The minimum recommended residence time is 20 minutes at the normal operating level of 50-60%. The lower the pressure, the more likely hydrocarbons will flash off, as pressure has a direct effect on the vaporisation point of hydrocarbons.

The pressure is set by the destination pressure of the flash gases. These gases are normally sent to flare, incineration, or a low pressure fuel gas amine absorber. Under no circumstances should flash gas be routed to the SRU, as the flash gas will have a continuous fluctuation in both flow and composition. Figure 9 presents a graphic visual of the potential effect of hydrocarbon load on reaction furnace operation. With excess heavy-end hydrocarbons the required air flow for combustion can double.

If the flash vessel uses weirs, they will typically be set at a height of 50-60% of the vessel. The water level should be maintained at 7-8 cm below the weir height, allowing liquid hydrocarbons to then flow over into the oil side of the weir. When both the size of the tank and liquid level are set, then the only option to increase residence time is to reduce the water flow to the vessel by critically evaluating all streams feeding this vessel.

One of the prevalent causes of SWS unit upsets is from large fluctuations in the composition and quantity of the sour process water. These fluctuations are inherent to refinery operation and can be prevented by a properly sized SWS feed stabilisation/buffer tank, with the water feed on one side of the vessel and the exit on the other.

The stabilisation/buffer tank also serves to partially remove suspended solids and liquid hydrocarbons. It is essential that the buffer tank has skimming facilities installed to remove these hydrocarbons. The buffer tank can be designed with a gasoil layer floating on the top, as a blanket, to avoid smell problems. A better option is to use an internal floating roof with hydrocarbon skimming facilities. This

Fig 9: **Effect of hydrocarbons on reaction furnace air flow**
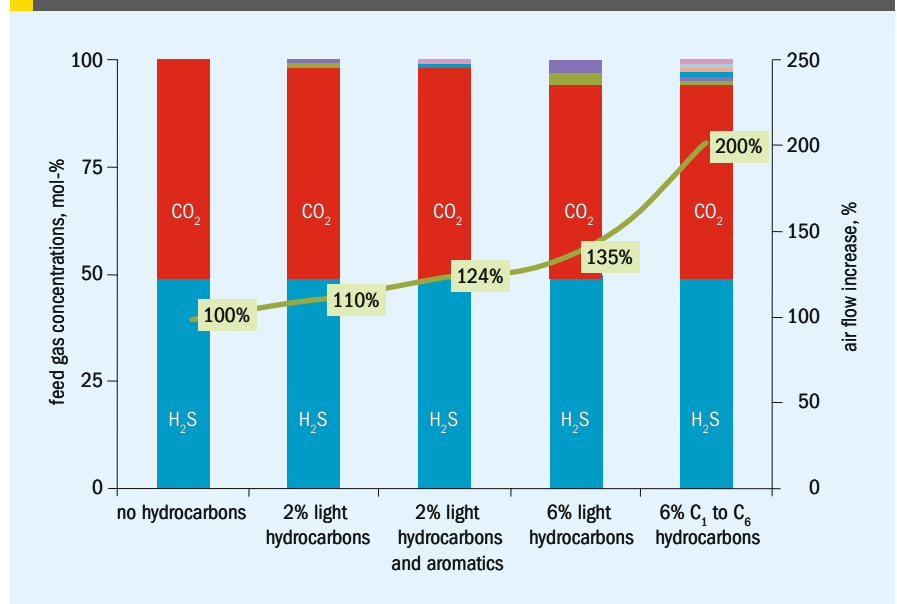
is a more costly option but it will significantly reduce the serious odour problems of SWS feed water.

Similar to the flash vessel, this stabilisation tank is normally operated 50% full. The correct level is however, always a compromise between the various functions: feed stabilisation, free storage capacity and separation. This tank must be partly empty, to allow for upsets of the stripper which can last hours or significantly longer. On the other hand, a longer residence time will improve hydrocarbon/solids separation and most importantly will stabilise the SWS feed composition and flow.

Along with the height of the liquid level, the location of the feed and discharge water lines play an important part in the stabilisation role. The inlet and outlet nozzles should be located at opposite ends of the vessel, so as to minimise potential bypassing of contaminants. The outlet nozzle is often 600 mm from the bottom of the tank so that precipitated solids or heavy oils are not pumped out of the tank along with the sour water. The buffer tank should be designed with a bypass to accommodate cleaning.

No. 5: Inadequate removal of solids and liquid hydrocarbons

Poor filtration of solids and inferior liquid hydrocarbon removal can result in fouling and corrosion problems of the SWS unit, which then leads to poor reliability and decreased run lengths between shutdowns. Additionally, hydrocarbons that are not separated at the source of the feed sour water can be present in the sour

water acid gas affecting the downstream sulphur recovery process.

Hydrocarbons
Hydrocarbons in water streams can be present essentially in three forms:
● free hydrocarbons;
● soluble hydrocarbons;
● emulsified hydrocarbons.

Free hydrocarbons
These will not interact with the bulk water and will tend to separate within a few minutes in the flash vessel. Free hydrocarbons are normally observed by the formation of a top hydrocarbon layer above the water phase (or below depending on the density difference). The levels of free hydrocarbons can vary from 100 ppmw to percentage levels. Their separation efficiency is calculated via Stokes Law, which has a large effect from the droplet diameter (Figure 10). Viscosity and density difference between the phases also plays a lesser role, with lower viscosities improving separation velocity. Generally, this indicates some benefit from running at slightly higher temperatures as the fluid viscosities decrease at higher temperatures.

Soluble hydrocarbons
All hydrocarbons will have a certain solubility in water phases. The extent of hydrocarbon solubility in water will depend on the pH of the water, water pressure, temperature and the type of hydrocarbon. It is impossible to observe dissolved hydrocarbon in a water phase as it is indistinguishable from pure water. In general, the solubility of hydrocarbon in water can

Fig 10: **Relationship between hydrocarbon droplet diameter & separation time**

Stokes Law:

$$V = \frac{gd^2(\rho_a - \rho_b)}{18\mu}$$

where:
V = separation velocity
g = gravitational force
μ = viscosity continuous phase (water)
ρ_a = density of solvent phase
ρ_b = density of liquid contaminant
d = diameter contaminant droplet

Droplet diameter, microns	Time
160	30 min
106	1 h
75	2 h
43	6 h
22	24 h
16	48 h
8	168 h

water + diesel-like hydrocarbon at the discharge of a centrifugal pump

range from a few ppm to a few hundred ppm. The solubility of hydrocarbon in sour water has a direct relationship with the pH; the higher the pH, the higher the solubility.

Emulsified hydrocarbon

Under normal conditions, hydrocarbons will be either free or dissolved in a water phase. However, when conditions are conducive (including the presence of surfactants and energy), the hydrocarbon contaminants can form very small droplets in the water phase (Fig. 11). These droplets are stabilised by molecular surfactants (similar to soaps or detergents) and also by small size suspended solids. Emulsion droplet sizes can range from a few microns to about 500 microns. Micro-emulsions are the most stable emulsion type and can take weeks to naturally separate. Micro-emulsions are typically found when droplet sizes are less than 10 microns.

Suspended solids

Suspended solids in the sour water feed are fairly common, especially in plants associated with coker units. To some extent these solids will settle in the upstream feed stabilisation tanks (also undesirable), however, a considerable portion can be present in the effluent. The effects of suspended solids can be somewhat similar to hydrocarbons, as they will stabilise foaming and deposit on metal surfaces leading to reduced flows and under-deposit corrosion.

Most refineries use stripped sour water as desalter wash water, particularly in FCC refineries to remove the phenols from the stripped water. The presence of solids will enhance emulsification, impacting the effectiveness of water and crude separation in the desalter unit. This can lead to increased salts in treated crude, generating higher corrosion rates in the crude unit overhead. Many crude unit corrosion problems, desalter upsets and increased additive usage can be tied to improperly stripped water.

Many solids are present at diameters less than the visual acuity of the human eye (<40 microns) and they are not detected until they precipitate out of the solution en masse (Fig. 12). These are the types of solids that can really stabilise a foaming condition, and there is a very good chance that these low micron solids and the larger visible solids will settle in any stabilisation tank, so it is generally recommended to include tank cleaning during any turnaround situation. Leaving excessive solids in the stabilisation tank can lead to the eventual transfer of these solids out of the tank with the process water if they are allowed to rise to the level of the outlet nozzle on the tank.

Possible remedies for the conditioning of sour water

Filtration is the basic technology for removing suspended matter from the sour water. For the removal of emulsified hydrocarbons, the technology of choice is a coa-
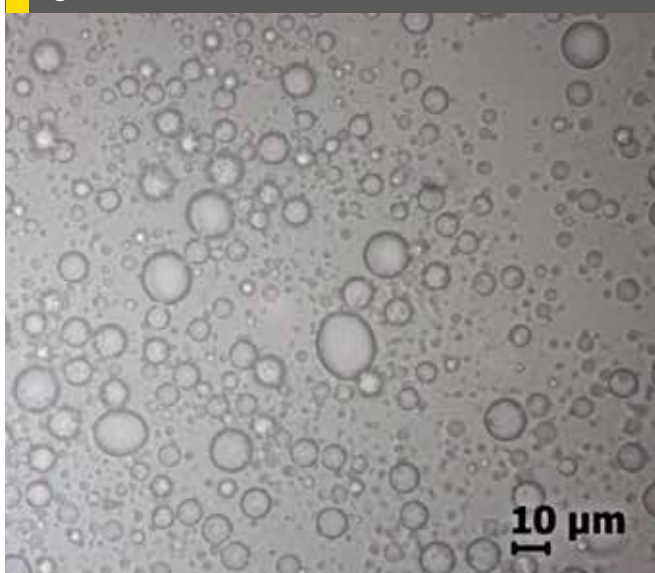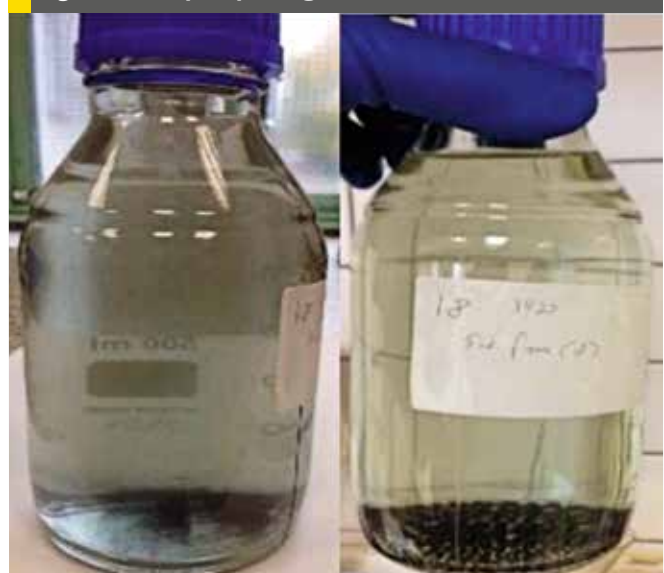

Fig 11: **Water and oil micro-emulsion**

10 μm

Fig 12: **Solids precipitating out of sour water after 12 hours**

lescer. Coalescence is the recombination of two or more small liquid droplets to produce a single entity larger in size.

A large stabilisation/buffer tank could be used to separate hydrocarbons and suspended solids from the various sour water streams. However, this is quite costly. A buffer tank rarely has sufficient residence time to accommodate effective separation of fine particulate and micro-emulsions (10 microns and smaller). It is therefore recommended to use filters and coalescers.

Due to the particle size and the high fouling properties of emulsified hydrocarbons in sour water streams, only disposable microfiber-based coalescers are able to provide proper emulsion separation. Other systems such as inclined plates and fibre mesh are not effective.

Suspended solids removal upstream of the hydrocarbon coalescer is mandatory. Particulate removal will protect the coalescer elements and also destabilise the emulsion, significantly improving overall system efficiency. The particle filter and liquid coalescer combination system should always be installed downstream of the sour water charge pump and upstream of the heat exchanger. This configuration is illustrated in Figure 13 and the effectiveness of such an arrangement is shown in Fig. 15. Figure 14 presents the deposition in a packed SWS caused by ineffective upstream solids removal.

No. 6: Lack of a detailed sour water analysis

The design specifications of a SWS often only list the H_2S and NH_3 content of the combined feed. The possible presence of other components is very rarely mentioned. These other contaminants can create significant problems because they could:

- bind H_2S to the water and reduce its tendency to be stripped;
- bind NH_3 to the water and reduce its tendency to be stripped;
- plug up the trays or packing or scale on hot surfaces;
- lead to foaming conditions in the stripper;
- affect the performance of the downstream bio-treaters.

Common "other" sour contaminants are listed below:

- Sulphuric acid, hydrofluoric acid, formic acid and other acids will bind NH_3 in such a strong way that it will be almost impossible to strip. The NH_3 can be liberated and subsequently stripped
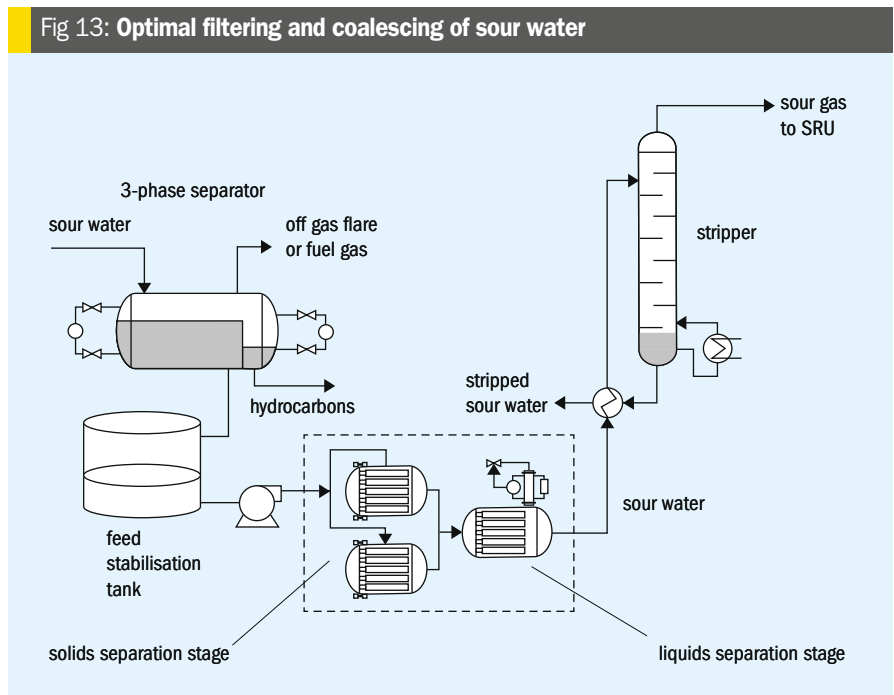
by addition of a strong base, normally caustic, to neutralise the strong acids.
- Calcium and magnesium can be present if hard-water has been used as process water. It is also possible that fire water or cooling water has been discharged to the SWS unit. As a result, calcium and magnesium carbonates will deposit as scale in the reboiler.
- Elemental sulphur or polysulphides are normally caused by air ingress to the process water system. H_2S will be oxidised to sulphur and polysulphides. This sulphur will deposit as a scale on the bottom trays of the stripper and in the feed/effluent exchanger.
- Phenols are present in the process water

from FCC units, cokers and thermal cracking units. Preferably this process water should be segregated in phenolic and non-phenolic water. Phenols are not properly removed in a SWS and therefore the phenolic water effluent should be sent to the crude desalter where the phenols are extracted to the crude.
- Nitrogen components such amines, filming corrosion inhibitors or HCN are very poorly removed in a SWS. Often the stripped effluent of the SWS is only analysed for NH_3 and therefore these other nitrogen components are missed. One of the important environmental goals of the SWS is to remove as much of the nitrogen components as possible.

Fig 13: **Optimal filtering and coalescing of sour water**

Fig 14: **Fouling in an SWS tower**

Fig 15: **Photograph of coalescer effectiveness in sour water service**

filtered sour water feed

recovered hydrocarbon

HYDROCARBON dissolved, emulsified and free

sour water feed

filtered and coalesced sour water feed
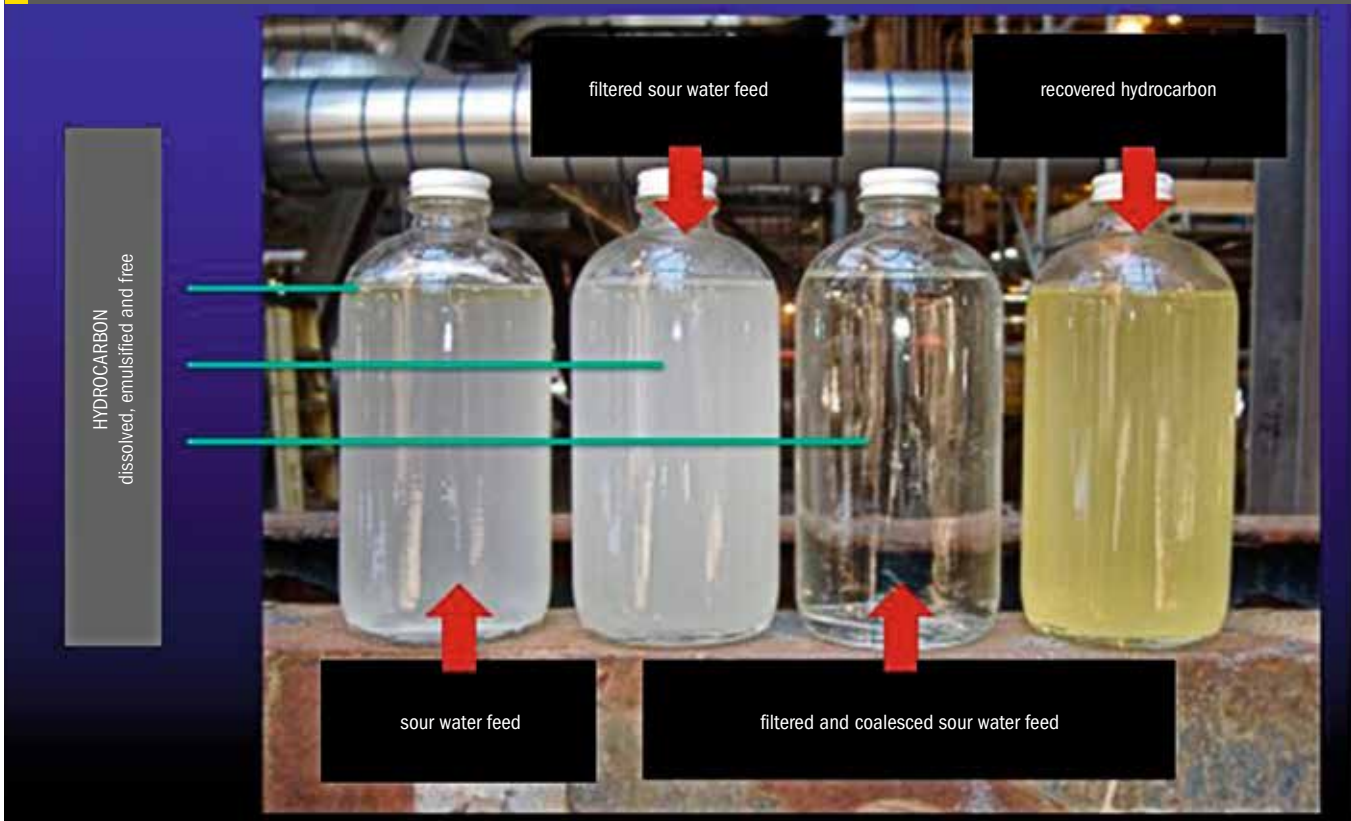
Fig 16: **Relative corrosion resistance for test materials in ammonium bisulphide environments[9]**

least resistant

most resistant

Alloy C-276
Alloy AL-6XN
Alloy 2507
Alloy 625
Alloy 825
Alloy 20cB-3
Alloy 600
Alloy 800
Alloy 2205
316 SS
304 SS
410 SS
Alloy 400
Carbon Steel
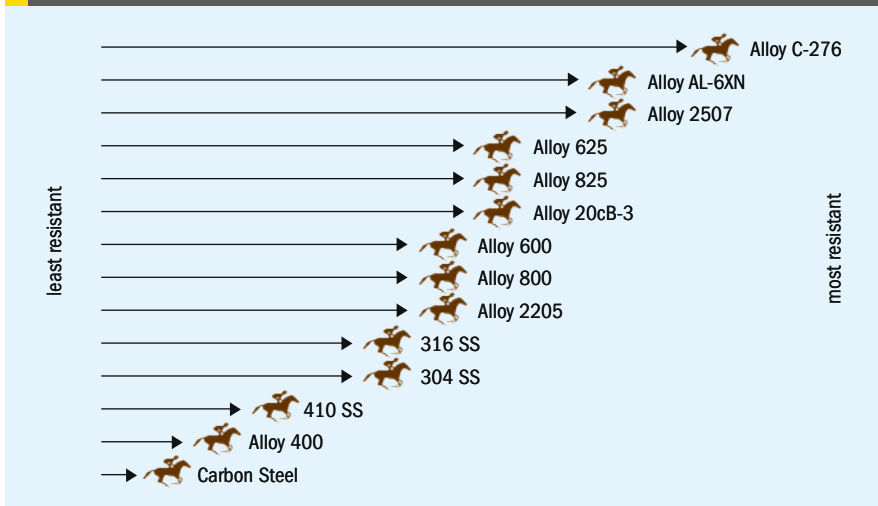
● Surfactants will certainly be present in the SWS feed, as they are removed by the various refinery wash-water systems. Analysis of these trace components is close-to impossible. As a consequence, the SWS needs to be designed with a safety margin to allow for foaming upsets.

● Mercaptans may also be present in the SWS feed, and will be removed in the stripper. As a result, they will contribute to the sulphur and hydrocarbon content of the acid off-gas going to the SRU. The overall design of the SWS and the SRU needs to allow for the additional air requirement for the SRU.

● Benzene, toluene, ethyl benzene and xylene (BTEX) will also be present in the SWS feed and removed in the stripper. BTEX compounds are well known to be detrimental to the life of catalyst in the SRU.

No. 7: Neglecting the sour water stripper metallurgy

The presence of ammonium bisulphide in sour water systems where both ammonia and hydrogen sulphide are present is the main driving force for corrosion. Ammonium bisulphide corrosion appears to be enhanced when flow rates are increased and also contributes to under-deposit attack. Flow-enhanced corrosion occurs at impingement points or after flow disturbances. The problem with corrosion in sour water strippers is that the corrosion has been historically hard to predict and most industry guidelines have been based on collected field experience with existing metallurgies. More recently, work has been done to build tools that will better predict sour water corrosion.

The following factors have been found to contribute to corrosion in sour water stripping systems:

● Ammonium bisulphide
  ○ Increasing concentrations result in increased corrosion
  ○ Some texts indicate a threshold level of 35 wt-%
  ○ Corrosion rates increase with water velocity
● Hydrogen sulphide partial pressure

Table 2: **Recommended metallurgy in sour water strippers**		
Location	**Minimum metallurgy**	**Notes**
Sour water flash vessel	Carbon steel with 6 mm corrosion allowance	
Feed pump	300 series stainless steel internals	
Feed / effluent exchanger	Carbon steel shell with 6 mm C.A. AISI 316(L) SS or Incoloy 825 tubes	
Stripping column	Carbon steel shell with 6mm C.A. Trays are 316(L) SS	400 series metallurgy not sufficient
Effluent pump	Carbon steel casing and internals	
Overhead cooler	Titanium or Avesta 254 tube bundle; headers can be 316(L) SS	
Overhead accumulator	Carbon steel with 6 mm C.A.	It is important to Control reflux temperature well to maintain an acceptable level of NH$_4$SH
Reflux pump	316(L) SS casing and internals	
Piping	Most piping can be carbon steel with 3 mm C.A.	Piping in the overhead section should have a more robust 6 mm C.A. due to high NH$_4$SH levels
General		If cyanides are present at ≥30 ppm then HIC resistant steel should be selected (cyanides are usually present in the sour water from FCC units)

❍ Corrosion rates increased with an increase in H$_2$S partial pressure; accentuated by higher velocities and higher ammonium bisulphide concentrations

❍ Effect was far more extreme for the least corrosion-resistant materials (carbon steel, Monel 400 and Type 410 SS) – Fig. 16

● Temperature

❍ As expected, an increase in temperature increased corrosion rates

Table 2 provides a quick review of recommended metallurgy.

Conclusions

In summary, sour water strippers have been designed and operated from simple systems with no buffer tank, minimal hydrocarbon removal, no filters, towers with few trays and live steam injection to deluxe systems with full pre-treatment stages (including flash tank, buffer tank, coalescer and filters) and segregated H$_2$S stripping and NH$_3$ stripping towers.

Ultimately, sour water systems should be designed to minimise operating problems, maximise on-line factor and optimise the SRU feed gas quality. In order to accomplish this the system should be designed with:

● a flash drum with three-phase separation capabilities and a minimum of 20 minutes residence time;

● a buffer tank with a minimum 24 hour residence time at 50% full;

● a filter followed by a coalescer for solids and hydrocarbon removal;

● a feed/effluent exchanger to heat up the feed stream and reduce the reboiler load;

● some consideration to segregating the ammonia fraction from the SRU feed stream (two-stage stripping);

● a reboiler (with the potential for live steam injection; a last resort as "dilution should not be the solution to pollution");

● reflux loop to control SRU feed temperature;

● insulated and steam traced piping to the SRU;

● a detailed feed water analysis;

● the correct metallurgy for the location in the system. ■

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