Impurities Removal Options in Sour Gas Field Developments

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To comply with both progressively tighter product purity specifications and stricter environmental regulations while at the same time handling feedstocks from more diverse and sometimes lower-grade sources, gas treatment plant operators in the hydrocarbon processing industries are having to adopt measures to deal specifically with minor impurities which would otherwise impair the efficiency of the main gas treatment unit or cause infractions of environmental emission standards. These include elemental sulphur, mercury, heavy hydrocarbons, ammonia, carbon sulphides and mercaptans, and sub-micron particulate solids such as ferrous sulphide. Depending on their nature and the set-up of the processing plant, these impurities may be dealt with by preliminary treatment upstream of the main gas plant or by final conditioning of the treated gas. This paper addresses the more significant impurities one by one and reviews the options for dealing with them. Staged co-processing of natural gas in the SRU is cited as a solution for such adverse conditions as lean feed, BTEX and extreme turn-down. The case is made for considering ammonia build-up in the amine regenerator reflux despite none in the feed gas.

Gas processing in gas industries and in oil and sour gas field facilities is becoming more complex owing to the increasing stringency of the emissions requirements established by environmental regulatory agencies. In addition, as components required on new wells become more complex and new sources of sour gases are developed, gas specialists are having to seek new technologies, new solvents, and new solutions to these new challenges. In response to this trend, gas preconditioning upstream or final step(s) for gas conditioning downstream of the gas-treating unit are emerging as the best options to comply with the most stringent regulations. The final steps of gas conditioning are a combination of different processes to remove impurities such as elemental sulphur, solids, heavy hydrocarbons, and mercaptans that current commercial solvents are not able to handle. In cases where there is no sulphur recovery / tail gas unit installed downstream of the gas plant to destroy the remaining impurities, meeting the product specification is very crucial. Solvents could be contaminated with undesired elements, causing any or all of solvent degradation, plugging, foaming, corrosion, and failure to meet the product purity specification. Over the years, many papers have been presented on the gas preparation required upstream of any gas treating system. There is no indication, however, of any unique process that is able to handle all of the impurities. [1]

In cases where sulphur recovery and tail gas units are installed downstream of the gas plant, gas preconditioning may not be required and most of the impurities will be destroyed in the sulphur recovery unit. However, with the increasing sulphur content in crude oil and natural gas and the tightening regulations on sulphur content in fuels, refiners and gas processors are being pushed to obtain additional sulphur recovery capacity. At the same time, environmental regulatory agencies in many countries continue to promulgate more stringent standards for sulphur emissions from oil, gas, and chemical processing facilities. It is necessary to
develop and implement reliable and cost-effective technologies to cope with the changing requirements. In response to this trend, several new Claus tail gas technologies are emerging to comply with the most stringent regulations. Feed gas compositions should be evaluated for the need for preliminary preparation measures upstream of any gas plant. The following are some of the unusual impurities that may require additional removal steps in gas treating.

- Elemental sulphur
- Mercury, Hg
- Heavy hydrocarbons (CnHm) and BTEX such as benzene and C8+
- Ammonia
- COS, CS₂, RSH, mercaptans, and solids such as FeS.

**Elemental Sulphur**

Several studies have been performed regarding elemental sulphur removal in natural gas production facilities from downhole to the gas processing facilities. Elemental sulphur causes a series of problems within the gas plant, such as plugging of exchangers, crystal forming, solvent contamination, and product quality deviation. The GPSA Engineering Data Book and the Perry and Chilton Chemical Engineering Handbook show that gravity-based scrubbers are not effective for particles smaller than approximately 1 micron, whereas filtration is effective for particles as small as 0.01 micron. Sulphur is one of the elements that has a tendency to bond extensively to itself and forms chains in a similar fashion to carbon to produce S₈ molecules. Chains can break and either react with other molecules such as H₂S (with which it forms sulphanes or hydrogen polysulphides – hence the high solubility of H₂S in molten sulphur) or produce solid sulphur, which goes into suspension in water. Sulphur also has the potential to act as a fairly strong oxidizing agent and causes corrosion in stainless steel equipment. Hydrocarbons could be used as solvents for H₂S because sulphur reacts with hydrocarbons to form mercaptans, which are present in sour gas. Sulphur is also highly soluble in carbon disulphide (CS₂). Other solvents include oily disulphides, amines, alkanolamines, and aromatic hydrocarbons. Amines and alkanolamines are extensively used in German sour-production schemes and depend on the following reaction for taking up sulphur.

\[ \text{RNH}_2 + \text{H}_2\text{S} \rightarrow \text{RNH}_3^+ + \text{HS}^- \]

Sulphur should be managed and it is reasonable to predict that a suitable chemical base might prevent sulphur deposition. Acid-base reactions are rapid compared with decomposition reactions and could act to capture the sulphanes as ionic polysulphides before decomposition occurs.

If water is contaminated with bicarbonate, it becomes corrosive. That suggests that aqueous sodium bicarbonate could be injected into the bottom of the well bore to control sulphur deposition until production matures and the formation water takes over.
If gas containing high levels of sulphur, say more than 10 tons per day, is to be removed, a regenerative H₂S adsorption/desorption process, allowing a Claus process to be used for converting the removed H₂S into elemental sulphur, is normally favored.

If less than a few hundred pounds per day of sulphur needs to be removed, fixed beds of chemical absorbents will remove H₂S to any level required. The used catalysts and absorbents can be sold to the metal recovery industry, and there are no disposal problems.

**Inline separator / Filtration system**

All gas-sweetening units should have a well-designed inlet separator. In-line separators have been used as a filtration system to remove particles and any entrained solids. The in-line separator should be designed not only on the basis of inlet fluid volumes but also on surge capacity to handle slugs of liquid hydrocarbons, water and well treatment chemicals. In cases where solids or liquids are known or expected to be a problem, a high-efficiency separator such as a coalescing filter separator should be used.

The inlet separator should be followed by a second-stage activated carbon filter for removing particles down to 5 microns. The carbon filter should always be located downstream because the deposition of solids would plug the carbon filter and prevent its regeneration.

The latest filtration system uses a special design of glass fiber medium which simultaneously separates the sulphur in conjunction with liquid aerosols. Depending on the quantity of entrained liquid, it may be necessary to spray in additional water upstream of the inlet nozzle of the filter to irrigate it. Owing to the hazardous (lethal, in fact) nature of the sour gas, it is advisable to have the ability to steam or nitrogen-purge the water injection system before servicing. This filter thus simultaneously water-washes the gas while collecting sub-micron elemental sulphur particles. These impinge on the filter medium and coalesce into progressively larger droplets until they become sufficiently massive to drain through the glass fibers. To prevent plugging of the glass fibers, a pleated paper pre-filter could be used.

**Once-through sulphur solvent injection**

DADs (diaryl disulphides) and DMDS (dimethyl disulphide) are well known as once-through sulphur solvents that could be injected into the well or into surface equipment (upstream or downstream of the choke valve) to absorb elemental sulphur. The rich fluid, which contains elemental sulphur, is collected in the gas plant separation equipment along with production water and disposed of with no regeneration. Carbon disulphide (CS₂) is another extremely effective sulphur solvent that has been used for gas well injection. It is not currently used because of its high toxicity and extreme odor.

**Sulphur scrubbing by using regenerable solvents**
Elemental sulphur can be removed using a regenerable mixed solvent known as absorption oil to control sulphur deposition in sour gas wells. This solvent is based on a mixture of alkyl naphthalenes diluted in a mineral oil; both can physically combine with the precipitated sulphur. With an oil-soluble inhibitor having proper phase behavior, it can effectively control corrosion in sour gas wells with high reservoir water production.

For application in sour gas wells a solvent should satisfy the following important characteristics:

- No corrosion with the well fluid
- Sufficient sulphur solubility
- No irreversible reactions with precipitated sulphur
- Stability under operating conditions
- Low vapor pressure
- Corrosion prevention
- Ability to separate from water
- Suitable uniform quality
- Suitable viscosity
- Ability to be regenerated and recirculated
- Simple recovery of the absorbent sulphur

The liquid is injected at the wellheads and travels by gravity through the annulus. The solvent mixes with the gas and formation water and returns to the surface with the well fluid. The annulus cross-section narrows around the couplings of the tubing connectors. At high injection rates, the annulus becomes partially filled up, forming a liquid column and creating slugs that travel through the tubing.

The produced liquid phases are separated at the surface by three 3-stage systems consisting of a free-water knockout drum, a separator and the scrubber of the glycol dehydrator. The formation-water/solvent mixture is collected in tanks at each well site.

Cooling shifts the solubility of sulphur in the gas to lower values. Depending on the particular degree of supersaturation of the gas, sulphur precipitation could take place in the cooler. To prevent plugging of the cooler tubes, a small volume of solvent is injected downstream of the free-water knockout drum; the sulphur loading capacity is about 30 g/L.

Elemental sulphur deposition can occur throughout sour gas gathering systems – formation, production tubing, pipeline and/or surface equipment. Based on extensive research by different sources, deposits can reasonably be quantified based on gas composition, temperature and pressure. In general, sour gases lean in hydrocarbons heavier than $C_{2+}$ tend to deposit elemental sulphur. Sour gases that are rich in heavier hydrocarbons and contain hydrocarbon liquid are much less likely to deposit sulphur. Both physical and chemical solvents can be employed, intermittently or continuously, to dissolve sulphur and prevent its deposition.

Physical solvents are generally hydrocarbons with high aromatic content – naphthalene, benzene, toluene and the xylenes, for example. Such solvents tend to be used in downhole and tubing wash applications, where
sulphur solubility is favored by the higher temperatures. A potential drawback in the case of lean sour gas streams, for example, is the tendency for relatively volatile aromatics to flash, thus reducing the volume of liquid solvent remaining to dissolve downhole sulphur. Another drawback is the tendency to re-precipitate solids at cooler downstream temperatures. Solvent requirements should thus be based on that required to dissolve the sulphur at, say, 20-25°C.

The quantities of simple physical solvents required are invariably greater than for chemical solvents, but field condensates may be a convenient source. Also, physical solvents are easier to handle and regenerate.

One family of chemical solvents utilizes the reaction of an aliphatic amine with the S₈ ring in the presence of H₂S to produce ionic polysulphides. The mechanism is thought to include intermediate formation of an ammonium bisulphide as follows: [2]

\[
\text{NRH}_2 + \text{H}_2\text{S} \rightarrow (\text{NRH}_3^+) (\text{HS}^-) + x\text{S}_8 \rightarrow (\text{NRH}_3^+) (\text{HS}_x^-)
\]

Polysulphides are polar and thus require additional polar solvents such as methanol or water to keep the sulphur uptake products in solution.

The other major, and generally preferred, class of chemical solvents are the organic disulphides (RSSR), where the R-group may be either an alkyl or aromatic residue. Predominant are dimethyl disulphide (DMDS) and mixtures of aromatic (diaryl) disulphides (DADS). A key advantage of the organic disulphides is their capacity – DMDS can dissolve 150% of its weight of sulphur at 20°C, and DADS can dissolve 25% of its weight. Despite the lower sulphur uptake capacity of DADS, it has the advantage of being less volatile and thus more easily recovered from the sour gas. DADS is also much less odorous than DMDS, though still objectionable.

Reactions of organic disulphides with sulphur are catalyzed by basic substances. Common catalysts are amines, which work only in the presence of H₂S. As in the case of amines as solvents, formation of the hydrosulphide anion, HS–, is necessary before sulphur uptake can occur. The overall chemistry can be summarized as follows. [3]

<table>
<thead>
<tr>
<th>Catalysis</th>
<th>H₂S + R¹R²NH → R¹R²NH₂⁺ + HS⁻</th>
</tr>
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<tbody>
<tr>
<td>Sulphur uptake</td>
<td>HS⁻ + RSSR → RS⁻ + RSSH</td>
</tr>
<tr>
<td></td>
<td>RS⁻ + S₈ → RSS₈⁻</td>
</tr>
<tr>
<td></td>
<td>RSS₈⁻ + RSSR → RSS₈SR + RS⁻</td>
</tr>
<tr>
<td>Overall</td>
<td>RSSR + xS₈ → RSS₈SR</td>
</tr>
</tbody>
</table>
At least two commercial sulphur solvent systems have been designed to provide the hydrosulphide anion directly in the absence of process $\text{H}_2\text{S}$.

Corrosion has proved to be a problem. To our knowledge, the mechanism is still not fully understood, and filming corrosion inhibitors are only marginally effective. The following are the methods in practice.

1. DADS and DMDS are not corrosive unless sour gas and water are present. The degree of corrosion increases with increasing $\text{H}_2\text{S}$ concentration and when sodium chloride is dissolved in the water.

2. $\text{CS}_2$ is another chemical solvent that could be used to establish a reaction with the elemental sulphur in the well. This solvent is not currently used because of its toxicity and high odor.

3. A mixture of alkyl naphthalenes diluted in a mineral oil is a regenerable solvent

The observations are:

4. The rate of corrosion increases considerably with increasing temperature and when elemental sulphur is dissolved in the disulphide solvent.

5. No corrosion occurs unless the steel surface is in direct contact with a liquid phase of water and organic disulphides.

Since corrosion is highly temperature-dependent, it is recommended that disulphides be injected into the wellstring only at a depth where sulphur deposition is predicted, and never at temperatures above 115°C, when sulphur is molten. When application is batchwise, solvent residence in the wellstring should be minimized.

Spent solvent is typically sent to disposal sites equipped to handle such chemical waste or is incinerated, the combustion products optionally being recycled to the SRU. Where solvent quantities are large, reclamation is possible, but to what extent the practice has been com-mercialized is unclear.

**Slug catchers**

If the elemental sulphur content in the feed gas is very high, slug catchers are highly recommended for removing the elemental sulphur. Slug catchers should be designed with enough capacity to remove all the particles.

**Gravity-based scrubber**

The elemental sulphur could be removed by using a gravity-based scrubber with a separation flash drum or settling storage tank that should be sized with sufficient residence time.

A typical diagram to study the potential for sulphur deposition in future planned offshore sour gas wells at about 8,000 psig and identify feasible processing options for mitigation of potential sulphur deposition and plugging. The produced gas from each wellhead platform is piped sub-sea to its respective tie-in platform,
combined and piped sub-sea to the onshore gas plant. Monoethylene glycol (MEG) is circulated continuously between the onshore gas plant glycol regenerator and tie-in platforms for hydrate prevention.

![Fig. 1: Simplified block flow diagram of offshore gas production, landing and treatment facilities](image)

Several options are available for the mitigation of sulphur plugging in natural gas wells. They are as follows:

- Manage or reduce pressure or temperature drops; try to manage sulphur deposition via production history of the formation
- Mechanical removal, pressure jetting
- Thermal removal
- Sulphur inhibitors / modifiers. No known commercially available crystal modifiers
- Sulphur dispersants. Work well in plant environments (controlled process with no other fluid mixing). Do not work well in well bore applications
- Sulphur solvents
The main treatment option for gas well sulphur plugging problem is solvent-based. Regenerable solvent techniques are available, but few companies seem to use them. They are not normally considered for offshore applications because they tend to be expensive and involve additional solvent separation and control equipment at the wellhead platform for sending the solvent ashore. (Space is too restricted on offshore platforms to allow onboard regeneration.) Further, they would require onshore regeneration equipment such as solvent surge vessels, sulphur crystallization and filtration equipment, pumps and subsea lines from and to the wellhead platform. This is similar to the MEG regeneration system.

The most common type of treatment uses a once-through application where the chemical is recovered with the well liquids but not re-used. The main chemical solvents are:

- DMDS (dimethyl disulphide) / DSO (disulphide oil) catalysed with a base, usually primary and/or secondary amines
- Naphthalene (ICTC Sulpha-Max with C.I.)
- Amine based with methanol (Baker Hughes)
- Alkyl naphthalene (aromatic hydrocarbons).

**Likely location of sulphur deposition**

For this particular client, downhole well samples were taken and the elemental sulphur content determined at downhole conditions. From the gas composition and from data accrued by a well-known research organization, a sulphur solubility phase diagram was constructed with pressure on the y-axis and temperature on the x-axis. On the solubility curves an operating line was constructed showing temperatures and pressures at various points in the well (bottom hole, well head, down-stream of chokes, at the tie-in platform, at onshore landing, and at the inlet to the onshore gas plant). As the pressure drops through the various pieces of the gas producing equipment, the temperature falls, decreasing the solubility of elemental sulphur in the gas and increasing its chance of coming out of solution from the gas and depositing. Where the operating line crosses one of the sulphur saturation curves, which corresponds to the value of the sulphur content of the well as analyzed, is the point where sulphur is likely to start coming out of gas solution and deposit. In this case it was estimated that the sulphur would begin to deposit in the wellhead choke valve. That being the case, it was decided the chosen solvent would be injected upstream of the well head choke valve.

*Figure 2 is a generic example of a sulphur solubility phase diagram for a hypothetical well.*
As stated previously, space is usually at a premium on offshore platforms; therefore an efficient sulphur solvent requiring the smallest amount of solvent was chosen to be injected on a continuous basis. The sulphur solvents considered are shown in Table 1.

As can be seen the most efficient solvent is DMDS / DSO (disulphide oil). This keeps the solvent requirement to a minimum and consequently the solvent injection equipment size to a minimum.

A source of DSO, from a nearby refinery, was discovered which may be able to be used instead of ICTC's DMDS. The DSO will be of varying quality and of varying sulphur content from the refinery so that it requires careful analysis to check if it is usable.
Equipment required

Each wellhead requires the following equipment for sulphur solvent injection:

- Inert gas-blanketed storage vessel
- High-pressure metering injection pumps
- High-pressure injection piping
- Injection quills.

Open issues

One issue that requires more analysis with the MEG vendors is whether the DMDS / DSO solvent needs to be separated off before commingling with the MEG or whether it can be separated at the MEG regeneration still.

Mercury

The oil and gas industry first became generally aware of the presence of mercury in the early 1970s with the advent of cryogenic processes utilizing aluminium-core heat exchangers, or “cold boxes,” which often failed owing to embrittlement by elemental mercury. Mercury contamination of natural gas has since become recognized as common, having been detected over a wide range of concentrations from the minimum detectable level of 0.01 µg/Nm³ to 5000 µg/Nm³ worldwide. By comparison, the OSHA mercury limit in air is 50 µg/Nm³ [4]. Virtually all mercury is in the elemental form.

Removal to <0.01 µg/Nm³, nominally corresponding to <1 part-per-trillion by volume, is considered necessary to avoid cold box aluminium corrosion. The suspected mechanism of mercury corrosion is multi-step, and it is insidious in its progressive nature. Following combination of aluminium with liquid elemental mercury, any trace O₂ present results in degradation of the amalgam to an aluminium oxide while freeing the mercury to attack the next layer of sound metal. Mercury is thus not permanently bound with the aluminium, but in effect acts as a catalyst for continued embrittlement – hence the need for essentially complete removal. [5]

Mercury does not typically form amalgams with steel and its alloys, and progressive corrosion is thus not the concern that it is with aluminium. However, mercury vapor nonetheless becomes adsorbed onto ferrous surfaces with a tendency to penetrate cracks and corrosion layers, thus requiring safety and environmental precautions when performing hot work (cutting, grinding, welding) on mercury impregnated steel. Also, special mercury stripping techniques may be required before recycling scrap steel [6].
Mercury removal from natural gas is perhaps most commonly achieved with activated carbon impregnated with sulphur to form non-toxic mercury sulphide (HgS). HgS is stable up to 450°C (840°F), and will not elute from the carbon bed under fluctuating conditions. The carbon is non-regenerable in situ, but a properly designed bed will reportedly last for many years. Owing to carbon’s affinity for water and heavy hydrocarbons, location is invariably downstream of dehydration and dew point control.

Johnson Matthey promotes their mixed-oxide Puraspec H₂S scavenging media as an alternative to carbon, preferably upstream of acid gas removal such that H₂S adsorbed from the raw natural gas reacts quantitatively with the mercury. This minimizes equipment contamination and avoids contamination of ancillary process streams such as acid gas, condensate and molecular sieve regeneration gas [6].

UOP’s regenerative HgSIV can simultaneously dehydrate and remove mercury. The product is made by coating the outside rim of an appropriate molecular sieve particle with elemental silver to a nominal depth of 1 mm, such that the silver occupies the outside but no more than 35% of the total particle. Mercury is captured by formation of the silver amalgam while water is adsorbed within the interior. Both are periodically regenerated with hot sales gas according to conventional dehydration practice.

The HgSIV adsorbent can be employed as a stand-alone unit, or in combination with an upstream bulk, non-regenerative mercury-removal bed such as sulphur-impregnated carbon. In the stand-alone case, mercury and water are condensed from the regeneration gas, with subsequent recovery of saleable liquid mercury.

When an acid gas removal plant is upstream, it may be desirable to precede it with non-regenerative bulk mercury removal. In this case, the downstream HgSIV bed is a polishing step and its regeneration gas is recycled to a point upstream of the bulk separation after condensation of water only. This reduces the size of both the bulk and HgSIV beds and permits maximum loading of the bulk bed without concern for minor breakthrough [4].

Heavy Hydrocarbon Removal

During phasing-in of new wells, feed gas is enriched with heavy hydrocarbons and oil. Hydro-carbon liquids are known to cause foaming in amine systems. It has been found that hydrocarbon liquid may reside in the piping; however, the liquid flow regime must be evaluated.

The first option is to drain these hydrocarbons from pipelines, for example by installing dip legs at different locations such as at the end of header, and between the final two branches.

Carbon filtration can be used upstream of the amine unit to further remove hydrocarbon molecules and other chemical contaminants which promote amine foaming.

Selective solvents have a capability of removing trace sulphur compounds, but hydrocarbon losses with the acid gas are high.

Hydrocarbons have a higher solubility in physical solvent than in water; therefore, a higher physical solvent concentration is likely to result in an increase in hydrocarbon content in the acid gas. There are other options that could be used for hydrocarbon removal, such as:

- Using physical solvent for gas treating if applicable.
• Draining the heavy hydrocarbons from pipelines upstream of the gas plant.
• Providing a water wash scrubber (with a separation flash drum with sufficient residence time, the dissolved hydrocarbon can gravity-separate from the bulk solution) and using baffles and weirs.
• Providing a gas carbon filter upstream of multi-cyclone separator and coalescing filter.
• Providing skimming facilities such as skimming pots for flash drums with sufficient residence time.
• Using a molecular sieve bed downstream of the gas treating (molecular sieves could be designed with multi-beds for the dehydration, aromatic removal, and Hg removal, etc. in one package).
• Adding one or two fractionation columns within gas treating for the removal of the remaining hydrocarbons, and to recover the C2-C4 and blend it back to the treated gas to maintain the required heating value.
• If the amine-based solvent is applicable, some hydrocarbon removal could be achieved by minimizing the lean amine, running stripper at a lower pressure, and using low circulation rate.

If the sulphur recovery unit is located downstream of the gas plant, the heavy hydrocarbons and BTEX could be destroyed by designing a suitable burner to achieve 2,200°F (1,200°C) minimum. If the acid gas feeding to the sulphur recovery unit has the low percent of H₂S (lean gas), oxygen enrichment is recommended.

If the gas has retrograde properties close to its hydrocarbon dewpoints, it is of particular importance to minimize pressure losses. Drums could be equipped with proper hydrocarbon condensate withdrawal, such as skimming pots.

**BTEX emissions**

An amine unit operates by contacting an amine solution with the sour gas or liquid feed counter-currently in an absorber column. H₂S and CO₂ in the feed are absorbed by the amine in the solution, and the sweetened gas exits the top of the column. Rich amine exits the bottom of the column and is sent through the regeneration system to remove the acid gases and dissolved hydrocarbons, including BTEX. The lean solution is then circulated to the top of the absorber to continue the cycle. The sweetened gas exiting the absorber is saturated by water from its contact with the amine. The overheads, including BTEX from the amine regenerator column, are sent to a sulphur recovery unit.

Aromatic hydrocarbons, including benzene, toluene, ethylbenzene, and xylene (collectively known as BTEX), are considered as hazardous factors in air pollutants.

If the raw gas contains appreciable amounts of H₂S, a sulphur plant is used to treat the overheads from the rich amine stripper. This treatment normally destroys any BTEX or other hydrocarbons.

Several operating parameters directly affect the amount of BTEX absorbed in an amine unit, such as inlet BTEX composition, contactor operating pressure, amine circulation rate, solvent type, and lean solvent temperature. MDEA absorbs the lowest amount of BTEX compared to DEA and MEA; therefore, it is recommended to use MDEA where BTEX is observed in the sour gas (if it is applicable).

Several operating parameters directly affect the amount of BTEX absorbed in an amine unit. These factors include the inlet BTEX composition, contactor operating pressure, amine circulation rate, solvent type, and lean solvent temperature. Following is a list of strategies that should be followed to limit the BTEX emissions from gas plant:
• Minimize the lean amine temperature. The amount of BTEX emissions in amine systems decreases with an increase in lean solvent temperature.
• Use the best solvent for treating requirements. (e.g. MDEA absorbs the lowest amount of BTEX).
• Minimize the lean circulation rate. BTEX pick up increases almost linearly with an increase in circulation rate.
• If the stripper pressure is higher, the overall BTEX emissions are lower.

Integration with membranes

Membranes are now being used widely for the purification of natural gas containing high levels of CO₂. For instance, a membrane-based process has been developed for separating and recovering hydrocarbons, including propylene and ethylene, from nitrogen and light gases. Unfortunately, the membranes available presently lack selectivity, and it is not possible to precisely control the rate of diffusion of the various components present across the membrane. Therefore, it is rare for the stripped gas to meet the sales gas specification.

Integration with molecular sieves

Molecular sieves are used extensively to dry natural gas. In this role, they will also remove H₂S but because water is significantly more powerfully bonded than H₂S, they are not very effective for the combined H₂S/H₂O removal duty. But new technology is using molecular sieves in a multiple-bed configuration, each for a specific duty. This combination could be a dehydration bed, in addition to a removal bed for heavy hydrocarbon(s), mercury, or any other impurities that could be effectively selected for removal technology. These beds should be cost-effectively designed.

Some of the problems caused by heavy hydrocarbons and some atypical solutions are set out below:

Silica gel and molecular sieves have been used to remove gas-phase C6+ hydrocarbons. Heavy hydrocarbon liquids are typically recovered from the cooled regeneration gas and stabilized. [2] In particular, BASF/Engelhard Sorbead™ oil-drop (referring to the manufacturing process) silica gel has been applied for decades to remove water, heavy hydrocarbons and mercaptans from natural gas in “quick-cycle” units, whereby said contaminants are preferentially attracted by molecular-scale forces to the adsorbent surface. In general (with the exception of water), adsorption capacity is directly related to molecular weight and boiling point. [2]

If only molecular sieve dehydration of a sweet gas stream is required, a common means of avoiding the negative effects (e.g.; coking on regeneration) of gas-phase impurities such as BTEX is the use of small-pore zeolites (3A or 4A). [2]

When using traditional membranes for CO₂ removal, heavy components such as aromatics, BTEX and heavy aliphatic hydrocarbons will tend to be trapped at the inlet. If they accumulate to the point of condensation, the liquids are often solvents for the membrane material. Even if the membrane fails to dissolve, condensed heavy hydrocarbons will coat the membrane surface and thus prevent permeation. The simplest treatment may be to heat the gas above the highest expected dewpoint, but often upstream adsorption or refrigeration is
required to remove the heavy hydrocarbons. Non-regenerable adsorbent beds are often used for trace heavy hydrocarbons levels.\[11\]

Surface active compounds such as aromatics are notorious for causing foaming in amine, glycol and physical solvent systems, but activated carbon usually solves the problem. Because fresh carbon adsorbs O\(_2\), carbon vendors generally advise heat soaking in condensate at 160-180°F (70-82°C) for several hours to desorb O\(_2\) before commissioning, but more often than not this detail is overlooked or disregarded. Carbon is also a Claus catalyst, and for sour acid gas removal systems (despite lean side filtration) we believe that failure to desorb O\(_2\) prematurely fouls the carbon pores with elemental sulphur.

The same surfactants that are conducive to foaming can also promote stable emulsions. Figure 3 (overleaf) shows the impact of a suspected aromatic/DEA emulsion on a refinery SRU. Surprisingly, regenerator operation remained stable, but Claus air demand and tail gas volume increased by 30% with a five-fold increase in TGU total reduced sulphur (TRS) emissions (presumably COS/CS\(_2\)).

For adequate BTEX destruction in the SRU, a reaction furnace temperature of at least 1,100°C (~ 2,000°F) is generally advised, and preferably 1,200°C (~ 2,200°F).

In the late 1990s, Saudi Aramco was faced with major aromatics in the lean DGA acid gas to their large SRUs at the Uthmaniyah and Shedgum gas plants. The classic solution, O\(_2\) enrichment, was considered unpractical on such a large scale in a hot climate. After a comprehensive evaluation of all options, activated carbon adsorption of heavy HCs from the acid gas was selected. Raw acid gas is heated to 65°C (150°F), corresponding to 50% relative humidity. Gas flow is upward in the adsorption cycle so that downflow of low-pressure regeneration steam avoids internal refluxing of condensate and, hence, BTX.\[12\]

**Gas-Phase Sub-Micron FeS**

An obscure case history suggests that TEG is an effective scrubbing medium for very fine ferrous sulphide (FeS particles which, for whatever reason, may be entrained in a gas stream. Herrin cites a small gas plant plagued with a chronic abundance of suspended sub-micron FeS, which passed
Fig. 3: Effect of aromatic/DEA emulsion formation in the acid gas removal unit on Claus SRU performance

through everything except adsorbent beds. The FeS had apparently accumulated on the walls of a 12” x 90-mile low-velocity wet gas pipeline over a period of 25 years.

The FeS deposits remained stable until dehydration facilities were installed upstream. As the downstream deposits subsequently dried out they were gradually eroded by the gas. Attempts to filter the particles were futile. Inspiration struck in the course of a conversation with an operator at another gas plant who complained that his glycol filters were continually plugging. Investigation revealed an inordinate amount of FeS in the raw gas, but none downstream of the glycol contactor.
A trial was conducted whereby a slipstream of FeS-laden gas from the original problem unit was passed through two packed TEG bubble towers in series. The 1st-stage glycol quickly turned black, while the 2nd-stage glycol remained clear, even after prolonged operation, thus confirming quantitative removal of the FeS.

A permanent trayed tower with recirculating TEG subsequently installed on the total stream proved equally effective. While some solids could be filtered out of the circulating glycol, sub-micron FeS accumulated until the liquid batch had to be replaced due to high viscosity after 3-4 months. [13]

**SRU Cofiring – Lean Feed, BTEX**

As a rule-of-thumb:

- Below 50% H$_2$S, reaction furnace temperature will be below the 1,100-1,200°C (~ 2,000-2,200°F) necessary for BTEX destruction.
- Below 30% H$_2$S, reaction furnace temperature will be below the 1,800°F (980°C) necessary for stable combustion, even with split-flow.

With no other choice, operators invariably resort to co-firing natural gas, very often sooting up the boiler tubes and catalyst beds in the process. At the least, abundant quantities of CS$_2$ are produced, potentially increasing sulphur emissions even with the benefit of a tail gas unit.

Refineries often employ two-zone reaction furnaces in which ammonia (NH$_3$) acid gas from the sour water stripper, start-up natural gas and combustion air are routed to zone 1, and amine acid gas is split between zones 1 and 2 so as to maximize the zone 1 temperature for enhanced NH$_3$ destruction. In a gas plant, the same design permits staged co-firing of natural gas in zone 1, with the entire acid gas stream routed to zone 2 so that the natural gas is cleanly burned to completion with surplus air, which is adjusted in the normal manner to maintain tail gas H$_2$S/SO$_2$ = 2/1.

In some cases this affords a convenient outlet for non-sales-quality gas, since a constant fuel quality is not required in this mode. In a gas plant with multiple SRUs, it can also be a convenient means of maintaining spare units on hot standby. Rather than sub-stoichiometric combustion of natural gas, requiring close operator attention to maintain the air/gas ratio within a narrow range, the natural gas is combusted with nominal excess air while routing enough acid gas to zone 2 to consume residual O$_2$.

The potential downsides are a reduction in both the capacity and the recovery efficiency of the Claus unit and increase in fuel consumption in the incinerator. Long-term co-firing is obviously more difficult to justify where there is no home for the additional waste heat steam.

**SRU Co-Firing – Extreme Turn-Down**

Excessive turndown can be temporary – as during start-up, curtailment or process upset – or permanent, as when reserves are declining. We typically guarantee SRU turn-down to 20-25% of design. At progressively lower rates, ambient heat loss accounts for a greater share of the process heat, eventually leading to one or
more of the following limitations. Virtually infinite turn-down is possible with staged co-firing, as previously described, to increase unit mass flow as well as furnace temperatures.

**Low reaction furnace temperature**

H₂S flame stability is strictly a function of furnace temperature. While operation at temperatures as low as 1,400°F (760°C) is feasible, the range 1,600-1,800°F (870-980°C) is more commonly considered the safe minimum (neglecting NH₃ destruction).

**Low converter temperature**

If converter temperatures are not maintained above the dewpoint, catalyst activity will eventually be lost as liquid sulphur fills the catalyst pores. Units employing, for example, auxiliary burners or hot oil for reheat can compensate with higher converter inlet temperatures, but HP steam reheaters most commonly employed in modern Claus plants have a limited temperature margin.

**Sulphur fog**

Sulphur fog consists of aerosol droplets so small that they behave like a gas and are not coalesced by demisters. Fogging tends to occur at low process rates because higher heat transfer flux rates cause supersaturation of the gas and condensation occurs by the formation of small droplets within the bulk stream rather than coalescence at the tube wall. Claus recovery efficiency suffers, but a hydrogenation tail gas unit (TGU), if existing, will compensate. However, upstream process gas dew points are also increased, thus increasing the likelihood of sulphur condensation on the catalyst.

**Low sulphur condenser temperature**

Below 10% of design, the last manifestation of excessive relative heat loss is plugging of the condenser tubes with solid sulphur. One solution is to sparge MP steam into the bottom of the condenser shell sides. Another is to drain the water and turn it into a LP steam condenser, although this may be ill-advised in situations where the process duty can abruptly increase.

Occasionally a new SRU will be installed at a gas field, for example, for which production is predicted to decline in the not-too-distant future. One consideration is to design the unit for initial O₂ enrichment – thus not only reducing capex but improving future turndown on air only. At most, 100% O₂ essentially doubles the capacity of a unit designed for air. [13]
Effect of NH₃ and Ammonia Build-Up In Amine Regenerator Reflux

When small amounts of ammonia are present in the sour gas, nearly all of it should be scrubbed from the sour gas by the amine solution. On account of the high solubility of ammonia in water, the ammonia may build up in the circulating rich amine solution and present several problems in the absorber and stripper. Some of the operational problems with ammonia are meeting the project specification; flooding in the stripper; and inability to hold the pressure control set points on the condenser or reboiler. Calculating the equilibrium vaporization ratio as a K value which is defined as a mole fraction of any components in the vapor phase to a mole fraction of any components in the liquid phase to determine the ammonia build up in the tower.

These problems all have the same root cause. Ammonia is absorbed at the pressure and temperature in the absorber, rich amine loaded with ammonia is fed to the stripper, and the K value for ammonia in the condenser is considerably less than one. Therefore, most of the ammonia is vaporized in the stripper and is returned in the reflux. This process continues to build up until steady-state ammonia either overcomes the low K value in the condenser or forces its way to the reboiler against the high K value in the tower.

By virtue of its high solubility in water, any ammonia in the raw gas will be absorbed by the amine solution. Dissolved ammonia will be readily stripped in the regenerator, only to be re-absorbed in the reflux, along with nominally equimolar amounts of H₂S/CO₂.

At around 2½ wt-%, ammonia typically starts to break through with the acid gas, and crystalline ammonium bicarbonate / bisulphide will deposit on any surface at a temperature below ~160°F (~70°C). Plugged instrument taps are usually the first sign, eventually followed by increased pressure drop. Under-deposit corrosion also results from capillary condensation of moisture saturated with NH₃, H₂S and CO₂. Fortunately, these deposits are readily decomposed at > 160°F, or dissolved with water.

As reflux ammonia ultimately approaches saturation levels of several wt-%, proportionate concentrations of H₂S/CO₂ become quite corrosive to carbon steel, and the higher reflux pH increases the tendency to emulsify surfactants conducive to foaming. Appearance is a useful indicator, progressively going from water-white to hazy to milky with increased emulsification. More dramatic, however, is the surprising extent to which reboiler duty is increased, often to the point where stripping efficiency is impaired.

Refiners expect ammonia to be present, and they routinely purge the regenerator reflux to limit NH₃ to 1 wt-% or thereabouts. While many measure actual NH₃, the procedure is laborious and it is instead sufficient to infer nominal NH₃ by simple M alkalinity determination (titration with acid to a methyl orange, or 4.5 pH, end point). In high-H₂S systems with an overhead condenser (as opposed to a pump-around system), H₂S determination by iodine-thiosulphate back-titration also suffices. Once signs of a regenerator problem appear, however, purging reflux is the first thing to try.

In our experience, regenerator troubleshooting efforts in the gas patch often fail to consider the build-up of ammonia, forgetting that ammonia is a likely product of thermal amine degradation in the reboiler. Furthermore, such degradation is invariably accelerated by the higher tube skin temperatures that are an inevitable consequence of the increased heat duty, particularly in the case of fired reboilers.
**COS /CS₂ Removal**

Some of the chemical and physical solvents are capable of removing COS/CS₂ at some level; however, the solvent may not be able to meet the product specification. In that case, using another conditioning process is feasible. The molecular sieve process could be used for COS/CS₂. An alternative is the amine reclaimer system. Reclaimer operation is a semi-continuous batch operation for removing both degradation products and suspended solids and impurities in the solution. The reclaimer operates on a side stream of 1-3% of the total solvent circulation rate. If a physical solvent is being used for the acid gas removal, COS/CS₂ levels could be improved by increasing the fresh solvent circulation rate, since the semi-solvent is already saturated, and providing an additional chiller system would increase the absorption process.

Any gas processed in the treatment plant, including natural gas and refinery off-gas, are contaminated with mercaptan and COS.

Several operating parameters directly affect the amount of COS absorbed in a gas treating unit, such as inlet COS composition, contactor operating pressure, solvent circulation rate, solvent type, and lean solvent temperature. The chosen solvent should be capable of absorbing COS in the absorption process and releasing it into the acid gas in the regenerator. The acid gas from the regenerator is sent to the sulphur recovery unit to decompose any sulphur compounds, including COS.

Pure physical solvents are particularly effective in high-pressure sour gas treatment systems for removing H₂S, CO₂, COS, organic sulphur species, and a wide range of other gas stream contaminants. Usually, physical solvent systems have two absorbers, one of them for removing mainly H₂S with semi-lean solvent and the other removing CO₂ and COS with lean, pure solvents. If more absorption of COS is required, additional COS-free, lean solvent should be fed to the H₂S absorber, or else it is necessary to cool semi-lean physical solvent before it is fed to the H₂S absorber.

The purpose of the amine reclaiming units is to distil the water and amine from the fouled solution, leaving behind the entrained solids, dissolved salts, and degradation products that cause foaming and corrosion problems.

The reclaimer is an integral part of a successful amine sweetening process. It normally operates on a side stream of the lean amine solution leaving the bottom of the stripper column. The temperature of the reclaimer is to be controlled through the cycle. The presence of COS, CS₂, FeS, free oxygen and other contaminants can poison the amine. In such cases, a reclaimer is often used to regenerate the degraded amine. Amine degradation depends on different factors. All of the feed to the reclaimer is assumed to go overhead except the degraded amine. A flash calculation would be essentially impossible since the composition and properties of the degraded amine vary widely and are never accurately determined. The reclaimer has only one inlet stream that comes from the reboiler, and two outlet streams (the reclaimer overhead and the reclaimer dump). The reclaimer operating temperature is in the range 300-350°F (150-175°C) and, usually, 1-5% of the lean amine would be fed to the reclaimer.
Conclusions

The key features affecting the selection of the acid gas processes are discussed. This paper also demonstrates the application of the most common technologies that are well known in the industry. In order to select the proper acid gas removal, the entire key parameters step-by-step should be considered. The selection criteria for gas preconditioning and the final steps of gas conditioning processes to meet the environmental regulations have been emphasized. Various contaminants and the removal process are discussed. Depending on the process route selected, all the criteria would be satisfied.

Many treating processes are available, and not one of them is ideal for all applications. The initial selection of a particular process may be based on feed parameters such as composition, pressure, temperature, and the nature of the impurities, as well as product specifications. The second selection of a particular process may be based on acid/sour gas percent in the feed whether all CO$_2$, all H$_2$S, or mixed and in what proportion; if CO$_2$ is significant; whether a selective process is preferred for the SRU/TGU feed; and by how much amine unit regeneration duty will be reduced. The final selection could be based on the content of C$_3$+ in the feed gas and the size of the unit (in a small unit the advantage of special solvents is reduced and conventional amine may be favored).

The final selection is ultimately based on process economics, reliability, versatility, and environmental constraints. Clearly, the selection procedure is not a trivial matter and any tool that provides a reliable mechanism for process design is highly desirable.

The variety of the acid gas sources that have different gas compositions, pressure, temperature, and nature of impurities and might require different means of gas processing to meet the product specification.

References


