THE IMPACTS OF TRACE COMPONENTS ON THE DESIGN AND OPERATION OF GAS TREATING AND PROCESSING PLANTS

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ABSTRACT

Our industry commonly expends a great deal of energy on determining the concentrations and how to remove CO₂ and H₂S from sour natural gas in the design of a gas treating and processing facility. Their presence normally drives the size and cost of much of the facility. However, troublesome trace contaminants such as
- mercury (Hg),
- carbonyl sulfide (COS),
- mercaptans (RSH),
- and aromatics (BTEX) and other high molecular weight hydrocarbons (HHC)

can strongly influence the design and successful operation of the various gas and recovered liquids treating systems – and ultimately the capital and operating costs of such facilities.

The fate of each of these components within a natural gas treating and processing facility will be discussed, along with a review of the design considerations for the following gas and liquids treating systems given a sample feed gas composition:
- Primary Gas Treating Unit (GTU) and Dehydration (DEHY),
- Acid Gas Enrichment (AGE) - optional
- Claus Sulfur Recovery Unit (SRU), including Tail Gas Cleanup Unit (TGCU) and Thermal Oxidizer
- Natural Gas Liquids Product Treating
Sour, Hydrocarbon-Rich Gas Processing Challenges

Many major producing oil and gas reserves throughout the world are characterized by gas that is fortunately rich with hydrocarbons and deserves processing for recovery of sales gas and natural gas liquid (NGL) products. The sales gas may be further processed to make LNG or provide feed to Gas-to-Liquids (GTL) and other gas monetization facilities. Unfortunately, many of these same producing reserves often contain up to a few percent each of \( \text{H}_2\text{S} \) and \( \text{CO}_2 \), and trace amounts of other components that complicate the gas conditioning and processing requirements. To commercially develop these reserves has involved some “lessons learned” and technology developments, particularly in handling the troublesome trace components such as mercury (Hg), carbonyl sulfide (COS), mercaptans (RSH), and aromatic hydrocarbons (BTEX). These trace components can strongly influence the design and successful operation of the various gas and recovered liquids treating systems, and ultimately the capital and operating costs of such facilities.

For further discussion in this article, a feed gas composition as shown in Table 1 has been assumed, which represents many sour, heavy hydrocarbon-rich gas reserves.

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{S} )</td>
<td>0.5 – 3% volume</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>3 to 15% volume</td>
</tr>
<tr>
<td>COS</td>
<td>100 ppm volume</td>
</tr>
<tr>
<td>RSH</td>
<td>300 ppm volume</td>
</tr>
<tr>
<td>BTEX</td>
<td>500 ppm volume</td>
</tr>
<tr>
<td>Mercury</td>
<td>100 µg/Nm³</td>
</tr>
</tbody>
</table>

Some primary challenges treating such gases are summarized below.

- \( \text{H}_2\text{S}-\text{CO}_2 \) ratio can be much less than 1:1 complicating and adding cost to the sulfur recovery process.
- At the above high concentration level, COS removal in the primary gas treating and dehydration systems is difficult and generally incomplete. The molecular sieve dehydration system may even produce additional COS. The cryogenic NGL recovery does remove most of the COS from the gas, but it then fractionates principally into the propane product and requires a more substantial product treating step.
- Mercaptans are also difficult to remove in the primary gas treating system. They too can be substantially removed into the mixed NGL product and in turn require a dedicated
product treating step for both the propane and butane products, and likely also the C5+ product(s). Alternatively, RSH can be removed using special molecular sieve material in the Dehydration System, but this adds considerable equipment, complexity, and capital and O&M costs.

- BTEX are unfortunately partially absorbed into most gas treating solvents in sufficient amount to contaminate the acid gas feed to the SRU. They can lead to short SRU catalyst life and poor sulfur recovery.
- Mercury, though present in very low concentration in natural gas (say 0.02 to 400 \( \mu g/Nm^3 \)), can accumulate inside equipment and concentrate in various internal process, effluent and product streams. This can lead to equipment failure, poison downstream processing catalysts and present health issues.

**Typical Gas Conditioning and Processing Configuration**

There are different variations on the gas conditioning and processing requirements depending on the ultimate products market and end use for the sales gas. Reference Figure 1 as a block flow diagram that depicts the basic processing steps and reflects many, but not all, of the options available. System depicted in black boxes are generally required, while systems shown in light gray boxes may not always be required or exist, depending on the level of contaminants in feed, the products desired, the product specifications, and the technology employed. For purposes of this paper it is assumed that in all cases ethane, propane, butane (separate normal and iso-butane products), and C5+ liquid products are produced from the gas processing steps, and that mercury removal is included to protect downstream aluminum equipment. Aspects of the diagram will be discussed individually in the sections below.

Numerous previous papers have considered some of the details with the various process systems (see references). Therefore, this paper will not go into such detail to explain the fundamentals of each. Instead, an overview will be provided to give some guidance as to the experience of the industry in dealing with various feed gas contaminants and their fate within a gas conditioning and processing facility.
Gas Conditioning

Plant Feed Stream Conditioning

Most gas conditioning and processing facilities will include an Inlet Gas Conditioning System upstream of the flow sheet as depicted in Figure 1. The Inlet System will typically remove free water and free hydrocarbon liquids. The water may be stripped of sulfur and other contaminants before re-injection or further processing for disposal.

The free hydrocarbon liquids are generally stabilized to recover a low vapor pressure C₅+ product. This product will also contain some amount of H₂S, COS and mercaptans so it requires treatment to obtain a saleable product. The rejected light ends from the stabilization system contain the stripped H₂S and some of the other sulfur compounds. The sour overhead stream is generally recompressed for further processing in the GTU. The COS remaining in the stabilized C₅+ product is likely within acceptable limits, while the RSH must be converted to disulfide oils (DSO) to render that product ‘sweet’. If necessary, the DSO can be removed as a byproduct. If
there are no market opportunities for the DSO stream, it must be processed separately or within the SRU/TGCU systems to recover the sulfur content.

**Mercury Removal**

Mercury occurs in produced natural gas streams in elemental (metallic), organic and inorganic form. The levels of mercury compounds are typically very low ranging from nominally 0 to 400 µg/Nm³ (about 0 – 40 ppbv). However, the required removal levels can be as low as 0.01 µg/Nm³ (about 0.001 ppbv), posing both processing and considerable analytical challenges. The design is further complicated by the fact that mercury levels are known to vary from one part of a formation to another, and may even vary from day to day with different well production patterns. Mercury also has a tendency to bond to surfaces it contacts such as piping and equipment, making it possible to be undetectable for a long period of time until it finally breaks through and is seen in the feed gas to a plant. In order to process a gas similar to the example feed gas stream and market the products, these mercury compounds must be removed.

In gas processing systems, mercury can accumulate and may form an amalgam with the aluminum used to manufacture plate fin heat exchangers (brazed aluminum construction, or BAHX) and other equipment that utilize aluminum components in cryogenic systems. Further, aluminum alloys are susceptible to Liquid Metal Embrittlement (LME), and the most common metal to cause embrittlement is mercury. LME can lead to structural failure. A number of mercury-caused BAHX failures have been validated and reported. Furthermore, mercury may act as a poison to catalysts in downstream facilities that process gas plant products.

Mercury also presents a health hazard when vented to atmosphere (e.g., in glycol or amine regenerator vents), and where liquid mercury may accumulate and expose workers. In its inorganic form, mercury dissolved in aqueous streams may be a health hazard when discharged through a waste water stream. Mercury in production sludge presents a disposal problem.

The Standards of Brazed Aluminum Plate-Fin Exchanger Manufacturer’s Association (ALPEMA) recommends a maximum acceptable mercury content of 0.1 µg/Nm³. However, where mercury removal is required, the removal technologies can generally achieve nearly complete removal, 0.01 µg/Nm³ or lower. This is also a generally accepted minimum concentration that can be measured by available analytical techniques. Therefore, 0.01 µg/Nm³ is the general specification stated for gas treating and processing applications and should provide extended life regarding mercury effects.

A mercury removal system is not shown in Figure 1 because the location and technology used are diverse. The mercury removal options available to the gas processor are based on three broad categories that can be applied to both gas streams and liquid products:

1. sulfur impregnated activated carbon,
2. metal oxides/sulfides dispersed onto a solid carrier, and
3. molecular sieve technology.

The activated carbon and metal oxide/sulfide technologies can both achieve <0.01 µg/Nm³, but cannot be regenerated in situ. Therefore, the adsorbent must be periodically replaced when it approaches its maximum loading of mercury. Activated carbon must be sent to a landfill or routed to an incinerator followed by mercury condensation from the flue gas. The metal sulfides can be sent to landfill, but also have the option of being recycled to vendors for metal smelting and recovery.
Molecular sieve systems can achieve <<0.01 µg/Nm^3 and are usually applied in combination with water removal (dehydration). This molecular sieve is regenerable with hot gases which drive the mercury (and water) off of the sieve and into the regeneration gas stream. At the end of the sieve’s life cycle, it can be disposed of as non-hazardous waste. The regeneration gas stream, say about 10% of the feed gas volume or less, may then be treated for mercury removal using one of the adsorbent technologies. One facility has reported success routing the mercury-laden regeneration gas without treatment to their sales stream, while staying within their sales gas specifications, and still protecting their cryogenic equipment. This latter option is likely the lowest cost and simplest of all options if done in combination with dehydration, and if the sales gas specifications on water and mercury will allow such re-blending.

The optimal mercury removal solution is one that is:

- The least affected by process conditions
- Situated in the process to protect as much of the equipment as possible from mercury contamination
- Minimizes the potential for mercury release to the environment
- Capable of meeting the specified mercury removal performance
- Installed in a system designed to minimize the handling frequency by operating personnel
- Supported by a supplier that can assist in disposal of the spent product
- The most economical over the plant life

If the inlet feed gas mercury content is low and the front-end gas processing systems do not require it, removal from the primary gas stream might be avoided. Where removal is required, AECOM (formerly URS) and others in the industry have conducted recent studies to understand where mercury removal should optimally take place in the overall gas processing scheme. For gas streams, removal can take place upstream or downstream of gas treating and dehydration units (using activated carbon and metal oxides/sulfides) or within the dehydration unit (using silver-impregnated and regenerable molecular sieve).

The results of reported studies for treating gas streams reflect that all of the fixed bed processes are very competitive, each with their own pros and cons, and the economic and optimal processing choice is dependent on the specific plant processing scheme and inlet mercury concentration. When dehydration of the gas is also required, and the regeneration gas can be re-blended with sales as discussed above, the regenerable molecular sieve technology likely offers the lowest absolute removal levels and lowest cost since additional equipment is not required and only a small amount of special adsorbent must be added. Where mercury content is higher and the regeneration gas cannot be re-blended with sales gas, and where mercury condensation may be expected in the regeneration gas cycle, other more common process configurations should be chosen.

The most common process configuration in previous years was to use sulfur impregnated carbon beds or metal oxide/sulfide beds to remove mercury from the treated and dried process gas stream prior to the NGL Recovery Unit. This was considered to be the simplest, and safest location in some aspects, as they generally handled a sweet and dry gas stream.
Most mercury removal vendors will quote designs with at least 3 to 5 year life for the adsorbent, perhaps up to 10 years for the metal oxide/sulfide option. Industry experience verifies these durations for clean, well operated systems. However, installations where entrained liquids are present can significantly reduce the adsorbent life.

Though specific plants’ design criteria and requirements have led to the selection of all of the above-mentioned process options for mercury removal, AECOM recommends consideration of locating the mercury removal system upstream of the Gas Treating Unit (GTU) and utilizing the metal oxide/sulfide adsorbent for the example gas composition. This solution may best satisfy the requirements listed above, is favorably received by clients, and offers the following significant benefits:

- The sorbent used for this application is not susceptible to damage from liquid hydrocarbons. Therefore it is tolerant to the wet, sour AGRU feed gas.
- Equipment in the acid gas removal, sulfur recovery, molecular sieve dehydration and other downstream systems will not be exposed to mercury contamination. As important, possible exposure of operating and maintenance personnel to mercury will be considerably reduced.
- Extraction upstream of the AGRU eliminates the chance that any mercury in the gas will enter the environment via the sulfur recovery or dehydration units’ effluent streams.
- The significantly higher concentration of mercury in a molecular sieve regeneration gas may cause the formation of liquid mercury. Subsequent release into the environment may occur with the condensed dehydration regeneration system water. Alternatively the liquid mercury would need to be periodically withdrawn and disposed. This would add to cost and increase the potential of exposing operating personnel to mercury.
- An expected bed life of up to 10-years significantly reduces personnel exposure to handling of the spent sorbent. Vendors offer a service to collect and reclaim the spent material.
- The long bed life provides an advantage over the lower bed life of carbon or molecular sieve options. The latter two options’ higher bed replacement frequency increases the labor, shipping, and handling costs of fresh and spent sorbent, and may increase the potential for lost production due to the increased downtime frequency, depending on gas plant shutdown planning and frequency.

Gas Treating and Dehydration

The primary gas conditioning and processing requirements will vary depending on the ultimate destination for the gas. The notes below provide some guidance regarding the level of contaminants that can generally be tolerated for various applications.

- CO₂
  - Pipeline sales gas may generally retain some amount of CO₂, up to about 1% to 2 % by volume.
  - For a high level of NGL recovery, specifically ethane recovery, the CO₂ may need to be reduced to less than 0.50 to 0.75%, although recent NGL process developments are increasing this allowable level.
  - For feed to LNG plants, the CO₂ should be reduced to less than about 25-100 ppmv to avoid freezing in the liquefaction process.
GTL plants may also benefit from low CO₂, though they likely have some resilience for higher levels without having a significant negative impact on the GTL process efficiency.

- H₂S
  - In all cases the H₂S must be removed to less than 2 – 4 ppmv.
  - While not necessarily required, lower H₂S concentration is often better for GTL feeds as sulfur will poison the GTL process catalysts.

- COS and RSH
  - In all cases, specifications may also require some or considerable COS and RSH removal from the gas, generally to meet low total sulfur content.
  - While not necessarily required, lower total sulfur concentration is often better for GTL feeds as sulfur will poison the GTL process catalysts.

- HHC and BTEX
  - Sales Gas specifications will usually only limit these components in terms of a heating value and dew point specification.
  - LNG specifications will require that these components are removed to very low ppm levels (often <1 ppmv), particularly BTEX and C₈+ hydrocarbons to avoid freezing in the liquefaction process.

As noted in Figure 1, the typical facility will include a primary Gas Treating Unit (GTU) for H₂S and CO₂ removal. The removed CO₂ and H₂S are regenerated into a concentrated acid gas stream that contains the co-absorbed CO₂ and H₂S along with some amounts of the troublesome trace components, depending on the characteristics, design configuration, and conditions of the GTU. The H₂S and other sulfur compounds must be processed to recover the sulfur to meet emission limitations as imposed by company, local and national regulations, or other imposed standards. Future facilities will likely be required to meet much better than 99% recovery of all sulfur entering the GTU, or certainly of all sulfur entering the SRU.

Physical solvents such as Selexol™ will remove COS and RSH but will also absorb a considerable amount of propane and heavier hydrocarbons. The reference gas composition is rich in hydrocarbons so there is economic value to accomplish high recovery of NGL liquids, regardless of the ultimate destination of the processed gas. Therefore, physical solvents are not applicable for the example feed gas. For gases similar to the referenced composition, an amine solvent likely represents the best available technology option for accomplishing H₂S and CO₂ removal from the plant feed gas.

There are various options within the broad category of amines, including non-selective and selective amine solutions. There are also so-called ‘hybrid’ solvents that include amine plus some amount of a physical solvent or additive to enhance both COS and RSH removal. However, the hybrid solvents may also co-absorb a large amount of BTEX and HHC compounds, similar to though less severe than with physical solvents, that result in lost hydrocarbon product revenue and complicate the acid gas processing in sulfur recovery units.

With traditional amine solvents and design criteria, little COS or RSH is removed in the GTU. When near-total CO₂ removal is desired, DEA, DGA or other specialty formulated solvents have the ability to remove significant amounts of COS and RSH. DEA may be able to remove more than 90% of the COS when operating at warmer operating conditions and with proper contactor design. Other specialty formulated solvents have also been developed to provide improved COS
and RSH removal. For example, solvent technology providers have reported data indicating that it is possible to achieve COS removal that is perhaps equivalent to the percent removal obtained for the CO₂. These technologies make it possible to achieve a high percentage removal of COS for LNG applications requiring very low CO₂ in the treated gas. Many factors will influence the choice of an optimal GTU solvent, including: the treated gas disposition and specifications, level of trace components, and the impact on overall facility complexity and cost.

Where the selected GTU design achieves only partial COS and RSH removal and product gas total sulfur specifications cannot be met, dedicated COS hydrolysis and RSH hydrogenation systems may be required in the gas treating scheme. Bulk H₂S and CO₂ removal would be done initially to support the hydrolysis and hydrogenation chemistry, followed by the reaction system to convert the COS and RSH to H₂S, and finally a polishing solvent wash to remove the remaining amounts of H₂S and CO₂.

Due to the complications associated with COS and RSH removal in the GTU, and where the treated gas can meet the total sulfur specification, the lowest cost option may be to allow the removal to occur downstream in the cryogenic NGL recovery step, where more than 90% of these components can be expected to concentrate in the NGL products and can be more effectively removed via dedicated product(s) treatment. The remaining contaminant will stay in the treated gas so further gas treatment may be needed to meet a stringent total sulfur specification.

Depending on the relative CO₂ and H₂S inlet concentrations, the gas treating scheme may require consideration of selective versus non-selective solvents. However, for the example composition, either choice may necessitate an Acid Gas Enrichment (AGE) system, as depicted in Figure 1, to provide a higher-H₂S acid gas feed to the downstream Claus Sulfur Recovery Unit (SRU).

The sweet gas from an amine-based GTU is water-saturated so it is directed through a dehydration (DEHY) system for water removal. Dehydration may consist of bulk water removal via glycol absorption if the product is pipeline gas. However, for NGL recovery or LNG feed, molecular sieve treatment is needed to achieve < 0.1 ppmv water content. This would be required for any GTU technology selection, not just when the upstream unit is an amine-based technology. The molecular sieve beds are regenerated in a batch-wise fashion, often with heated natural gas product. Regeneration gas is ideally recycled back into the process to retain its hydrocarbon value.

While an amine-based GTU is ineffective at removing RSH, and cannot typically achieve complete RSH removal essentially complete RSH removal can be achieved in the DEHY system with the addition of a second type of molecular sieve material in the adsorbers. In this case, the regeneration gas will contain the removed RSH and must be treated. Physical solvents, for example Selexol™, have been used for this service, although a hybrid solvent could also be used. The regenerated acid gas from the regeneration gas treating system must be directed to the SRU for sulfur recovery.

The following sections discuss some specific considerations for GTU and DEHY designs as they relate to each of the contaminants being addressed.
**CO₂ and H₂S Considerations**

Amine circulation rate is a primary factor in establishing the size and cost of most every equipment item in the GTU. Because CO₂ is often the predominant acid gas contaminant in the feed, as it is in the example composition, the amount of CO₂ absorbed into the solvent is one of the primary drivers of circulation. The less acid gas absorbed, the less circulation needed, the smaller the equipment, and the lower the capital and O&M costs.

**Selective Gas Treating Opportunities**

When treating to pipeline sales gas specifications, where CO₂ content can remain relatively high in comparison to the tight H₂S specifications, a selective GTU solvent, such as MDEA, can be used to minimize CO₂ pickup. The selective solvent GTU can be tailored through amine(s) composition, operating conditions or mechanical design features to “slip” much of the feed CO₂ into the treated gas stream. This will often substantially reduce total acid gas removal, due to less CO₂ absorption, and will therefore require less solvent circulation. In addition to reduced acid gas flow, this CO₂ slip allows for a higher H₂S to CO₂ ratio feeding the SRU, perhaps minimizing or eliminating the need for an AGE, and allowing for better SRU operation.

Amine regeneration energy requirement is a strong function of the amount of acid gas absorbed. The less acid gas absorbed, the lower the solvent flow, and the less energy is needed. The selective amines also have lower heats of reaction, further lowering regeneration energy requirements.

All of the factors described above primarily impact sizing of the GTU regeneration system (solvent circulation rate and regeneration energy), reducing both capital and O&M costs. However, such advantages are not only realized in the GTU, but are also magnified significantly in the AGE, SRU and TGCU systems.

A selective solvent can also often be used where high levels of ethane are recovered in an NGL Recovery, depending on how much CO₂ the process can allow. If some large portion of the feed CO₂ is allowed to “slip” through the GTU in this case, a large amount will condense into the liquids stream in an NGL Recovery unit, and ultimately concentrate in the ethane product after NGL fractionation. CO₂ can be removed from the ethane using an amine or other process technology, but this adds complexity and cost to the NGL Treating System. These added costs should be included in any cost analysis to determine the project’s optimum GTU and overall processing arrangement.

Allowing appreciable CO₂ slip in the GTU also limits the opportunities for the DEHY system. CO₂ competes strongly with RSH for molecular sieve capacity. This competition negates the opportunity for the DEHY system to provide both water and RSH removal as the system design becomes economically infeasible.

**Non-Selective Gas Treating Opportunities**

In contrast, LNG and GTL applications most often require a “non-selective” GTU solvent, such as MDEA plus piperazine, which removes essentially all H₂S and CO₂.
For such systems, solvent selection and operating conditions must be chosen to meet the stringent treated gas specifications, with little regard for impacts on the sulfur recovery system configuration and cost. Including an AGE in the process configuration may provide the most benefit in these situations.

**Other Considerations**

When large pore molecular sieves are used for downstream dehydration (e.g. 4A sieve, which is very common), some of the remaining CO\textsubscript{2} and H\textsubscript{2}S may be co-adsorbed along with water, even when CO\textsubscript{2} and H\textsubscript{2}S have been treated to low levels upstream. However, because the sieve is less ‘selective’ to CO\textsubscript{2} and H\textsubscript{2}S than water (they are not adsorbed as readily, and are held more loosely), they are released much faster during regeneration, resulting in a concentration spike of CO\textsubscript{2}, and even more so H\textsubscript{2}S. Some COS may also form during the regeneration from reaction of the CO\textsubscript{2} and H\textsubscript{2}S (see COS Considerations section below). If the regeneration gas is not treated (e.g. H\textsubscript{2}S scavenger bed), or recycled back to the GTU, and instead recycled to the front of the DEHY or combined with the sales gas stream, the resultant concentrations of H\textsubscript{2}S in the sales gas product may even spike to levels greater than specifications allow. This is a scenario which should be considered in design. Use of smaller pore size sieve (e.g. 3A sieve), or changing the structure of the sieve to reduce basicity (i.e. 5A), will minimize CO\textsubscript{2} and H\textsubscript{2}S adsorption, COS formation and thus concentration spikes in the regeneration gas.

**COS Considerations**

Traditional amine solvents remove little COS in the GTU, and the DEHY system does not remove effectively COS. In general, near complete COS removal can only be achieved in the GTU with a non-selective or formulated amine-based solvent that removes CO\textsubscript{2} down to ppm levels. Hybrid solvents are often considered to maximize COS removal; however, additional GTU design features may be needed as hybrids have higher solubility of heavy hydrocarbons, resulting in hydrocarbon products loss.

Some existing Middle East projects utilize the hybrid (amine plus physical solvent additive) Shell Sulfinol® solvent for the GTU. Without considerable effort, Sulfinol® will remove only a portion, but not nearly all of the COS and mercaptans. Therefore, the lowest cost option may be to allow the removal to occur naturally via the cryogenic NGL recovery step – concentrating these components in the NGL products and requiring NGL product treatment. The acid gas containing COS that is regenerated from the NGL treating system would be directed to the SRU for sulfur recovery.

BASF (see reference) and other solvent suppliers have developed specific MDEA formulations that can accomplish deep COS removal in the GTU in near equal proportion to CO\textsubscript{2} removal. LNG systems can likely tolerate the COS leakage from such systems. However, GTL feeds require near complete removal of all compounds that contain sulfur, so they must include a “sulfur guard” system in the front end to protect against any leakage from the gas conditioning and processing systems.

Even if the GTU removes a majority of the COS, or there is little to no COS in the natural gas feed to the GTU, there is some risk of downstream COS formation if molecular sieve dehydration is used, which is typically required upstream of liquids recovery. As discussed
above, when large pore sieves are used for dehydration, larger concentrations of CO₂ and particularly H₂S can be seen for short periods during regeneration. The molecular sieves can thus catalyze the reverse hydrolysis reaction due to the absence of water:

\[
\text{H}_2\text{S} + \text{CO}_2 \rightleftharpoons \text{COS} + \text{H}_2\text{O} \quad \text{(Equation 1)}
\]

The high regeneration temperatures also drive this equilibrium reaction towards COS formation. Use of smaller pore size sieve (e.g. 3A sieve), or changing the structure of the sieve to reduce basicity (i.e. 5A), will minimize CO₂ and H₂S adsorption and thus COS formation.

Most COS left in the dry treated gas will concentrate in any NGL product containing significant amounts of propane. COS can be removed from the propane product, but this represents additional complexity and cost. The optimal location for COS removal must be considered to ensure the most economical facility configuration.

**Mercaptan Considerations**

Simple solubility plays a large role in the removal percentage of mercaptans. For that reason, non-selective solvents, which require a relatively larger circulation rate due to their complete removal of acid gas, will often achieve better RSH removal than selective solvents. Generally speaking, amine solvents are not very effective at removing these trace components.

Because physical solvents exhibit greater solubility for RSH, hybrid solvents provide improved RSH removal. However, hybrid solvents also have higher solubility of heavy hydrocarbons, resulting in hydrocarbon products loss. Unless the selected solvent can achieve near complete mercaptan removal, further treatment may be required downstream of the GTU.

Another alternative first practiced in the Middle East is to install additional special molecular sieve material into the DEHY molecular sieve beds to accomplish both essentially complete water and mercaptans removal. This option increases capital and O&M costs but does provide some added assurance against mercaptans leaking into the GTL. It also provides a good treating option if NGLs are not to be recovered or if the NGL Recovery system might be bypassed for maintenance.

If this option is chosen, the molecular sieve regeneration gas will contain the removed mercaptans and must be treated to recover the sulfur and hydrocarbon content. If the GTU can remove a sufficient amount of RSH, the regeneration gas may be recycled directly back to the GTU without further treatment. This recycle increases the GTU feed gas RSH concentration and enables net total recovery in the GTU acid gas.

Alternatively, stand-alone physical solvents have also been used for treating the regeneration gas, though a hybrid solvent could also be used. For a GTL Project, the treated regeneration gas may need to be recycled to the GTU for re-treatment, as the physical solvent cannot meet the very tight treated gas sulfur specifications. The RSH is recovered in a concentrated acid gas stream from the physical solvent regenerator, which is routed to the SRU for recovery of the sulfur. The introduction of this stream into the SRU reaction furnace must be carefully considered, as it will be rich in hydrocarbons and have relatively higher oxygen requirements than the GTU acid gas.
**HHC and BTEX Considerations**

BTEX removal from the feed gas must be considered during design, but is generally not required unless they contribute to a treated gas dew point issue, or if they pose a risk of freezing in the liquids recovery section or liquefaction unit.

Removal of a substantial portion of BTEX and HHCs upstream of the GTU would be beneficial to the overall plant performance and add volume of valuable liquid product. However, the methods for significant recovery also involve significant cost and existing facilities have not found these methods to be commercially attractive.

A portion of the heavy hydrocarbons (HHC), and especially aromatics such as Benzene, Toluene and Xylene (BTEX), is soluble and will be absorbed by most amine treating solvents; some estimates indicate about 25% pickup. Hybrid and physical solvents will pick up even more. However, hybrid solvents are being developed to simultaneously maximize RSH absorption with a low level of hydrocarbon co-absorption.

Any absorbed BTEX is rejected in the acid gas from the solvent regenerator, which then feeds the SRU. BTEX concentrations of 500 ppmv or greater in the SRU feed require increased furnace temperatures. If the acid gas is not rich enough in H₂S to achieve the furnace temperature required for BTEX destruction, special design features and/or fuel gas co-firing will be required, representing additional CAPEX and OPEX.

**Sulfur Recovery**

The acid gas mixture from the GTU is principally H₂S and CO₂, but contains some of the contaminants discussed. It is assumed that the reference gas feed stream contains over 50 tpd of sulfur, and that regulations require better than 99% recovery of all sulfur entering the GTU or certainly essentially all sulfur entering the SRU.

Most high tonnage sulfur recovery facilities utilize the modified Claus process to convert the H₂S to elemental sulfur vapor and then condense the sulfur into molten form for separation from the process tail gas stream (mostly N₂, H₂O and CO₂). The modified Claus process consists of an initial air or oxygen fired partial combustor (SRU burner) that achieves perhaps 70% conversion of the H₂S to sulfur. Downstream, there are a series of catalytic converters that complete the overall H₂S conversion to approximately 94% to 97%.

High sulfur recovery applications, as required for our sample facility, also require a tail gas cleanup unit (TGCU). Numerous TGCU process options are available that might meet the required sulfur recovery level, but this paper emphasizes the industry recognized hydrogenation/quench/amine (H/Q/A) process arrangement that is likely required to meet most future sulfur recovery operating permits.

Finally, the treated tail gas from the TGCU passes through a thermal oxidizer to oxidize all remaining sulfur compounds to SO₂, and to destruct all VOC hydrocarbons and aromatics, before being vented to atmosphere. This can normally be accomplished by fuel gas supplement to operate at 1000 – 1200°F, though a high concentration of aromatics may require 1400°F or higher to achieve adequate destruction.
The acid gas from the GTU could be as low as 3 – 50% H₂S on a dry basis for the referenced gas composition, if a non-selective solvent is utilized in the GTU. This is low for an SRU and requires some special design features to ensure long term, stable operation that provides high sulfur recovery. Options include acid gas and air pre-heat or supplemental fuel gas firing. Oxygen enrichment may be used but is often not justifiable based on economics.

A split-flow configuration can also be implemented in the SRU to increase the furnace temperature; however in this case, a portion of any acid gas feed contaminants will not have the opportunity for destruction or conversion in the furnace.

For these reasons, it is often economical to route a lean acid gas through an acid gas enrichment (AGE) unit upstream of the SRU, in order to further concentrate the stream in H₂S. A significant advantage of the AGE is that the amount of ‘slipped’ CO₂, often referred to as the CO₂ vent gas, might be substantially removed from the SRU and downstream TGCU process stream and sent directly to the thermal oxidizer. The enriched acid gas stream is therefore much smaller in volume and mass flow. This decreased volume enables debottlenecking of existing SRU equipment, and allows for smaller equipment in new facilities, saving considerable capital cost and improving sulfur recovery efficiency. However, the disposition of the vent gas can be impacted by the presence and concentration of trace contaminants such as COS and RSH.

Unfortunately, for our reference gas composition a majority of all RSH, COS, BTEX and other hydrocarbons contained in the raw acid gas from the GTU predominantly slip through the AGE Absorber with the CO₂. In addition, the AGE Absorber cannot fully remove the H₂S from the rejected CO₂. Typically about 150 to 300 ppmv H₂S remains, although it is feasible to design for much lower (see references).

Figure 2 and Figure 3 illustrate the sulfur recovery configuration with and without and AGE.

![Figure 2 – Sulfur Recovery without AGE](image-url)
In order to serve its function, the AGE and TGCU must use a selective solvent, since any co-absorbed CO₂ is routed to the SRU and simply adds volume, and increases the size and cost of all associated systems. The main objectives of the AGE in treating the raw acid gas are:

- To reduce the concentration of H₂S in the CO₂ rich gas to very low levels; a low concentration (approximately 150 ppmv) of H₂S must generally be achieved in this CO₂ rich stream to ensure acceptable total plant sulfur emissions.
- To minimize the co-absorption of CO₂ (i.e. maximize CO₂ slippage); the Claus process is least costly and most efficient when the feed acid gas is approximately 80% H₂S or higher.

MDEA has proven to offer selectivity for H₂S over CO₂ and offers generally higher loadings without corrosion and with reduced regeneration energy requirements. However, MDEA has some limitations in reaching very low concentration specifications for the acid gases, particularly at the low operating pressures of an AGE or TGCU. A number of solvent vendors have developed additives to improve MDEA’s performance. The concept of using mixtures of certain amines in an MDEA base solution has been commercialized with good success. A series of solvents offered by BASF, Ineos, Huntsman, Dow, Shell and others are examples of this continuing trend. The ExxonMobil developed Flexsorb® series of ‘sterically hindered’ amine solvents have also become established in the marketplace to perform enhanced selective H₂S removal.

The various solvents also react in differing means, degree of completeness and irreversibility with COS and RSH. This can be a significant factor in determining the optimum solvent for a given application.

Configuration of an AGE is similar to a GTU or TGCU amine section. Economics and plant simplicity are generally improved when an integrated AGE/TGCU solvent arrangement is used.

**COS Considerations**

*Sulfur Recovery without AGE*

Any COS absorbed by the GTU solvent will be regenerated into the acid gas feed to the SRU. A portion of the absorbed COS may be hydrolyzed to H₂S and CO₂ in the AGRU solvent regeneration system, particularly if the solvent contains piperazine, which enhances COS hydrolysis (see references). Any COS remaining in the acid gas feed to the SRU does not
materially complicate the design or operation of the sulfur recovery process. This is true even in a split-flow SRU, since COS is actually formed in the SRU reaction furnace, particularly for acid gases with high concentrations of CO₂.

The first converter in the SRU may be operated at an elevated temperature to enhance COS conversion to H₂S via the hydrolysis reaction. If the COS concentration in the first converter feed is significant, specialized catalyst (e.g. titania) may be required to improve kinetics and conversion to CO₂ and H₂S. Any COS remaining in the SRU tail gas has one last opportunity for conversion in the TGCU reactor. However, some small quantity often remains in the TGCU reactor effluent, especially at end of run catalyst conditions.

The TGCU solvent will only absorb a very small percentage of the COS in the feed to the unit. Practically speaking, any COS remaining in the TGCU reactor effluent is a direct contributor to sulfur emissions.

**Sulfur Recovery with AGE**

Like the TGCU solvent, the AGE solvent will absorb very little of the incoming COS. If the AGE vent gas is routed directly to the thermal oxidizer, as depicted in Figure 3, then a large majority of the COS in the GTU acid gas will directly contribute to sulfur emissions.

If the amount of COS in the AGE vent gas is inhibiting the ability to meet sulfur recovery requirements, the vent gas must instead be routed to the TGCU, upstream of the reactor; refer to Figure 4. The TGCU reduction reactor converts the various sulfur compounds remaining in the SRU tail gas, including COS in the vent gas from the AGE, to H₂S. COS is the most significant sulfur contaminant other than SO₂ in this stream and can be present in concentrations well over 1000 ppmv. In this case, much of the COS can be hydrolyzed to H₂S, and the H₂S can be absorbed by the TGCU solvent for recycle to the SRU, improving sulfur recovery.

However, high levels of CO₂ contained in the feed to the TGCU drives the equilibrium of the COS hydrolysis reaction to the COS side, resulting in lower COS conversion for leaner gases. This is important because essentially all unconverted COS passes through the rest of the TGCU. Little, if any, is absorbed in the TGCU absorber. COS remaining in the TGCU absorber overhead tail gas is oxidized (along with other sulfur species) to SO₂ in the thermal oxidizer and exits in the plant tail gas. This COS can often be responsible for a significant portion of the total sulfur emissions.

Additionally, in this configuration, the TGCU will not benefit from the volumetric capacity decrease offered when routing the AGE vent gas directly to the thermal oxidizer, and the TGCU capital cost will increase.
There are additional design considerations that may come into play if this configuration is pursued. Depending on the solvent used in the AGE unit, there will be varying amounts of heavy hydrocarbons and/or aromatics present in the AGE vent gas. If the concentration is significant, consideration can be given to the installation of a second, dedicated hydrogenation bed for the AGE vent gas. This second reactor would be smaller than the main TGCU hydrogenation reactor. Providing the second reactor limits the risk of contamination by heavy hydrocarbons or aromatics in the AGE vent gas to the smaller bed. This configuration would particularly merit evaluation if the TGCU did not include a Reducing Gas Generator (RGG), which also has the potential to deposit hydrocarbons on the TGCU reactor due to the reducing environment of the combustion.

**Mercaptan Considerations**

**Sulfur Recovery without AGE**

Any RSH absorbed by the GTU solvent will be regenerated into the acid gas feed to the SRU. Assuming that the SRU is a straight-thru configuration, the presence of RSH in the SRU acid gas feed does not materially complicate the unit’s design or operation, as RSH will readily oxidize in the SRU burner.

If the SRU is designed with a split-flow configuration, the portion of RSH bypassed around the reaction furnace will directly reduce the sulfur recovery percentage of the SRU. If there are heavy mercaptans in the acid gas feed, a split-flow SRU is not recommended as these contaminants could deposit on the first converter bed, negatively impacting activity and life.

In recent years, it has been demonstrated that a significant portion of RSH can be converted to H$_2$S in the TGCU reactor via the following hydrogenation reaction:

\[
\text{RSH} + \text{H}_2 \rightleftharpoons \text{H}_2\text{S} + \text{RH} \quad \text{(Equation 2)}
\]

In this way, the hydrogenated portion of the RSH that bypasses the furnace in a split flow configuration will increase the H$_2$S load on the TGCU absorber.

Most TGCU solvents will only absorb a very small percentage of the RSH. Therefore, in general, any RSH remaining in the TGCU reactor effluent is a direct contributor to sulfur emissions.
**Sulfur Recovery with AGE**

Like the TGCU solvent, most AGE solvents will absorb very little incoming RSH. Therefore, generally, if the AGE vent gas is routed directly to the thermal oxidizer, then a large majority of the RSH in the GTU acid gas will directly contribute to sulfur emissions.

If the amount of RSH in the AGE vent gas is inhibiting the ability to meet sulfur recovery requirements, the vent gas can instead be routed to the TGCU, upstream of the reactor; refer again to Figure 4. In this case, a significant portion of the RSH can be reduced to H₂S via hydrogenation, and the H₂S can be absorbed by the TGCU solvent for recycle to the SRU. However, in this configuration, the TGCU will not benefit from the volumetric capacity decrease offered by routing the AGE vent gas directly to the thermal oxidizer and the acid gas load on the TGCU increases. For these reasons, the TGCU capital cost will be higher.

As discussed previously in the COS section, if the AGE vent gas contains heavy hydrocarbons, consideration may be given to a second hydrogenation reactor that is dedicated to the AGE vent gas. This would have the most merit in a TGCU that did not contain an RGG.

**BTEX and HHC Considerations**

**Sulfur Recovery without AGE**

If BTEX is present in significant (>500 ppmv) concentration in the SRU acid gas feed, the reaction furnace temperature must be elevated to ensure complete destruction. Otherwise, these hydrocarbons (principally the toluene & xylenes) will deposit and form coke on the first stage converter bed, negatively impacting catalyst performance and life. This is a well documented cause of SRU underperformance.

If the SRU acid gas is not rich enough to support the required reaction furnace temperature, special design features including oxygen enrichment, acid gas or air preheat, and/or supplemental fuel firing are required, representing increased capital and operating costs. The option to bypass some acid gas around the burner to elevate the burner temperature cannot be employed, as this bypasses some BTEX that would deposit almost directly onto the downstream catalyst and render it ineffective.

**Sulfur Recovery with AGE**

As with RSH, most AGE solvents will not absorb a significant percentage of BTEX. However, their presence in the AGE vent gas does warrant consideration.

The AGE CO₂ vent gas is most commonly routed directly to the thermal oxidizer. If the concentration of BTEX to the thermal oxidizer is significant, increased operating temperatures could be required to ensure complete destruction to meet environmental permitting requirements, increasing capital and operating costs. Operating levels of 1200-1400°F or higher have been reported.

If the CO₂ vent gas is routed to the TGCU to increase sulfur recovery as discussed above, any BTEX in the stream could deposit on the TGCU catalyst, decreasing activity and catalyst life.
This is specifically the reason why consideration may be given to a second hydrogenation reactor that is dedicated to the AGE vent gas, to limit contamination to a single, smaller bed, thereby minimizing operating costs.

**General Sulfur Recovery Considerations**

If the previously discussed strategies do not yield an acceptable level of sulfur recovery, installation of an SO\(_2\) removal system on the thermal oxidizer flue gas can be considered. All sulfur compounds would be oxidized to SO\(_2\) in the thermal oxidizer. A NaOH scrubber or some other liquid solvent or solid sorbent system could be utilized (see references).

**Impact of GTU Solvent Selection on SRU**

Two example designs are presented briefly below to depict the impact of the choice of a non-selective versus selective GTU solvent system has on the design of the SRU.

**Example 1: Non-Selective GTU Solvent**

A sour gas at 900 psig and containing less than 10% total acid gas requires treating to meet a pipeline sales gas specification of less than 2% CO\(_2\) and overall sulfur recovery of 99.8%. A significant amount of COS and RSH are predicted over the life of the project. The total acid gas content will vary by a factor of two, as will the CO\(_2\)-to-H\(_2\)S ratio. A “non-selective”, mixed physical/chemical (hybrid) amine has been specified to meet total sulfur removal specifications.

Figure 2 and Figure 4 illustrate two process options considered for the subject facility. Figure 2 depicts a GTU, modified-Claus SRU, followed by a TGCU. With the “non-selective” GTU and no AGE, the SRU/TGCU process gas volumes are large and equipment is costly. Also, a split-flow Claus with air and acid gas preheat is required to achieve stable operation at the low H\(_2\)S acid gas concentration.

Figure 4 depicts the optimum arrangement, including an AGE and TGCU using an integrated AGE/TGCU process. The Claus/TGCU process gas volume is shrunk by a factor of over 5:1 as only 10-15% of the CO\(_2\) in the raw acid gas is co-absorbed with the H\(_2\)S.

Table 2 summarizes process parameters for each non-selective option: one for a design without an AGE; a second that includes an AGE; and for both a high and low feed acid gas concentration was investigated. Table 3 defines the relative costs for these two non-selective alternatives. The AGE clearly reduces SRU and TGCU process gas volumes by about one-half and reduces capitalized cost by about 15-30%.
Table 2 – Process Impacts: Non-Selective Versus Selective GTU (With and Without AGE)

<table>
<thead>
<tr>
<th>PROCESS OPTION</th>
<th>CO₂-TO-H₂S RATIO IN FEED GAS TO UNIT</th>
<th>PERCENT OF CO₂ CO-ABSORBED FROM UNIT FEED</th>
<th>RELATIVE VOLUME OF PROCESS GAS TO UNIT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GTU</td>
<td>AGE</td>
<td>SRU</td>
</tr>
<tr>
<td>A: NON-SELECTIVE GTU + SRU/TGCU</td>
<td>6:1</td>
<td>N/A</td>
<td>3:1</td>
</tr>
<tr>
<td>B: NON-SELECTIVE GTU + AGE + SRU/TGCU</td>
<td>6:1</td>
<td>3:1</td>
<td>1:3</td>
</tr>
<tr>
<td>C: SELECTIVE GTU + AGE + SRU/TGCU</td>
<td>50:1</td>
<td>30:1</td>
<td>1:1</td>
</tr>
</tbody>
</table>

Table 3 – Cost Benefit of AGE

<table>
<thead>
<tr>
<th>PROCESS OPTION</th>
<th>CAPITALIZED TIC PLUS O&amp;M</th>
<th>BASE</th>
<th>HIGH H₂S</th>
<th>LOW H₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: NON-SELECTIVE</td>
<td></td>
<td>100%</td>
<td>100%</td>
<td>79%</td>
</tr>
<tr>
<td>B: NON-SELECTIVE WITH AGE</td>
<td></td>
<td>78%</td>
<td>84%</td>
<td>69%</td>
</tr>
<tr>
<td>C: SELECTIVE WITH AGE</td>
<td></td>
<td>75%</td>
<td>N/A</td>
<td>80%</td>
</tr>
</tbody>
</table>

Example 2: Selective GTU Solvent

A sour gas at 1000 psig (69 barg), containing up to 5% volume CO₂ and less than 0.1% H₂S, requires treating to meet a pipeline sales gas specification of less than 4 ppmv H₂S and 2% CO₂. A small amount of trace sulfur compounds (COS, RSH) are present, but their removal is not required to stay below the allowable levels per sales gas specifications. The CO₂-to-H₂S ratio is about 50:1 and is predicted to remain relatively constant over the life of the project. Total sulfur recovery is required to exceed 98.5%.

A “selective” amine was an obvious choice for the GTU and it achieves a CO₂ “slip” of just under 2% into the sales gas. Even using the selective amine, the resulting acid gas from the GTU is only concentrated to about 30:1 (say 3% H₂S), since over 60% of the feed gas CO₂ has to be removed along with the very small amount of H₂S.
The primary area for cost reduction and process optimization for this project was in the downstream SRU and TGCU systems. Several process options, including oxygen enrichment, were thus investigated to find the optimum SRU/TGCU configuration. Most options involved use of a selective solvent to fully optimize the SRU/TGCU configuration. The most competitive design configuration investigated is summarized in Figure 5.

As depicted in Figure 5, the process could be improved to 99.3% sulfur recovery by inserting an AGE system upstream of a modified-Claus SRU, followed by a “hydrogenation/quench/amine” TGCU. The AGE and TGCU can use a common “selective” amine solvent, though probably not the same solvent as used in the GTU. For further sulfur recovery improvement to 99.8% or higher, the rejected CO2 from the AGE Absorber can also be processed in the TGCU. This would increase the equipment size and cost in the TGCU, and would increase the recycle stream size to the SRU, negating much of the savings achieved by the AGE.

The integrated AGE/TGCU process configuration receives the 30:1 raw acid gas and includes the same special design feature in the AGE to achieve acid gas enrichment to a CO2-to-H2S ratio of about 1:1, shrinking the total SRU/TGCU process gas volume by a factor of about 15:1. Table 2 reflects these advantages for the designated Case C. In this arrangement, over 60% of the feed CO2 is absorbed by the selective solvent in the GTU, while in the AGE a different selective solvent absorbs only a net 3% of the CO2. With the integrated arrangement, the TGCU uses the same solvent as the AGE; however, in order to meet the treated tail gas H2S specification the solvent is unable to limit CO2 co-absorption to less than about 30% of the CO2 entering the TGCU.

Table 2 summarizes some primary process parameters that differentiate the most advanced selective design that includes an AGE. The ability of the selective solvent(s) to achieve enrichment (decreasing CO2-to-H2S ratio), amount of CO2 co-absorption, and process gas volume shrinkage are illustrated, showing the benefits of matching “selective” solvent designs within appropriate AGE/SRU/TGCU design configurations. Clearly, the lowest cost process choice is the integrated AGE/TGCU “selective” solvent design.
**GTU Solvent Selection Summary**

Selective gas treating solvents offer significant cost saving and operating advantages. They may be used in the primary GTU, the AGE, and the TGCU to meet treated gas specifications with smaller equipment and lower operating costs versus non-selective solvents.

Separating the CO₂ from the H₂S in a lean acid gas using acid gas enrichment can reduce the overall cost of the sulfur recovery system as well as improve its performance. Acid gas enrichment can significantly reduce the volume of gas to be processed in the SRU; allows the use of a simple, straight-through Claus unit; operation of the TGCU is simplified; and the overall sulfur recovery is improved.

**Gas Processing**

**NGL Recovery**

The sweet, dry gas, particularly when rich in hydrocarbons as in the example feed composition, will often be sent to a cryogenic NGL Recovery unit to extract ethane and heavier hydrocarbons (C₂⁺) for sale as liquid product. Sometimes only propane and heavier hydrocarbons (C₃⁺) are recovered, driven by product values and the local market for LPG products. NGL recovery may be done either to increase the overall product value, in the case of high margins for liquid products, or to meet heating value or Wobbe index specifications for the sales gas product. The level of ethane recovery is closely tied to the sensitivity of the design to CO₂ freezing in the process, which can particularly become an issue when high ethane recovery is desired. This will impact the GTU treating requirements for CO₂ content and is discussed in more detail earlier.

NGL Recovery is included accomplished in a non-proprietary turboexpander unit technology such as the popular Gas Subcooled Process (GSP), or through various proprietary turboexpander unit technologies designed to increase product recovery, purity, process flexibility, and/or process energy efficiency. Other technologies such as straight refrigeration chilling, lean oil, and others are also commonly used.

**Contaminants in NGLs**

When NGL recovery is employed at a facility treating high CO₂ and/or sour gas, the recovered NGL stream will contain some amount of the subject trace contaminants (CO₂, H₂S, COS and RSH), even if they were specifically targeted and removed to low concentration during upstream gas treating. These contaminants largely distribute into the NGLs rather than the natural gas product after processing in a turboexpander plant. Because the liquid NGL stream is a much smaller fraction of the overall gas conditioning facility feed, these contaminants significantly concentrate in the NGLs, often to levels exceeding product specification limits.

Table 4 provides some high level estimates of the portion of each contaminant feeding a turboexpander-based NGL recovery unit that ends up in the NGL products.
Table 4 – Estimated Contaminant Disposition in Turboexpander NGL Recovery Unit (Compared to Residue Gas)

|                | CO₂   | H₂S  | COS  | MeSH | EtSH | iPrSH | Heavier
|----------------|-------|------|------|------|------|-------|         |
| C₂+ NGL        | >1/3  | >90% | >95% | >99.5% | 100% |
| (Ethane Recovery) |       |      |      |       |      |       | RSH      |
| C₃+ NGL        | <0.5% | 1–15% | 75–90% | >95% | >99.5% | 100% |
| (Ethane Rejection) |       |      |      |       |      |       |

Notes:
1. Depending on the level of C₂ rejection (e.g. C₂ content in C₃+ NGL stream)

The following two key observations can made from the table above.

1. CO₂ will generally distribute between methane and ethane during separation by cryogenic distillation, having a slightly higher affinity for the methane rich stream. Thus, a significant portion of the CO₂ fed to an NGL Recovery unit will end up in the C₂+ NGL stream (during ethane recovery), while almost no CO₂ will end up in a C₃+ NGL stream (during ethane rejection).

2. Most of the sulfur bearing contaminants will follow the propane and heavier fraction of the stream, ending up in the NGL stream regardless of whether the unit operates in ethane recovery or ethane rejection mode. The exception is H₂S, which will stay with the mostly with the ethane fraction, similar to CO₂, but to a much lesser extent.

While nearly the entire amount of COS and RSH that are fed to the NGL recovery unit end up in the NGL stream, regardless of the mode of operation (C₂ recovery versus C₂ rejection), the more ethane that is recovered, the higher the quantity of all trace contaminants in the mixed NGL stream produced from the NGL Recovery system. This is particularly the case for CO₂ and H₂S, introducing them as trace level contaminants in the mixed NGLs to a greater extent for ethane recovery operations. Because the volatility of each of these contaminants is scattered across the range of the individual NGL hydrocarbon components, they are ultimately distributed throughout the various final liquid products, concentrating to an even higher level in one or multiple products. The concentration of trace contaminants in the final liquid products can potentially increase up to ten times the level in the treated gas feeding NGL recovery, or more, if not at least partially removed in gas treating.

CO₂ and H₂S are nearly always targeted for removal in the GTU. H₂S is generally targeted for removal to less than 4 ppmw, but CO₂ may only be removed to anywhere between 50 ppmv and 2 mole % to meet LNG or pipeline sales gas specification, respectively. COS and RSH may not necessarily be targeted for removal as many commonly-used GTU technologies have difficulty removing these trace contaminants to low levels. While some may count on NGL Recovery to remove COS and RSH to a sufficient level to meet natural gas product specifications, these contaminants are simply moved from one product to another and must often be addressed by treating the liquid products. Facility design should always consider whether specialty solvents could more economically be used for RSH and COS removal in the GTU versus removal from the NGL products.
**NGL Fractionation and Treating**

The C\(_2^+\) or C\(_3^+\) NGL stream exiting NGL Recovery is further processed by fractionation into various products such as ethane, propane, butanes (either mixed butanes or split into normal and iso-butane), and natural gasoline (C\(_5^+\)). Fractionation increases the overall product value, and may occur at either the gas conditioning facility itself, or at a third party facility. Figure 6 depicts a typical fractionation unit. Units shown in dark boxes are generally required, while units in light gray boxes, or streams with dashed lines may not always be required or exist, depending on feed composition (e.g. C\(_2^+\) versus C\(_3^+\)), products desired, location of treating, and the level of contaminants in feed.

![Figure 6 – Typical NGL Fractionation Train](image)

**NGL Product Specifications**

Each liquid product has limitations on the amount of the subject contaminants that can be present for sale, just as with natural gas. These contaminant level specifications, along with limitations in water content, are intended to ensure products can be safely transported and handled. These specifications are also in place, along-side hydrocarbon composition specifications, to ensure the liquid products can perform sufficiently and safely in their end-use markets, and meet emissions requirements (minimize total sulfur emissions). CO\(_2\) and sulfur components are primarily removed to extremely low levels to prevent corrosion in transportation systems. H\(_2\)S in particular is a bad actor in promoting corrosion, especially in the presence of elemental sulfur. H\(_2\)S, RSH, and ultimately COS – when it hydrolyzes in the presence of water to H\(_2\)S – may also result in odor issues if not sufficiently removed from liquid products.

Table 5 shows some general ranges of specifications on trace contaminants for NGL liquid products is included below. Indicated under each product specification range in the table are some specification values seen more commonly in the industry. While Table 5 is intended to show typical contaminant limitations in liquid products, primarily for the US, these limitations can vary. They could even potentially vary outside of the range presented depending on the specific plant location and sales contracts. These values are provided for illustration only and should not be used as a basis of final design.
### Table 5 – Typical Liquid Product Specification Ranges

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Y-Grade NGL (C₂+)</td>
<td>100 - 3500</td>
<td>6 - 10</td>
<td>5 - 70</td>
<td>75 to No Free Water</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>[500]</td>
<td>[10]</td>
<td>[30 - 50]</td>
<td>[No Free Water]</td>
<td></td>
<td></td>
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<tr>
<td>Ethane</td>
<td>10 - 5000</td>
<td>0.5</td>
<td>100 - 185</td>
<td>13 to No Free Water</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>[10 or 1000]</td>
<td></td>
<td>[10-30]</td>
<td>[76]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propane (Commercial – US)</td>
<td>1 - 2</td>
<td>1 - 10</td>
<td>30</td>
<td>No Free Water</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propane (Export Grade)</td>
<td>&lt;1</td>
<td></td>
<td>10</td>
<td>[10-30]</td>
<td></td>
<td></td>
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<tr>
<td>Mixed Butanes (Commercial – US)</td>
<td>140</td>
<td></td>
<td></td>
<td>No Free Water</td>
<td></td>
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<td>Mixed Butanes (Export Grade)</td>
<td>&lt;1</td>
<td>1 - 10</td>
<td>30</td>
<td>[30]</td>
<td></td>
<td></td>
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<tr>
<td>Iso-butane</td>
<td>140</td>
<td></td>
<td></td>
<td>No Free Water</td>
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<td>140</td>
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<td></td>
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<tr>
<td>Natural Gasoline</td>
<td>5000</td>
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<td>No Free Water</td>
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</tr>
</tbody>
</table>

[GPSA Data Book 13th Edition, Section 2]

**Fate of Contaminants in NGLs**

Over the past several years, the exact distribution of contaminants into the various NGL products in a fractionation unit has been the subject of much debate, and in a real plant some surprises can occur. To make the issue more challenging, while process modeling software has improved over the years, predictions of the distribution of these trace contaminants have not proven fully reliable.

However, as discussed earlier, the volatility of the contaminants is spread throughout the range of the NGL product hydrocarbon volatility. Figure 7 illustrates this by showing the pure component vapor pressure of each contaminant and the various hydrocarbons in an NGL feed mixture. This information could be used to help predict the likely disposition of each contaminant in the various liquid products, with an expectation that lighter contaminants will end up in the lighter products and heavier contaminants in the heavier liquid products. More specifically, one might expect each contaminant to mostly distribute between the two hydrocarbons with immediately higher and lower vapor pressures during fractionation.
While the Figure 7 is intended to give an idea of where contaminants end up in an NGL fractionation unit, it does not accurately describe contaminant distribution in practice, nor does it address the quantity of contaminants that distribute to which products. For example, one might surmise from the figure above that methyl mercaptan (MeSH) would primarily distribute between the butane and natural gasoline products only, and perhaps primarily to the butane products as the vapor pressure of MeSH is closer to that of normal butane. However, in practice, MeSH happens to distribute primarily between the butane and propane products, even ending up in the iso-butane product rather than normal butane when mixed butanes are split. On the other hand, one would expect all of the CO$_2$ to end up in the ethane product, H$_2$S and COS to distribute between ethane and propane (with more H$_2$S to ethane than COS), and iso-propyl mercaptan to be fully in natural gasoline, all of which are correct in practice. Again, the figure above is generally helpful, but mostly illustrative to show each contaminant tends to distribute to various liquid products, primarily driven by similarities in component volatility. Non-idealities of various components do however factor into component distribution, causing some departure from the expected behavior described above, supporting the difficulties in prediction where contaminants end up in an NGL fractionation unit.

To make tracking some of these components through the fractionation train even more difficult, much of the literature even suggests formation of some amount of H$_2$S due to the decomposition of other sulfur compounds, and formation of methyl mercaptan in the depropanizer and/or debutanizer, likely due to decomposition of dimethyl disulfide (DMDS), when present in the NGL feed.

The following sections discuss the disposition of the various contaminants in more detail, and how the distribution impacts treating requirements, technology selection, and unit design.
The Fate of CO$_2$ and H$_2$S

With high pure component vapor pressures, similar to that of ethane, H$_2$S and CO$_2$ will generally only be present in significant quantities in the liquids from an NGL recovery unit if the NGL liquids have a significant portion of ethane. Even if a plant is operating in a partial ethane rejection mode, there is some significant amount of ethane left in the predominantly C$_3+$ NGL liquids produced, and these contaminants will be also be significant in the liquids. However, when operating in ethane rejection mode, there will essentially be no CO$_2$ in the NGL liquid stream, and very little H$_2$S.

Similarly, all of the CO$_2$ in the mixed NGL feed stream will end up in the ethane product stream as it is an even more volatile component than ethane itself. H$_2$S, although less volatile than ethane, will primarily end up in the ethane product stream, with only trace amounts of H$_2$S normally distributing to the propane product stream, if any.

The treated natural gas specification significantly influences the level of contaminants that end up in the mixed NGL stream feeding fractionation. In general, when contaminants are removed to a lower level in the GTU, less will end up in the NGL. This is most notable for CO$_2$ because H$_2$S is generally removed to the same very low levels in natural gas (often 4 ppmw or less), regardless of whether the natural gas product has to meet pipeline specifications, or whether it is being fed to an LNG or GTL facility. On the other hand, CO$_2$ content in the treated natural gas may range from below 50 ppmv to 2 mole % or greater.

As an example, assume the feed gas to an NGL Recovery system has 2% CO$_2$, 4 ppm H$_2$S, 75% Methane, 12% ethane, and the rest is C$_3+$ NGL components. In the case of ethane recovery, Table 4 presented earlier suggests that about 1/3 of the CO$_2$ might distribute to the NGLs, causing CO$_2$ to concentrate to almost 3% in the C$_2+$ stream. After fractionation, it would further concentrate totally into the ethane product to a level greater than 5%, much above the upper limit of typical ethane product specifications. In a case where the treated gas composition looks identical, except with 50 ppmv CO$_2$, the CO$_2$ ultimately concentrates to only about 140 ppmv in the ethane product, potentially within product specification limitations such that further treating for CO$_2$ would not be required. H$_2$S on the other hand would concentrate to about 15 ppm in the C$_2+$, and further to about 30 ppm in the ethane product in either case; this is a level that is likely to require further treating. As illustrated, while CO$_2$ and H$_2$S were removed to a sufficient level in the GTU, the concentrated levels in the final NGL product is substantially increased compared to the natural gas product. This may or may not require further liquid product treating, depending on GTU removal level (natural gas product specifications), and downstream liquid product specifications.

An item of special note is that while H$_2$S may not be present in significant amounts in the NGL feed, and does not generally distribute to products other than ethane, some literature suggests that it can and often does show up in almost any of the NGL liquid products due to decomposition of other sulfur compounds and/or hydrolysis of COS (when water is present). Care should be taken in any design to consider whether H$_2$S may be present in levels significant enough to require treating, despite low H$_2$S feed content, and not simply considering which product it will distribute to. As discussed in a later section, most liquid treating technologies will remove H$_2$S to low levels, so if treating is already included on a product, the addition of a small amount of H$_2$S should not be a problem, but some should be accounted for in the design if it is expected.
The Fate of COS

Based on pure component vapor pressure alone, one would expect COS to distribute between the ethane and propane products, and perhaps more so with the propane as the vapor pressure of the two components (COS and propane) are more similar. In fact, in practice it is observed that COS distributes within the deethanizer with only some of the COS in the NGL mixture distributing to the ethane product, while most will principally distribute to the propane and heavier stream at the tower bottoms.

However, in the case where an ethane-propane mixture is produced off the top of the deethanizer, more COS will end up in the tower overhead. Further, higher quantities of COS will distribute to the ethane-propane mix at the overhead of the deethanizer tower as propane content increases in this product. In fact, if an ethane-propane mixed product is produced, it may be likely to see more COS in the deethanizer overhead, rather than in the bottoms.

As expected, COS does not distribute in the depropanizer. All of the COS feeding the depropanizer will end up in the propane product.

The Fate of Mercaptans

As discussed above, methyl mercaptan (MeSH) is expected to distribute primarily in the debutanizer and butane splitter between the butane and natural gasoline products, based on its pure component vapor pressure. In practice, MeSH does not follow expectations and is primarily distributed between the propane and butane products in the depropanizer. Some minimal distribution may even be found in the deethanizer, with trace amounts of MeSH in the ethane product, but distribution in the deethanizer is generally only significant if an ethane-propane mix product is being made, with some MeSH following propane into the tower overhead. Additionally, to continue its departure from expected behavior, distribution of MeSH is not typical in a butane splitter, with all of it going overhead to the iso-butane product.

Distribution of MeSH is further complicated by the fact that some amount of it can be generated in a fractionation unit, particularly in the depropanizer and debutanizer when operating at temperatures greater than 212°F, due to the decomposition of DMDS, when present. Some publically available plant test data even suggest that up to 80% additional MeSH has been generated compared to the feed composition (see references). The distribution of MeSH in a fractionation unit has proven very difficult to predict and is often not accurately modeled by process simulation software. It may be appropriate in design to consider that a large portion of MeSH ends up in both the propane and butane product streams, perhaps as much as 80% of the feed MeSH to each product (ignoring the material balance of this component) to ensure downstream treating units are adequately sized, particularly when the presence of DMDS is suspected, and depending on the its quantity.

The distribution of ethyl mercaptan (EtSH) is less challenging to predict in a fractionation unit. Pure component vapor pressures suggest EtSH would tend to end up either mostly or fully in the natural gasoline product, and in practice it is indeed observed to distribute between normal butane and natural gasoline products. While the bulk of the EtSH does tend to end up in the
natural gasoline, a larger fraction than one might expect may stay in the mixed butanes or normal butane product.

Isopropyl mercaptan (iPrSH) would be fully expected to end up entirely in the natural gasoline product based on vapor pressure alone. In practice, there may be some slight distribution of iPrSH in the debutanizer, but only trace quantities of this contaminant are expected in the mixed butane or normal butane products. Almost all iPrSH will indeed end up in the natural gasoline.

All heavier mercaptans (and most other sulfur contaminants not discussed) will end up exclusively in the natural gasoline product.

**Summary of Contaminant Distribution**

Table 6 is intended to qualitatively summarize the distribution of trace contaminants that is observed in practice in a fractionation unit. It would be best for an engineer designing an NGL Treating unit to consider experimental and plant test data to ensure the predicted quantitative splits of trace components within the fractionation unit are correctly modeled in simulation software.

<table>
<thead>
<tr>
<th>Contaminant Disposition in NGL Fractionation Train</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CO₂</strong></td>
</tr>
<tr>
<td>Ethane</td>
</tr>
<tr>
<td>Propane</td>
</tr>
<tr>
<td>Mixed Butane</td>
</tr>
<tr>
<td>Iso-butane</td>
</tr>
<tr>
<td>N-Butane</td>
</tr>
<tr>
<td>Natural Gasoline</td>
</tr>
</tbody>
</table>

Notes:
1. H₂S and significant amounts of MeSH may be generated in the fractionation unit due to hydrolysis of COS and/or decomposition of other sulfur compounds.

**NGL Product Treating**

Both the quantity of each contaminant present in an NGL liquid stream, and the specific products specifications (there are various purity grades of all of the liquid products) drive how contaminants are removed and what technology is selected (e.g. bulk removal versus polishing). The following sections discuss some of the more common technologies. It is not intended to be exhaustive or all inclusive. Rather, it is provided to help familiarize the reader with some of the more common or typical technologies used to treat NGLs with a basic description of their capabilities, pros and cons.

**Amines**

Various alkanolamines (‘amines’) can be used to treat NGL liquids, just as they are commonly used for acid gas removal from natural gas in the GTU. Amines are particularly good at
removing CO₂ and H₂S to very low levels, and are flexible enough to economically handle contaminant removal from low inlet concentrations (polishing) and high inlet concentrations (bulk removal), although amines are most economical for bulk removal. While tertiary amines (e.g. MDEA, especially ‘activated’ versions) have gained great popularity for gas treating applications due to their higher loading ability, lower regeneration energy requirements, and ability to slip CO₂, primary amines (e.g. MEA, DGA®) and secondary amines (e.g. DEA, DIPA) remain more prevalent for liquid treating applications. However, activated MDEA is still sometimes used, particularly for high levels of CO₂ removal from ethane.

Primary and secondary amines have the main advantages for liquid treating because they are stronger bases than tertiary amines, allowing them to remove some COS (more for primary amines than secondary). This also allows for lower residence time in the contactor to sufficiently remove CO₂. RSH are much weaker acids than CO₂, H₂S, and COS, and are thus not effectively removed by amines. However, some recent project history suggests that some primary amines could remove up to 50% of RSH, and some secondary amines could remove up to 15% RSH.

Because amine solutions are aqueous, their use will result in a water-saturated treated NGL liquid that might otherwise be dry, necessitating downstream dehydration.

Pros
- High removal capability for CO₂ and H₂S, with some potential capability to remove COS (quantity and treated level dependent on amine selection);
- Can often meet tight product specs for CO₂ and H₂S;
- Suitable for bulk removal due to high loading capability;
- Regenerable, resulting in lower operating costs compared to non-regenerable treating options (no chemical consumption/replacement, low chemical losses/makeup, and no disposal required)
- Widely used technology, even perhaps in the same facility for gas treating, allowing for some potential overall facility integration.

Cons
- Does not sufficiently remove RSH;
- May not remove sufficient quantities of COS to meet product specifications;
- Because amines are aqueous solvents, they will saturate the otherwise dry NGL liquid products with water, which will then require downstream drying to meet product specifications;
- Corrosive.

Caustic

Often sodium hydroxide (caustic) can be used to chemically remove CO₂ and sulphur-bearing contaminants from NGL streams in a similar manner to amines. Caustic solutions are more basic (alkali) than amines, making it very effective for contaminant removal, particularly to very low levels. This also makes caustic very effective at removing RSH (weak acids). However, if CO₂ and H₂S are removed with a caustic solution, non-regenerable and/or stable by-products are formed (e.g. Na₂CO₃, NaSH, Na₂S). These render the caustic solution spent, and it must be
disposed of appropriately. Further, if H₂S is in the system, the spent caustic solution is considered hazardous because the reaction with H₂S is reversible, and H₂S can be released when mixed with other waste streams. The presence of CO₂ in any significant quantity in a caustic treating system results in high chemical loss and continuous make-up requirements, increasing the system OPEX.

Caustic solutions are not very effective at removing COS, however, some applications have used a non-regenerable mixture of caustic and MEA to avoid the need for downstream COS removal, and this combination of technologies can meet tight COS specifications. Recent project history suggests that total chemical consumption and disposal costs are higher for this combination of technologies, compared to when they are used separately (MEA used for CO₂, H₂S, and COS removal, followed by a caustic for RSH removal). Disposal of this spent solvent can even be more challenging than for caustic alone.

Pros
- Stronger base than amines so very good at removing CO₂, H₂S, and RSH, even to the tightest of product specifications;
- Regenerable when little contaminants are removed other than RSH.

Cons
- Does not remove COS, unless used on combination with other solvents (e.g. MEA);
- The presence of CO₂ and H₂S results in production of non-regenerable and/or stable, hazardous waste product resulting in high costs for appropriate waste disposal and chemical consumption. This technology is best suited for removal of only RSH and only trace levels of CO₂ and H₂S;
- May not be economical to regenerate if contaminants other than RSH are removed;
- Because this is an aqueous solvent, it will saturate the otherwise dry NGL liquid products with water, which will then require downstream drying to meet product specifications;
- Corrosive.

**Molecular Sieve**

Just as a molecular sieve is used commonly in gas conditioning to remove water, it has a high affinity to adsorb all of the subject trace contaminants, driven largely by sieve pore size and component polarity. Although each of these contaminants is adsorbed, some are more strongly held by the sieve than others. Specifically, water is most strongly held, followed by RSH, H₂S, CO₂, and finally COS (which has very low polarity). As a result, molecular sieves are great for dehydration. They are also effective at removing many of the other subject contaminants, and can meet very low concentrations of these contaminants. However, removal of COS from the NGL liquids stream is much more difficult, particularly when in the presence of other contaminants that are more strongly held by the sieve.

Because the contaminants removed from the NGL liquids continually load onto the sieve, with regeneration only occurring as in a batch cycle (not continuously regenerated as in solvent systems), molecular sieve systems must be proportionally larger as the total quantity of contaminants to be removed increases (more so than for changes in quantity of liquid to be
processed). As a result, molecular sieve systems are generally only applicable when the total level of contaminants in the feed is low.

Molecular sieves are a regenerable technology, however, all of the contaminants that are removed from the NGL liquids will be contained in the regeneration gas. Unlike in dehydration, where the water contained in the regeneration gas can simply be condensed and purged from the system, the regeneration gas in a molecular sieve system must be treated with another technology to ultimately capture and dispose of the contaminants. This could be done using a small solvent system. The regeneration gas could also be recycled back to the GTU if it has some contaminant removal capability, blended into a product that can handle some level of impurities, or burned as fuel if environmental and equipment design limits permit.

Pros
- Can remove all subject contaminants, although some less than others (e.g. COS);
- Can meet the tightest of product specifications;
- Regenerable.

Cons
- While molecular sieves have some COS removal capability, it is more difficult to adsorb on most molecular sieve materials than other subject contaminants, which tend to displace COS from the bed when present in any significant amount;
- Bed sizes start to become extremely large at high contaminant concentrations, so only economical for trace removal;
- Regeneration gas contains all contaminants removed and requires further treating by another technology.

**Chemical Adsorption (e.g. Mixed Metal Oxide)**

Chemical adsorption systems generally consist of a blend of mixed metal oxides (e.g. copper and zinc oxides), sometimes in an alumina binder. They chemically react with various sulfur species, such as COS and H$_2$S, to form stable metal sulfides as described by the following reactions.

\[
\text{Metal-O + COS} \rightarrow \text{Metal-S + CO}_2 \quad \text{(Equation 3)}
\]

\[
\text{Metal-O + H}_2\text{S} \rightarrow \text{Metal-S + H}_2\text{O} \quad \text{(Equation 4)}
\]

This is a non-regenerable process capable of ensuring very high purity specifications, possibly considerably lower than export grade specifications. Some vendors even claim that they can reduce COS to ppb range. The spent media, consisting of a stable metal sulfide, can either be disposed of as non-hazardous waste, or in certain circumstances it may be more economical to recycle them for metals recovery.

Because there is no regeneration of the adsorbent, this system is very simple. In some cases, pre-heat and post-cooling may be required for operation at elevated temperatures to ensure optimal loading of the adsorbent bed, but some adsorbents are designed to operate at ambient temperatures, making them even simpler.
Estimated bed life for typical designs is only 3 to 6 months, requiring regular bed replacement and disposal. Bed life may be further reduced if sulfur species that are not primarily being targeted are present, which co-load the adsorbent, such as H₂S and perhaps RSH. In such a case, an upstream bulk contaminant removal technology is generally the most economical solution to minimize bed replacement and disposal costs. Care must also be taken to monitor for sulfur breakthrough from the bed; however, operating in a lead-lag bed arrangement allows for saturation of the bed to occur before replacement is necessary.

Non-regenerable chemical adsorbent systems tend to have an economic advantage over regenerable technologies only when a small amount of COS is present, but may be required if product specifications for COS are extremely low. The capital cost for these systems is often low, while O&M costs are high.

**Pros**
- Simple design (no regeneration equipment required);
- Can meet the tightest of product specifications, primarily targeting COS, but is also effective at removing H₂S;
- Waste is non-hazardous.

**Cons**
- Non-regenerable, resulting in high capital (large bed sizes), disposal, and replacement costs at high inlet sulfur contaminant concentrations - only economical for trace removal;
- The presence of significant levels of H₂S and RSH co-load the adsorbent and make this technology not economical;
- Bed life likely limited to 3 to 6 months, requiring regular disposal.

**Hydrolysis**

In applications where higher concentrations of COS exist, and removal is critical, a COS hydrolysis reactor can be used to convert COS to CO₂ and H₂S by the aforementioned hydrolysis reaction. When the concentration of CO₂ and H₂S is very low, and at optimal temperature, COS conversion can be maximized. Catalysts promote this otherwise slow reaction to make the reactor size reasonable. Hydrolysis is generally only considered when either a molecular sieve (or other technology) is not sufficient or economical to meet very low COS specifications. A downstream treating unit is also likely required to remove H₂S, water that may have been added to shift equilibrium in the proper direction, and potentially CO₂ to meet all liquid product specifications.

**Pros**
- Can meet the tightest of product specifications for COS.

**Cons**
- May require downstream treating to remove the CO₂ and H₂S created;
- May require the addition of water, potentially adding the requirement to dehydrate the liquid product stream downstream.
**Summary NGL Treating and Design Considerations**

Table 7 provides a qualitative summary of common NGL treating technology capabilities.

**Table 7 – NGL Treating Technology Summary of Capabilities**

<table>
<thead>
<tr>
<th>Technology</th>
<th>Removal Capability</th>
<th>CO₂</th>
<th>H₂S</th>
<th>COS</th>
<th>RSH</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemical Solvents</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Primary Amine (e.g. MEA, DGA)</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓ (&lt; 50%)</td>
<td>× (Saturates)</td>
</tr>
<tr>
<td>Secondary Amine (e.g. DEA, DIPA)</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓ (&lt; 15%)</td>
<td>× (Saturates)</td>
</tr>
<tr>
<td>Tertiary Amine (e.g. MDEA)</td>
<td>✓ (Selective)</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>× (Saturates)</td>
<td></td>
</tr>
<tr>
<td>Caustic (Non-Regenerable OR Regenerable e.g. Merox)</td>
<td>✓ (undesirable)</td>
<td>✓ (undesirable)</td>
<td>✓</td>
<td>✓</td>
<td>× (Saturates)</td>
<td></td>
</tr>
<tr>
<td>Molecular Sieve (1)</td>
<td>✓ (4)</td>
<td>✓ (3)</td>
<td>✓ (5 – Marginal)</td>
<td>✓ (2)</td>
<td>✓ (1)</td>
<td></td>
</tr>
<tr>
<td>Chemical Adsorption (e.g. Mixed Metal Oxide)</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Hydrolysis</td>
<td>✓ (Added)</td>
<td>✓ (Added)</td>
<td>✓</td>
<td>✓</td>
<td>× (Added)</td>
<td></td>
</tr>
</tbody>
</table>

Legend:
✓ = Removed (at least partially)
× = Contaminant added/re-introduced during treating

Notes:
1. Numbers indicate the order of selectivity for physical adsorption with 1 being the easiest contaminant to remove (and hardest to regenerate), and 5 being the hardest contaminant to remove (and easiest to regenerate).

One thing that should be evident from Table 7, and the supporting technology discussions above, is that the best NGL treating solutions will often require a hybrid process, utilizing more than one technology to remove all contaminants as required to meet product specifications. This is particularly true for propane treating, and potentially even ethane treating, where more than one type of contaminant is present. Even when more than one technology is not required, it may be more economical depending on the level of contaminants to be removed and/or how strict the product specifications are (e.g. bulk removal, trace removal/polishing).

In any case, the contaminants that end up in the NGL stream feeding a fractionation unit can either be removed from the bulk NGL stream before it is fractionated into separate liquid products, or each liquid product could be treated separately downstream of fractionation (or perhaps even other intermediate locations). Treating the bulk NGL feed stream would require one larger treating system, compared with multiple smaller treating units in the case of treating the specific liquid product streams, with one system for each product. While the single large treating system would appear to be the economical choice, taking advantage of economies of scale, there are a number of reasons to consider treating the individual liquid products instead.
Because multiple treating technologies/steps are likely required to treat the bulk NGL stream sufficiently enough to meet all product specifications, a single large bulk NGL treating system is likely made up of multiple large treating units in series. This may, or may not, have an economic advantage over multiple small treating systems, depending also on whether the individual product treating systems also require multiple treating steps (this is often required for propane product treating, but is not as common for treating other liquid products).

Removal of contaminants from the bulk NGL stream must often be done to a lower level than when treating the individual product streams because contaminants become further concentrated in the final liquid products in a fractionation train. This makes sufficient contaminant removal more difficult, and perhaps not achievable, for many technologies.

If fractionation were to occur at a separate facility, particularly when processed by a third party, treating of the bulk NGL stream within the gas conditioning facility may be required to meet a Y-Grade NGL specification before it is shipped and fractionated, regardless of where it would be desired or most economical.

Many of the referenced treatment technologies require a regeneration material or may produce effluent streams that require disposal or recycle within the overall plant configuration. The upstream GTU and DEHY technologies have a major impact on the quantity of contaminants that make their way to the NGL Recovery and Treatment systems and distribute to the regeneration or byproduct effluent streams.

CONCLUSION

The presence of Hg, COS, RSH, and BTEX in produced gases can significantly alter individual gas conditioning and processing systems design and the project’s overall process configuration. Proper technology selection requires an engineer to consider all aspects of the plant design including (in no particular order):

- Technology capabilities in relation to:
  - What contaminants must be removed
  - Quantity of contaminants to be removed (bulk versus trace removal)
  - Product specifications
- Impacts on other processes in the facility
- Location for treating
- Process complexity
- CAPEX versus OPEX
- Reliability and maintainability
- Waste disposal and environmental impacts
- Safety (corrosion and handling requirements)

Existing and emerging technologies are available to optimize a plant design to meet a project’s specific requirements. The task for the process designer is to understand their project’s feed gas composition and end use product gas and NGL liquids specifications – then optimize the
application and arrangement of technologies to the best commercial advantage. The following roadmaps can be used as a general guide, in conjunction with the paper in determining

- the disposition of the subject trace contaminants, and
- the various treating strategies to consider depending on the different feed gas compositions, and considering the technologies chosen in other portions of the facility.

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**Figure 8** – Roadmap for Handling Mercury in Gas Conditioning and Processing Plant
Figure 9 – Roadmap for Trace Contaminant Disposition in Gas Treating and Dehydration Units

Notes:
* When large pore sieves are used (e.g. 4A), COS may be formed by hydrolysis of CO₂ and H₂S during regeneration.
** While the chart indicates that "No" or "All" RSH, HHC, or BTEX end up in a stream, there may actually be small amounts (<1%) that end up in the stream indicated to have none.
Figure 10 – Roadmap for Trace Contaminant Disposition in Sulfur Recovery Unit
Figure 11 - Roadmap for Trace Contaminant Disposition in NGL Recovery and Fractionation Units
REFERENCES


