11. Mercaptans Removal

- Whereas deep removal of carbon dioxide (CO_2) and hydrogen sulfide (H_2S) is now mastered, mercaptans (R-SH) removal from a sour natural gas stream is considered a challenge, depending on the concentrations involved.
- To meet sales gas product specifications, and avoid operating problems with corrosion and damage to downstream equipment, typical total sulfur specifications generally range from 30 to 100 ppmv.

11.1. Gas Treating Unit

- Amine can remove some mercaptans via chemical and physical absorption. The removal mechanism varies from system to system and is dependent on the operating conditions and the specific types of mercaptans in the feed gas.
- From a chemical perspective, mercaptans have acidic properties, like H_2S, but because of the hydrocarbon functional group, they are much weaker acids than H_2S. Mercaptans behave less like acids and more like hydrocarbons as the hydrocarbon chain length increases.
- Mercaptans chemically react with amines, but these chemical bonds are weak and are readily dissociated by more acidic compounds (e.g., H_2S and CO_2).
- The solubility of mercaptans in amine solutions increases with increased solvent alkalinity (less absorbed H_2S and/or CO_2), and decreases with increased temperature.
- Physical solvents can be used to remove H_2S and CO_2, and are also very effective in removing mercaptans and organic sulfurs.

11.2. Molecular sieve unit (MSU)

- The Molecular sieve unit (MSU) generally removes water from the gas, but can also be designed to remove trace components such as mercaptans.

- Molecular sieves (4A, 5A, and 13X) have polar internal surfaces that interact favorably with polar molecules such as water or mercaptans, making it possible to adsorb very low concentrations of mercaptans.
- During the regeneration cycle, the mercaptans are desorbed which can be removed with **the use of a physical solvent** and can be sent to the sulfur recovery unit for conversion.
- Depending on the acid gas contents and the levels of mercaptans, the molecular sieve unit can be used in combination with the gas treating unit for mercaptan removal.

11.3. Process Options

Three gas-treating options for the combination of gas treating and molecular sieves process are considered here.

Option 1: Removal of H_2S and CO_2 in a promoted MDEA unit and dehydration/ mercaptans removal in a molecular sieve unit.

Option 2: Removal of H_2S and CO_2 and all mercaptans in Fluor DGA unit and dehydration only in a molecular sieve unit.

Option 3: Partial removal of R-SH in a hybrid (mixed) solvent unit plus polishing with a molecular sieve unit.

12. Mercury Removal

- Mercury, which is present in varying concentrations and as a variety of species in many of the world’s natural gas fields.
- In fact, even low levels of mercury pose a health hazard (because it is toxic) and will damage aluminum heat exchangers, such as those used in cryogenic gas processing plants, which are susceptible to corrosion attack by mercury.

12.1 Mercury in Natural Gas Stream

- Mercury (Hg) is a trace element often found in natural gas and natural gas liquid streams. It can be present as organometallic and inorganic compounds, and/or in the elemental form depending on the origin of the gas.
- The concentration of mercury in natural gas streams can range from a few ng/Nm^3 to a few hundreds of mg/Nm^3 among different production fields.
- It is very difficult to predict or measure the concentration of mercury at the low levels present in production reservoirs. Furthermore, elemental mercury needs to saturate tubulars and piping, so it may take some time before the mercury is detected in the facility.
- This means in the design stage; operators will often have no idea of its steady state concentration. This can lead to either not including a mercury removal system or installing a system that is under designed. Conversely, it may lead to the installation of an unnecessarily large mercury unit for those who design plants conservatively. In the former case, the operator may be unaware of impending trouble until failure of an equipment item due to mercury-induced corrosion.
- Methods that involve flowing of a known quantity of gas past a gold foil to accumulate mercury over time can give a good idea of the average mercury content.

12.2. Mercury Removal Technologies

- Any mercury removal process must be effective at very low concentrations of mercury due to the low vapor pressure of elemental mercury and its low solubility in water and liquid hydrocarbon.
- The majority of currently used methods for removing mercury from natural gas and hydrocarbon liquids employ fixed-bed technologies. Mercury can be removed using either **regenerative adsorbents** or **nonregenerative sorbents**.

12.3. Regenerative Mercury Adsorbents

- Regenerative mercury removal processes utilize the high affinity of mercury for precious metals such as gold and silver. The relatively high cost of gold has resulted in silver being the metal of choice for the duty.
- An example of its use in practice is silver deposited on the surface of molecular sieve material (UOP HgSIV).
- The silver-coated zeolite is installed as a layer within the molecular sieve unit utilized for natural gas dehydration, saving the cost of an additional vessel and adsorbent, as well as reducing the overall pressure drop.
- In operation, the unit is used to remove both moisture and mercury from the main process stream. Then regenerated by hot regeneration gas then cooling to process temperature prior to returning the sieve to service and the mercury concentrated in the regeneration stream.
- The requirement for further processing of the regeneration stream to completely remove trace amounts of mercury leads to the molecular sieve method rarely being applied as a stand-alone system for mercury removal.

12.4. Nonregenerative Mercury Sorbents

Nonregenerative mercury removal processes utilize the chemical reaction between mercury and sulfur (or metal sulfides) which forms cinnabar (HgS), the most stable form of mercury in nature. The most common nonregenerative mercury removal processes are **sulfur-impregnated activated carbon** and **mixed metal sulfides**.

12.4.1. sulfur-impregnated activated carbon

- Sulfur-impregnated activated carbon is a proven commercial process for effectively removing the mercury from natural gas.

- In this process, a thin layer of sulfur covers the internal surface of the activated carbon. The reaction between mercury and sulfur forms nontoxic, stable mercury sulfide (HgS), which is then retained in the pores of the carbon bed.

$$\text{Hg} + \text{S} \longrightarrow \text{HgS}$$

- Activated carbon typically has a very large surface area and relatively small pore size. Both factors contribute to a higher potential for capillary condensation, leading to a free liquid phase within the system. Although there have been recent improvements in this area, this still limits the use of sulfur-impregnated activated carbon to lean and dry gas streams.

12.4.2. Mixed Metal Sulfides

- The mercury removal reaction using mixed metal sulfides (i.e., copper and zinc sulfides) is as follows:

$$\text{MS}_x + \text{Hg} \longrightarrow \text{MS}_{x-1} + \text{HgS}$$

- In these systems, the reactive metal is incorporated in an inorganic support, and the absorbent is supplied with reactive sulfide component.
- However, potential retrograde condensation will have a similar effect to the sulfur-impregnated activated carbon.
- Mixed metal sulfides are not affected by the presence of water or hydrocarbons accompanying the mercury in the gas. Therefore, the mercury removal unit may be installed upstream or downstream of dehydration/heavy hydrocarbon removal units.
- Any oxygen present in the feed gas will react with the mixed metal sulfides and reduce the capacity of the mercury removal bed.
- The nonregenerative methods require simpler systems both in construction and in operation because no regeneration equipment or special valving is required.
- At the end of life of the material, disposal of the spent sorbent can be challenging as it will contain the trapped mercury and be considered a hazardous waste.

12.5. Mercury Removal from Natural Gas

There are four possible options for mercury removal from the feed gas, as described below:

Option 1: Installing a mercury removal unit utilizing a nonregenerative sorbent at the plant inlet, upstream of the AGRU. This option removes all the mercury and ensures no contamination in any downstream processing units. The system is simple both in construction and operation. Although potentially larger volumes of sorbent are required due to the large volumetric flow of feed gas (including acid gases), this does not affect in any way the process or the absorbent and the overall plant performance.

Option 2: Installing a mercury removal unit utilizing a nonregenerative sorbent downstream of the AGRU and upstream of the molecular sieve unit. This option reduces the size of the beds to some extent (as the stream being treated does not include the acid gases). It does not eliminate the risks of mercury contamination in the AGRU solvent.

Option 3: Installing an additional layer of a special, regenerable silver-impregnated mercury sieve section to the molecular sieve beds. This option can operate to remove water and mercury at the same time without a separate mercury bed. It does, however, present problems with a high mercury content in the regeneration stream and the condensed water that would pose operating hazards, unless treated by another mercury removal step. Other considerations would be the regeneration system and the additional size requirement for the molecular sieve bed.

Option 4: Installing a mercury removal unit utilizing a nonregenerative sorbent after the molecular sieve unit. This option yields good mercury removal performance However, in this case, mercury contamination in the AGRU and other upstream units can still occur and may pose operating hazards.

13. Nitrogen Rejection and Helium Recovery

- Nitrogen (N_2) may naturally occur in high concentration in certain gas production fields. Approximately, 15% of the non-associated gas reserves in the world are high in nitrogen content and would not meet the specification for normal pipeline quality gas (typically 3- 4 mol%).
- Nitrogen, being an inert gas, will not support combustion. So, when a gas with too much nitrogen is burned, it may lead to unstable combustion. When high nitrogen gas is processed in a gas plant, recovery of NGL content will be reduced as nitrogen will act as a stripping gas. Additional nitrogen content will increase the compression equipment and size of the transmission pipeline. In an LNG plant, high nitrogen is not desirable as it lowers the LNG temperature, increasing the power for natural gas liquefaction, in addition to increasing the quantity of boil-off gas from the LNG storage tanks.
- In production areas where nitrogen injection is used for enhanced oil recovery, nitrogen content in the produced gas will gradually increase over time as nitrogen breaks through from the injection wells to the producing wells.
- Nitrogen rejection methods can be classified into **cryogenic** and **noncryogenic processes**.
- In some cases, natural gas rich in nitrogen contains a relatively high concentration of helium (He), which may improve the gas plant economics by adding a helium recovery unit (HeRU). Helium is a unique gas and is in high demand, commanding high values in the gas market.

13.1. Cryogenic Processes

- Cryogenic nitrogen rejection technology, which is the most common method of removing nitrogen from natural gas, uses the difference of boiling points between nitrogen and methane for separation.

- Cryogenic processes use Joule-Thomson (JT) cooling of the high-pressure gas and separation in a distillation column to produce a nitrogen overhead product and a methane-rich bottom.
- The nitrogen product contains 1 mole% or lower methane content, which minimizes the greenhouse gas impact, and can be discharged to the atmosphere.
- The methane rich bottom can contain 1 to 3 mole% nitrogen that can meet the typical natural gas pipeline specifications.
- Cryogenic processes are proven processes to process natural gas containing more than 5 to 10 mole % nitrogen with gas flow rates ranging from 30 MMscfd up to 900 MMscfd.

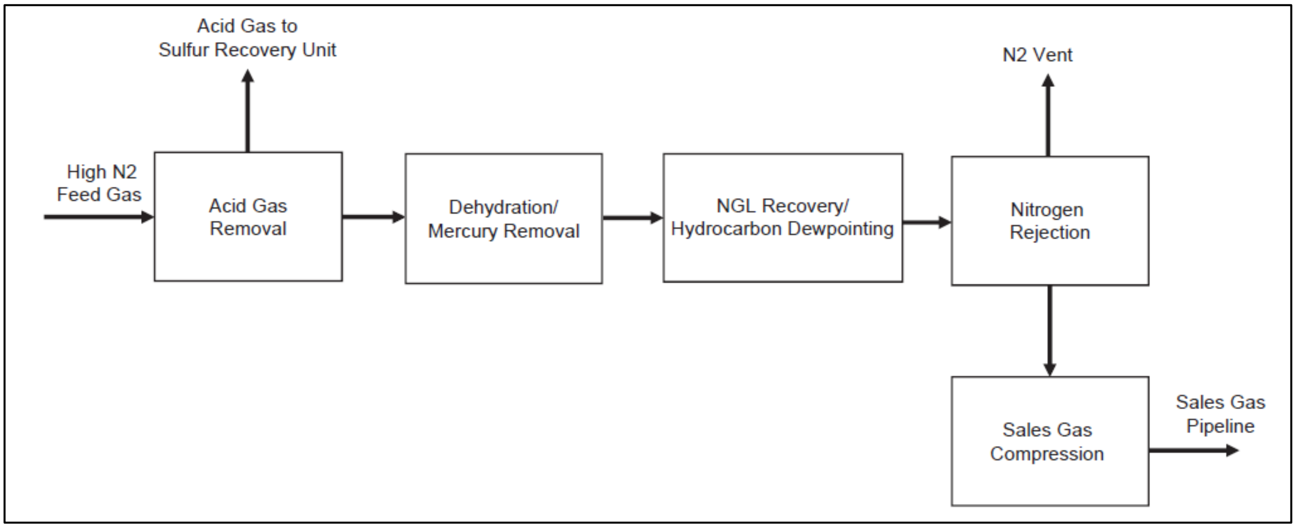
13.2. Noncryogenic Processes

- Noncryogenic nitrogen separation processes include mainly **pressure swing adsorption (PSA)** and **membrane separation**.
- PSA uses a zeolite adsorbent to selectively separate nitrogen from methane in a cyclic process. The adsorbent can be regenerated with a combination of pressure and thermal changes.
- PSA technology is limited in capacity and can typically handle 2 to 15 MMscfd gas flow rate. The drawback of this process is that natural gas is produced at low pressure requiring recompression to pipeline pressure.
- Also, the hydrocarbon content in the rejected nitrogen is significant which represents a production loss, and will contribute to significant carbon emissions if vented to atmosphere.
- In membrane process, the feed gas is compressed and passed across the surface of the membrane elements. It separates the hydrocarbon permeate which is compressed back to the pipeline pressure, while the nonpermeate, nitrogen-rich waste gas can be used as fuel. Membrane can handle small flow rates varying from 0.5 to 25 MMscfd.

- The membrane units are compact and can be supplied in modules, suitable for offshore installation.
- However, membrane separation systems would require feed gas pretreatment such as aromatics removal and dew point depression to remove impurities that may cause damage to the membrane.
- Membrane has the same drawback as PSA process, that is, the hydrocarbon losses in the nitrogen waste stream is relatively high, and will contribute to greenhouse gas emissions if vented to atmosphere.
- PSA and membrane separation methods are limited in commercial applications and have not found acceptance, especially for larger NRUs.

13.3. Nitrogen Rejection Integrated with Natural Gas Liquids Recovery

- Since NRU operates at cryogenic temperatures, the feed gas pretreatments as shown in Figure below are required.



Nitrogen rejection integration with NGL recovery.

- Pretreatment generally consists of an amine scrubbing unit to remove carbon dioxide (CO_2) and hydrogen sulfide (H_2S), and a molecular sieve unit for removal of water, mercaptans and undesirable contaminants.

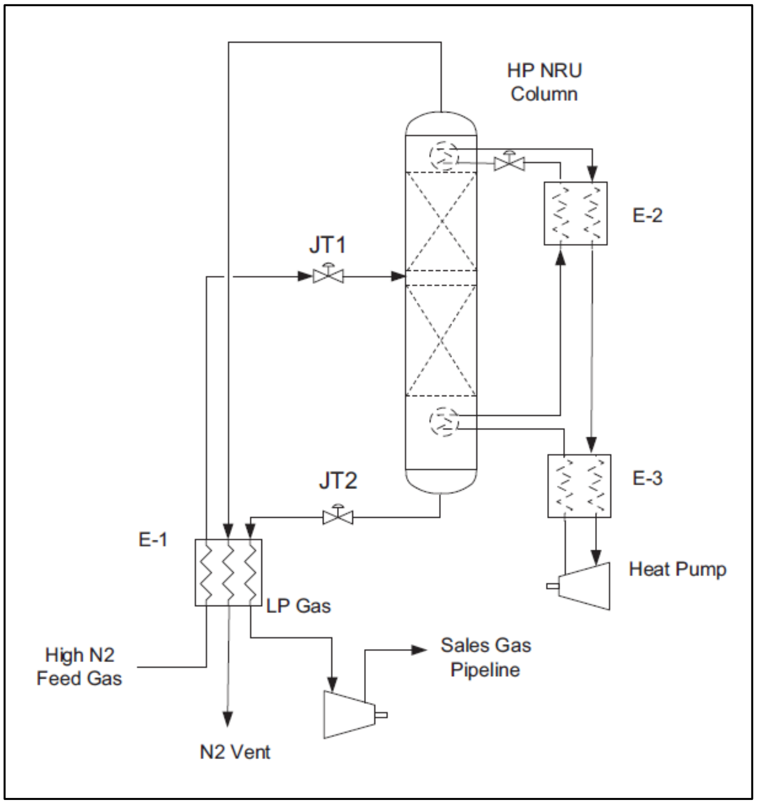
- Mercury removal bed may also be necessary if the gas shows presence of mercury.
- The feed gas to a nitrogen rejection unit must be depleted of the heavy hydrocarbons, typically C4+ hydrocarbons, as the presence of the heavier components will result in freezing in the column overhead that operates at cryogenic temperature.
- For rich gas streams, an NGL recovery unit is located downstream of the dehydration unit. This unit ensures removal of most of the C_3^+ hydrocarbons, producing a lean gas depleted of heavier hydrocarbons. For lean pipeline gas sources with low C_4^+ contents, a hydrocarbon dew pointing unit can be used.
- The residual C_4^+ hydrocarbons, benzene, toluene, ethylbenzene and xylene (BTEX) and heavier components can be removed in the feed chilling exchanger of the NRU.
- In the nitrogen rejection unit, the inclusion of a feed separator, will condense most of CO_2 and heavier hydrocarbons, bypassing the fractionation column. This design will avoid heavy hydrocarbons from reaching the NRU column.
- For conventional feed gas, the NRU unit is more efficient when integrated with an NGL recovery unit as the lean gas requires less compression and produces a nitrogen reject stream low in hydrocarbons content, which would minimize carbon emissions. For a lean gas, a deep hydrocarbon dew pointing unit may also be used, provided a downstream separator integrated in the cold box, to remove these components, avoiding heavy hydrocarbon losses in the nitrogen vent gas.

13.4. Cryogenic Nitrogen Rejection

Several cryogenic distillation schemes are known to reject nitrogen from natural gas stream. The state of the art of cryogenic nitrogen rejection processes are single column process, double-column process, and two-column process. These processes vary in complexity and efficiency.

13.4.1. Classical Single-Column Design

- The classical single-column nitrogen rejection process uses a heat pump to provide the reflux duty and reboiler duty of the fractionation column, as shown in Fig. below.



Single-column nitrogen rejection process.

- The single column typically operates between 300 and 400 psig. Methane can be used as the working fluid that is compressed to supply the reboiler heating duty, condensed and then evaporated at low pressure providing the condensation duty.
- Brazed aluminum heat exchangers (BAHXs) are used to achieve a close temperature approach required by the process. Feed gas is typically supplied at 800 to 1000 psig.
- The gas is chilled by several effluent streams and then letdown in pressure to the high pressure (HP) column in a JT valve, JT1. The column produces a nitrogen overhead vapor, and a bottom methane-rich liquid. The column bottom is letdown in pressure using valve JT2, providing further chilling to heat exchanger E-1.

- The low pressure (LP) gas is then compressed to the sales gas pressure. Due to the large boiling point difference between nitrogen and methane, sharp separation of nitrogen from methane is feasible.
- Typically, the single-column design can produce a nitrogen overhead product with less than 1% methane and a methane bottom product with less than 1 mol%

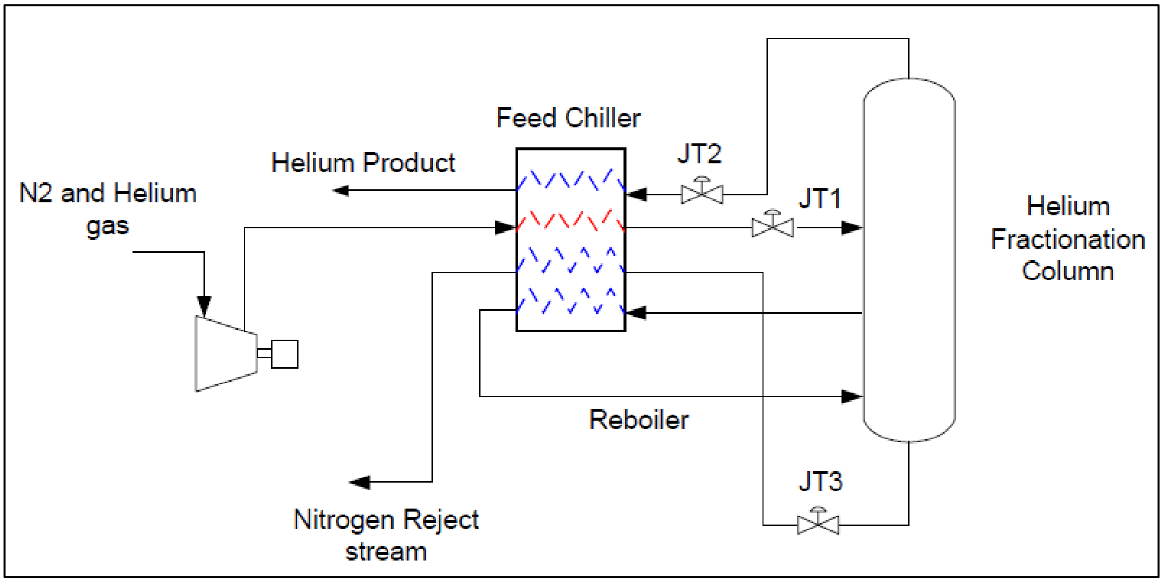
13. Helium Recovery

- Helium is found in natural gas, typically in concentrations from a few parts-per-million up to a few percent in certain fields.
- The helium is the result of radioactive decay of thorium and uranium in granite near the reservoir.
- Only a few natural gas fields world-wide have high enough helium content that can be considered to be economical viable for extraction.
- When the feed gas contains higher than 0.5 vol% helium content, it may be economical to justify helium recovery.
- Depending on the applications, helium recovery product purity specification can vary; from low purity about 50% to 99.99 % purity.

13.1. Helium Recovery Unit

- A typical helium recovery unit is shown in Fig. below.
- Feed gas is compressed to a higher pressure and chilled in the feed chiller exchanger to the cryogenic temperature.
- The feed chiller is a brazed aluminum exchanger or equivalent exchanger which can achieve a close temperature approach, such as 2 °F.
- A very close temperature design is required due to the cryogenic operating temperatures operation.

- The chilled gas is letdown in pressure in valve JT-1 and is chilled. The chilled gas is fractionated in the helium fractionation column, which uses the feed gas for reboiling.



Helium recovery unit.

- The refrigeration process is provided by JT expansion of the bottom stream via valve JT3, and overhead vapor stream via valve JT2, in addition to the reboiler.
- There are other separation processes that can be considered, such as **PSA or membrane system.**
- PSA and membrane are bulk removal system, and the recovery levels in a single pass operation can be 50 to 80%, depending on the feed gas composition.
- To improve recovery and purity, multiple units operating in series are required.
- There are other innovative schemes, such as hybrid membrane and cryogenic system.