Contaminant Removal from Natural Gas Liquid Streams
UOP Adsorbent Solutions Help Remove Contaminants from Natural Gas Liquid Streams
NATURAL GAS LIQUIDS

Contaminant removal from NGL streams

Natural gas liquids (NGLs) include ethane, propane and butane and other heavier hydrocarbons that make up natural gas. NGLs are valuable as separate products, and it is critical to remove contaminants from these streams, which either reduce their market value or compromise reliability of downstream catalytic processes and equipment. Gas plant operators experience new and sometimes unique challenges as they source feed gas from unconventional resources or from aging wells. Some of the concerns posed by contaminants in NGL streams are:

• Meeting strict specifications for NGL products
• Mitigating health, safety, and environmental hazards within the gas plant as well as in downstream pipelines and equipment
• Preventing corrosion and equipment reliability issues
• Maintaining catalyst life and activity at downstream processing facilities

Common contaminants found in NGL streams are:

• Water
• Sulfur Compounds
  - Sulfides
    • Hydrogen Sulfide (H₂S)
    • Carbonyl Sulfide (COS)
    • Carbon Disulfide (CS₂)
    • Organic Sulfides and Di-sulfides
    - Mercaptans species
• Oxygenates
  - Alcohol (methanol and isopropanol)
  - Other oxygenates (glycols, ethers, aldehydes and ketones)
• Mercury
• Contaminants seen in unconventional and/or pipeline feed gas
Adsorbents for contaminant removal from NGL

UOP has offered a variety of contaminant removal solutions to the natural gas industry for more than 60 years.

Our portfolio of regenerative and non-regenerative adsorbents specially designed and formulated for contaminant removal from NGL streams include zeolite molecular sieves, modified activated aluminas and non-regenerative metal oxide/sulfide products.

Zeolite molecular sieves are uniform microporous crystalline adsorbents which adsorb molecules based on their size and polarity. Zeolites have a strong affinity for polar molecules and demonstrate a selective preference for polar molecules relative to their degree of polarity. The combination of size and polarity-based selective removal makes zeolite molecular sieves an ideal option for removing contaminants from NGL streams. A majority of contaminants found in these streams, such as water, light mercaptans and low molecular-weight oxygenates, can be removed using molecular sieves.

Activated alumina adsorbents are synthetically-produced transitional-phase aluminas. These aluminas exhibit lower crystallinity compared to zeolites and have a non-uniform pore distribution and structure. Contaminant removal capacity of the alumina adsorbent depends on the ability of the activated alumina to effectively chemisorb contaminants, in addition to the polarity of the contaminants. Capacity also depends on the surface activity of the alumina, which is carefully tailored using special manufacturing techniques. Contaminants like COS and H₂S are thus effectively chemisorbed and removed from the NGL stream using activated alumina adsorbents.

Guard bed adsorbents are high capacity, non-regenerative metal oxides or sulfides for removing mercury (Hg), hydrogen sulfide (H₂S) and carbonyl sulfides COS to parts per billion (ppb) levels in NGL streams. These adsorbents are carefully formulated with a pore structure designed to maximize mass transfer and enable high contaminant removal capacity.
Mercury is commonly found in natural gas in varying concentrations. Many NGL plants require mercury removal upstream of cryogenic processing to avoid corrosion damage to aluminum metallurgy in the cryogenic section of the plant and the potential for catastrophic failure.

Various NGL fractionation facilities source their feedstocks from “Y grade” NGL pipelines that collect NGL products from multiple gas plants and condensate units. This common stream is then separated into C_2, C_3, C_4 and heavier fractions at the fractionation plant. Insufficient upstream mercury removal (in feeder gas plants) leads to mercury contamination of the C_2, C_3, C_4 and heavier streams. Mercury-contaminated NGL streams:

- Adsorb or form amalgams with equipment metallurgy, copper and aluminum internals
- Are a known poison for noble metal catalysts and thus limit the use of contaminated NGL streams in downstream processes
- Are traded at a discount thereby reducing profitability

**UOP SOLUTIONS:** Regenerative options: UOP HgSIV™ 3 or UOP HgSIV 1

Sulfur compounds naturally occur in natural gas as sulfides, disulfides or mercaptans. Given the various types of sulfur compounds and their chemical characteristics, customized removal techniques are needed, since no one treatment technique is sufficient for all types of sulfur compounds in NGL streams. Sulfur compounds pose operational, corrosion, environmental and marketing challenges for NGL plants. Sulfur contaminants found in NGL streams include:

Mercaptans pose not only corrosion concerns but also specification challenges for NGL producers. High mercaptan content increases the total sulfur in the stream which is commonly limited by a sale specification.

**Sulfur**

Sulfur compounds are sometimes used to remove H₂S from NGL streams. These are liquid tertiary or quaternary amines which react with H₂S to form a thermally-stable salt. These salts travel with the NGL streams and pose contamination risk for downstream processing.

**UOP SOLUTIONS**: Regenerative options: UOP RK-29, UOP RK-29HP
Non-regenerative options: UOP GB-417 and UOP GB-420 Adsorbents

**Hydrogen sulfide** (H₂S) is usually treated upstream in natural gas treatment processes using liquid amine based scrubbing systems. Natural gas plants limit H₂S content to below 1ppm in the dry gas feed to NGL recovery. However, H₂S can sometimes be found in NGL streams which can cause corrosion issues and failure to meet established NGL product standards.

A common test method for H₂S corrosivity is ASTM D 1838 (12-A), for copper corrosion potential of the stream. Copper corrosion test results of >1a are considered off-spec.

**UOP SOLUTIONS**: Regenerative options: UOP RK-29 II, UOP RK-29 and UOP RK-29HP Adsorbents

Carbonyl sulfide (COS) can be present in the feed natural gas or could be formed on the molecular sieve surface due to the catalytic activity of the zeolite. UOP offers liquid solvent technology for selective removal of COS from natural gas, upstream of natural gas drying. UOP also offers its COSMIN series of molecular sieves to reduce COS formation on the molecular sieve surface.

COS that is not removed upstream fractionates with the cryogenically-separated C₃ NGL stream. COS gets hydrolyzed on contact with trace water contamination in pipelines, leading to the formation of H₂S and CO₂, which pose operational and marketing challenges for the NGL streams.

**CONTAMINANTS**
As mentioned, propane, butane, and mixed LPG streams can be treated to meet industry specifications for dryness, volatile sulfur and petrochemical feedstock purposes in a single molecular sieve process unit. Most units treat propane or butane streams separately, but the process principles are the same for mixed LPG streams, as well as NGL streams.

**Steps in the Treating Process**

The flow sheets in figure 1 show a typical process for a 2-bed molecular sieve system. While one bed is adsorbing (treating), the other is being regenerated. Typical steps in the process are listed below.

1. **Treating (Fig. 1A)**
   
   Liquid feed, flowing either up or down (upflow is preferred) travels through a molecular sieve bed. To maintain liquid phase flow sufficient feed pressure should be applied (e.g., typically 15-20 bara for propane). The molecular sieve, based on its adsorption selectivity, first removes water and then the most strongly adsorbed oxygenates/sulfur compounds (methanol, mercaptans, hydrogen sulfide, carbonyl sulfide). The quantity of molecular sieve required depends on the amount and type of contaminants in the feed stream, and process design variables.

2. **Drain (Fig. 1B)**
   
   After the adsorption step, typically ranging from 8 to 24 hours, the beds are switched and, by using a pad gas, the liquid is drained downward from the bed being taken off line. Drained liquid may be sent to the product storage unless upflow treating is being carried out, in which case the liquid must be recycled to the feed.

3. **Depressurize**
   
   After draining, the vessel must be depressurized to the heating gas pressure. This is done at the same time that the heating step is started – usually it will be in the same flow direction as heating, and pressure changes should be limited to 3.5 bar/minute maximum. During the depressurization step, liquid held on the bed flashes, and the effluent lines of the vessel may become noticeably colder.
4. Heating (Fig. 1C)
To regenerate the molecular sieve, a sweet, dry fuel gas at moderate pressure is generally used, flowing countercurrent to the adsorption step. Temperature and flowrate depend on the quantities of water and other contaminants to be removed, on the hydrocarbon stream being treated, and the quality of the regeneration gas. Typical operating conditions fall in the ranges of 3-20 bara and 230-290 °C inlet to the bed. The regeneration gas usually is cooled and returned to the plant fuel gas system.

5. Repressurization
Repressurization is required after heating if the liquid product is to be used for cooling. It can follow the cooling step if ambient temperature purge gas is employed for cooling. Repressurization with product liquid actually occurs as the first part of the cooling step. A slipstream of product liquid for cooling is slowly bled into the hot molecular sieve bed. As the liquid flashes, the vessel is represurized to the treating pressure.

6. Cooling and Filling (Fig. 1D)
Liquid product from the on-stream treater is usually used for cooling, with the flow concurrent to the treating step. Cooling takes place as the liquid flashes upon contact with the hot bed, and continues as a liquid level builds in the bottom of the vessel. Effluent cooling vapor condenses in a cooler before blending into the product stream. With down-flow treating, the entire vessel must be filled with liquid before switching in order to drive all the gas from the void spaces. This ensures that no channeling occurs from a two-phase flow. This problem can be avoided in up-flow adsorption.

Purge gas also can be used for cooling, after which the product liquid is bled into the bed to represurize. When the cool and fill step is complete, the beds are switched, and treating starts on the cooled bed. The vast majority of process units use a liquid product slipstream for cooling the bed.
System Design
Proper system design is, of course, imperative in any critical process area. This is particularly true of hydrocarbon product treating. This is the last step in processing before the product is shipped to the customer. A sound design basis must be established for optimum system performance, and the adsorption unit design must be considered by the producer or primary contractor in the early stages of project planning to insure getting the best overall process package.

UOP sizes the beds and vessels for product treaters, as well as other molecular sieve treating or dehydration systems. Table 1 lists the process data that should be prepared for the design basis.

When there are several adsorption systems in the plant, their designs should be considered at the same time, to get the benefit of any possible system integration. For example, UOP has designed systems with different adsorption units using a common regeneration gas heater. This both reduced regeneration gas requirements and capital equipment costs.

Effects of Variables on Treating Process
The section below gives a better understanding of the importance of the different process variables, and how they may affect the system’s design and operation.

Temperature Effects
At the same partial pressure, the lower the temperature the greater the capacity of the molecular sieve for a given contaminant (isotherm behavior). A major increase in capacity can be achieved just by operating at a lower temperature, this is especially true when removing low polarity contaminants like COS.

TABLE 1 – Process Design Data Required for an LPG/NGL Treater

<table>
<thead>
<tr>
<th>ADSORPTION</th>
<th>REGENERATION</th>
<th>MISCELLANEOUS DATA</th>
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<tbody>
<tr>
<td>• Flowrate</td>
<td>• Type and maximum flow and temperature of available regeneration gas</td>
<td>• Available equipment (if any)</td>
</tr>
<tr>
<td>• Temperature</td>
<td>• Pressure</td>
<td>• Special considerations for your process</td>
</tr>
<tr>
<td>• Pressure</td>
<td>• Contaminants to be removed (i.e. H₂O, H₂S, COS, C₂SH, C₂SH, etc.)</td>
<td></td>
</tr>
<tr>
<td>• Feed composition</td>
<td>• Contaminant concentration</td>
<td></td>
</tr>
<tr>
<td>• Contaminants to be removed</td>
<td>• Required effluent specification</td>
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</table>
Concentration Effects
As the concentration of a contaminant increases, the adsorption capacity increases. Thus, as the inlet sulfur concentration to the unit varies, the loading capacity of the molecular sieves also will vary. This self-compensating effect will permit satisfactory treating in cases of fluctuating inlet contaminant concentrations.

Co-adsorption Effects
Other adsorbable compounds in the stream such as unsaturated hydrocarbons can hamper adsorption of a contaminant that is to be removed. For this reason, a detailed feed composition is needed in order to properly design the system.

Residual Moisture Effect
Residual moisture on the molecular sieve will adversely impact on it’s capacity to adsorb lower polarity contaminants. Therefore, whenever possible, use a bone-dry regeneration gas. When a water-free regeneration gas is not available, a change in the molecular sieve may be justified to optimize performance.

Summary
It has been demonstrated that over the past decades UOP adsorbents have offered an economical and relatively maintenance free method for treating and drying liquid hydrocarbon streams. In particular, UOP’s adsorbent portfolio breadth, strong process knowledge and experience ensure a safe and trouble free solution for your liquid phase treating needs.
UOP is a leader in developing and implementing adsorbent solutions for contaminant removal in the oil and gas industry. UOP developed the first commercialized zeolite molecular sieve application and continues to commercialize a range of innovative and advanced adsorbent removal technologies. With more than 2,100 total active patents worldwide, our research and development efforts continue to drive important advances in the oil and gas industry.

Backed by strong research and development support, UOP’s adsorbent Sales Technical Support (STS) team provides experienced advisors supported by a troubleshooting team. UOP’s STS team supports 1,000 customers in nearly 100 countries around the globe. We maintain this reach through our regional service centers in Houston (USA), Antwerp (Belgium), Dubai (UAE), Kuala Lumpur (Malaysia), Dhahran (Kingdom of Saudi Arabia), Moscow (Russia) and Shanghai (China).

UOP’s STS team is committed to providing service designed to advise you about pre-startup problems, get you on-stream faster and keep your operation running at peak performance.

Call your UOP representative to assist you in:

**Pre-Application Support**
- Adsorption process design
- Review existing unit designs for improved operation with UOP adsorbents
- Vessel inspection, loading and start-up assistance

**Performance Evaluations**
- Contaminant analysis in feed and product streams
- Adsorption cycle and regeneration optimization
- Performance life projection
- Spent adsorbent analysis

**Troubleshooting**
- Simulation studies on operating plants
- Troubleshooting operating issues with unit surveys, performance evaluations and shutdown experience
UOP ADSORBENTS

Decades of experience responding to your commercial needs

Count on UOP to provide reliable, high-performing products with low life-cycle costs and continuous product renewal to meet the changing needs of your business.