SYLOBEAD® Adsorbents for Natural Gas Processing

Introduction

Natural gas (NG) is a vital component of the world's supply of energy. It is one of the cleanest, safest, and most versatile of all energy sources.

Raw natural gas is not only saturated with water, but also contains acid gas components such as CO₂, H₂S and other sulphur compounds in varying concentrations, depending on the source.

Therefore, it is often necessary to condition the raw gas to:

- adjust the composition to the required market standards (sales gas)
- recover its by-products (e.g., condensates, NGL - Natural Gas Liquids)

Since the early 1950s, the natural gas industry has utilized solid adsorption materials such as silica gels, molecular sieves and aluminas for dehydration and purification of various product streams.

Grace has a long history of developing, producing and marketing various types of zeolites and silica gels for both industrial scale adsorption and catalyst applications.

SYLOBEAD® molecular sieve and silica gel products have been used successfully in natural gas processing for many years. Our product portfolio includes several products of beaded and granular silica gels, beaded molecular sieves and ceramic balls (for support layers).

Key natural gas applications for the use of SYLOBEAD® include:

- Drying
- Contaminant removal
- Sweetening
- Adsorber bed protection
- Dewpointing

This Technical Information document focuses on the different applications of molecular sieves and silica gels in the natural gas industry.
SYLOBEAD® – The Products

SYLOBEAD® Molecular Sieves
Zeolite molecular sieves are crystalline, highly porous materials belonging to the class of aluminosilicates. The crystals are characterized by a three-dimensional pore system, with identical pores of precisely defined diameter. This structure is formed by tetrahedras of \((\text{AlO}_4)\) and \((\text{SiO}_4)\), which are the basic building blocks for various zeolite structures, such as zeolite types A and X, the most common commercial adsorbents.

Due to the presence of alumina, zeolites have a negatively charged framework, which is counter-balanced by positive cations. These cations can be exchanged to fine tune the zeolite’s pore size or adsorption characteristics. For instance, the sodium form of zeolite A has a pore opening of approximately 4 Ångstrom, called 4A molecular sieve.

Adsorption takes place at the precisely dimensioned micro-pores of the zeolite crystals. The size of these pores plays a significant role: it allows or hinders the entrance of molecules into the pore system, effectively acting as a molecular sieve.

Due to their hydrophilic surfaces, zeolites preferentially adsorb polar or polarizable molecules. They have an extremely high adsorption capacity for such components, even at very low concentrations.

Zeolite crystals are mixed with a clay binder in order to form beads. The binder ensures a number of important characteristics of the final adsorbent bead:

- The right diffusion pore structure
- High mechanical stability
- Low catalytic activity

The adsorption is fully reversible. Molecules that have been adsorbed can be released at high temperature and/or reduced pressure or concentration in the regeneration phase.

The main applications for molecular sieves in natural gas processing are:

- **Drying**
  - Water outlet concentrations of 0.1-1 ppm are achievable
- **Sweetening**
  - Hydrogen sulphide, carbonyl sulphide, mercaptans (RSH) removal
- **Contaminant removal**
  - Carbon dioxide, nitrogen, hydrocarbons and oxygenates removal

Below is a summary of Grace’s most common products for different applications. A complete product overview can be found in our SYLOBEAD® portfolio leaflet.

### SYLOBEAD® Molecular Sieve Portfolio

<table>
<thead>
<tr>
<th>Main Applications</th>
<th>Specific Properties</th>
<th>Type</th>
<th>Average Particle Size</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dehydration and purification of natural gas, LPG and other industrial gases</td>
<td>High selectivity, good mass transfer, low pressure drop</td>
<td>4A</td>
<td>4.0 mm</td>
<td>SYLOBEAD® MS 512 Molecular Sieve</td>
</tr>
<tr>
<td>Dehydration and purification of natural gas</td>
<td>Low lost bed mass, low pressure drop</td>
<td></td>
<td>4.0 mm</td>
<td>SYLOBEAD® MS 512 NGD Molecular Sieve</td>
</tr>
<tr>
<td>Sweetening</td>
<td>Strong COS minimization</td>
<td>5A</td>
<td>2.0 mm</td>
<td>SYLOBEAD® MS C 534 Molecular Sieve</td>
</tr>
<tr>
<td>Removal of CO/CO₂/H₂S and other impurities from hydrogen and other gases</td>
<td>High adsorptivity for several impurities, suitable for thermal regeneration</td>
<td>5A</td>
<td>2.0 mm</td>
<td>SYLOBEAD® MS C 522 Molecular Sieve</td>
</tr>
<tr>
<td></td>
<td>High adsorptivity for several impurities, suitable for pressure swing units</td>
<td>5A</td>
<td>2.0 mm</td>
<td>SYLOBEAD® MS S 624 Molecular Sieve</td>
</tr>
<tr>
<td>Removal of oxygenates and other impurities from air, isomerization feed and other gases; Sweetening of LPG (mercaptan removal)</td>
<td>High adsorption capacity for water, CO₂, oxygenates and higher mercaptans</td>
<td>10A (13X)</td>
<td>2.0 mm</td>
<td>SYLOBEAD® MS 544 Molecular Sieve</td>
</tr>
</tbody>
</table>
|                                                                                                |                                                                                   | 10A (13X) | 4.0 mm | SYLOBEAD® MS 542 Molecular Sieve
**SYLOBEAD® Silica Gels**

Silica gel is a porous, amorphous form of silica (SiO₂). Although it has the same chemical composition as sand, silica gel is radically different from other SiO₂-based materials, due to its unique internal structure.

The internal structure of silica gel is composed of a vast network of inter-connected microscopic pores that attract and hold water, alcohols, hydrocarbons and other chemicals on their surface through phenomena known as physical adsorption and capillary condensation. These phenomena can be reversed by changing the conditions under which adsorption takes place, a process called regeneration.

Unlike zeolites, silica gels have larger pores with a wide range of diameters – typically between 5 Å and 300 Å – and do not allow for the separation of molecules by size alone.

Under certain operating conditions, the adsorption capacity of silica gel may be higher than molecular sieves due to the higher internal pore volume.

This, together with other properties, such as chemical inertness, high purity and mechanical stability, makes silica gel a widely used adsorbent material in natural gas processing, often in combination with molecular sieves and aluminas.

Silica gel may be used for the following applications:

- **Drying**
  - When adsorption capacity is greater than molecular sieve for the specific operating conditions
  - When the required water outlet concentration is not very low
- **As buffer layer for adsorber bed protection**
- **In dewpointing or hydrocarbon recovery units**

Grace silica gels are available as granules or beads (SYLOBEAD®) in various particle size distributions. An overview of all available products can be found in the SYLOBEAD® product portfolio leaflet. The most important products are shown in the table below.

### SYLOBEAD® Silica Gel Portfolio

<table>
<thead>
<tr>
<th>Main Applications</th>
<th>Specific Properties</th>
<th>Particle Shape</th>
<th>Type</th>
<th>Average Particle Size</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dehydration and purification of gases</td>
<td>Good mass transfer</td>
<td>narrow porous</td>
<td>4.5 mm</td>
<td>SYLOBEAD® SG 127</td>
<td>Silica Gel</td>
</tr>
<tr>
<td>Hydrocarbon dewpointing</td>
<td></td>
<td>macro porous</td>
<td>4.5 mm</td>
<td>SYLOBEAD® SG 59</td>
<td>Silica Gel</td>
</tr>
<tr>
<td>Liquid carryover adsorption</td>
<td>Unique protection properties, applicable for buffer layers</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dehydration and purification of gases</td>
<td>Dehydration, low dust and attrition, low pressure drop</td>
<td>narrow porous</td>
<td>3.2 mm</td>
<td>SYLOBEAD® SG B 127</td>
<td>Silica Gel</td>
</tr>
<tr>
<td>Hydrocarbon dewpointing</td>
<td>High adsorption rates</td>
<td>macro porous</td>
<td>3.2 mm</td>
<td>SYLOBEAD® SG H 127</td>
<td>Silica Gel</td>
</tr>
<tr>
<td>Liquid water adsorption</td>
<td>Unique protection properties, applicable for buffer layers</td>
<td></td>
<td></td>
<td>SYLOBEAD® SG W 127</td>
<td>Silica Gel</td>
</tr>
</tbody>
</table>
SYLOBEAD® – The Applications

Natural Gas Drying
Dehydrating raw natural gas in order to meet sales gas specifications and transmission pipeline specifications (typically 30 - 110 mg/Sm³) can be achieved with:

- Glycol dehydration units
- Adsorption units with silica gels or aluminas
- Molecular sieve dehydration units

Dehydration of natural gas for downstream cryogenic processing (e.g., liquefaction plant for LNG production) calls for more stringent water vapour concentrations, typically in the range of 0.1 - 1 ppm. This specification can be met by using molecular sieve adsorbers, either downstream of the silica gel adsorbers or glycol dehydration units, or completely replacing these units.

Typically, silica gel units can economically outperform glycol dehydration units, where large and fluctuating flow rates (summer and winter conditions) and/or changes in the gas composition are expected. Both conditions are typical for the gas supply chain, making gas processing more difficult, especially at ageing gas fields. The main performance benefit of silica gel units is attributed to the fact that silica gel adsorbers can be operated in a much more responsive mode to feed gas changes without extensive unit revamping.

Modern natural gas processes, such as expander technology and cryogenic separation used for LNG production and NGL extraction, require a low level of water, typically < 1 ppm, which can only be achieved with zeolitic adsorption technology.

The SYLOBEAD® 4Å molecular sieve adsorbent is the most widely used Grace adsorbent for natural gas drying, covering more than 90% of all NG and NGL drying applications.

To meet the growing demand for longer cycle times and longer unit life, Grace has recently launched an improved version of its long established 4Å molecular sieve.

The new SYLOBEAD® MS 512 NGD and MS 514 NGD products offer superior performance compared to standard 4 Ångström grades:

- Excellent kinetics
- High crush strength
- Low attrition

Contaminant Removal
When NG and NGL contain reactive compounds from the gas well, such as H₂S, CO₂, COS and RSHs, or olefins recycled from downstream process units, and the product gas specification does not allow any contaminant spikes, SYLOBEAD® 3Å type molecular sieves are recommended.
**Natural Gas Sweetening and NGL Sweetening**

Processing of natural gas streams that are contaminated with sulphur compounds is becoming more common to the natural gas industry. Several gas sweetening technologies have been developed, one of which uses 5A and 13X type molecular sieves.

The molecular sieves can be used in stand-alone units or in combination with other sulphur compound removal technologies acting as a final polishing step, for example when very low sulphur levels of <1 ppm for each sulphur compound are required. The composition of sulphur compounds in the natural gas feed together with the final outlet product specification will determine the selection of the most appropriate 5A and/or 13X SYLOBEAD® product application.

**Adsorber Bed Protection**

Adsorber beds in natural gas industrial processing operations might be exposed to liquid water and liquid hydrocarbons carried over from upstream units, or formed in the pipeline through condensation.

Since liquids would severely damage the first adsorbent layers close to the inlet of the vessel, guard beds are used to protect the bed. The function of the guard bed is to pick up these free liquids, thus protecting the following adsorbent layers.

Macroporous SYLOBEAD® silica gel has excellent pick-up capacities for free water and heavy hydrocarbons and glycols. The removal of free water carryover from upstream by macro-porous gel minimizes the potential for formation of carbonic or sulphuric acid, which could otherwise damage molecular sieve beds.

**Dewpointing or Hydrocarbon Recovery**

Besides water, in most cases natural gas streams also carry heavy hydrocarbons (C6-plus) that have the tendency to condense, depending on the operating conditions.

Together with the product gas, a two-phase flow will be formed, which not only causes malfunctions to the pipeline system due to slugs of liquids, but also leads to fouling and plugging of major equipment.

Silica gel has a high adsorption capacity for both water and heavy hydrocarbons, with preference for the more polar adsorbates (i.e., water and heavier hydrocarbons will be picked up first). Depending on the water/hydrocarbon ratio, the silica gel adsorber bed will simultaneously retain water and heavier hydrocarbons.

To ensure that the target impurity levels in the product gas can be met continuously, before breakthrough at the outlet of the adsorber bed, the feed gas has to be switched to a freshly regenerated bed, and the saturated adsorber has to be thermally regenerated. This can be accomplished by passing a hot flow of feed or product gas through the bed.

Due to the temperature increase, the bed loses its affinity towards adsorbates and releases the impurities into the gas flow, which acts as a regeneration fluid. After completion, the adsorber bed will be cooled down, regaining its adsorption capacity. The unit is now ready for the next cycle.

**SYLOBEAD® – Further Info**

For more information on products and applications, please don’t hesitate to contact our global Technical Customer Service (TCS) team, who will be more than happy to guide you through our product portfolio.

Several of our products are used for other purification processes; please refer to our SYLOBEAD® technology brochure for more information.
Grace is a leading global supplier of catalysts; engineered and packaging materials; and, specialty construction chemicals and building materials. The company's three industry-leading business segments – Grace Catalysts Technologies, Grace Materials Technologies and Grace Construction Products – provide innovative products, technologies and services that enhance the quality of life. Grace employs approximately 6,000 people in over 40 countries.

Grace has met all REACH requirements for the given deadline for Tier 1, December 1, 2010, and can hereby assure today's and future customers full REACH compliance of its products. This assurance also includes the very diverse use of a spectrum of our products.