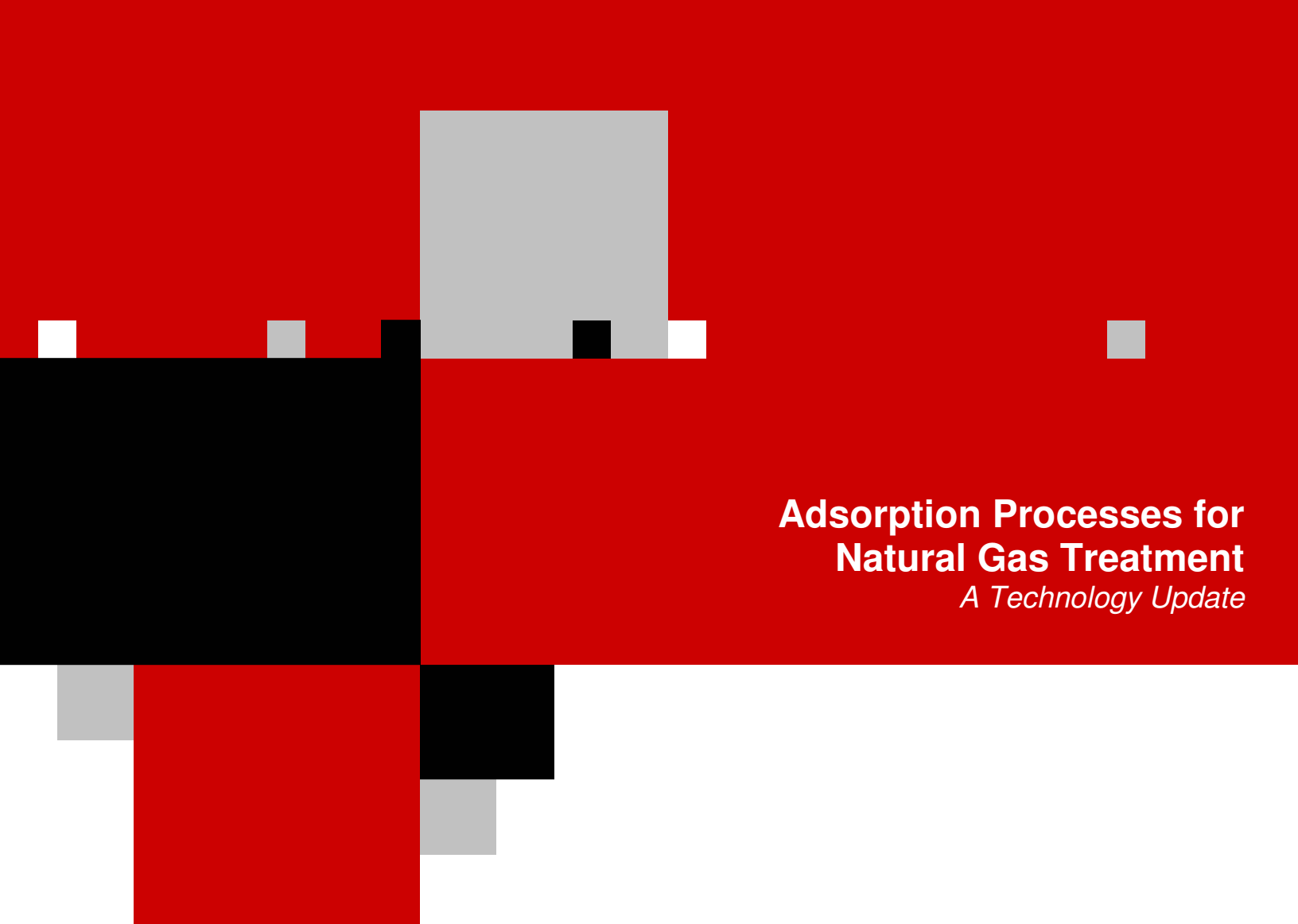




Adsorption Processes for Natural Gas Treatment

A Technology Update

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ENGELHARD 

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1. Introduction

1.1 Overview

This technology update outlines commercial applications of PSA (pressure swing adsorption) and TSA (temperature swing adsorption) in natural gas treatment.

Applications include:

- Water dew pointing (TSA)
- Hydrocarbon dew pointing (TSA)
- N₂ removal from natural gas (PSA)
- CO₂ rejection (PSA)

Fundamentals and basic design considerations of each application will be elaborated. The features and benefits of processes and adsorbents will be highlighted and compared to other technologies. Engelhard is a leading surface and materials science provider with a rich legacy of producing a wide variety of high quality adsorbents with over 200+ references worldwide. As an experienced and reliable supplier of specialized molecular sieves and silica gels, Engelhard also offers comprehensive technology packages and turnkey units.

1.2 Natural Gas Components

Natural gas, as naturally occurring, is an astonishingly complex mixture containing such diverse components as (not a complete list):

- Hydrocarbons (light, heavy, aromatic)
- Water
- Sulfur-components (H₂S, mercaptanes)
- Carbon dioxide
- Nitrogen
- Mercury

The final end-product, natural gas, as we know it from the pipeline, is a relatively homogeneous product traded globally as a commodity. Therefore, before it reaches the marketplace, numerous separation processes must occur. In the future, this need for cost-effective separation processes will increase as more and more remote and marginal fields will be looked at for exploitation.

1.3 Adsorption Mechanisms and Adsorbents

Adsorption is one of the many separation technologies used in treating natural gas. Adsorption can be broken down into several different categories:

- Chemisorption (usually irreversible; no regeneration) – not discussed in this paper. Example: Mercury removal with promoted activated carbon, H₂S polishing with ZnO.
- Physisorption (reversible adsorption on the surface of a material). Example: Water or hydrocarbon removal with silica gel – regeneration by heat.
- Size exclusion (the molecules of the contaminant fit into the pores of the adsorbent, the rest passes by.) Example: Removal of N₂ or CO₂ with Molecular Gate® – regeneration with heat or pressure swing.

Other classes of adsorbents such as activated carbon, molecular sieves, and activated alumina all have their own niches in treating natural gas which will not be elaborated upon in this discussion.

The focus will be regarding separations with silica (Engelhard Sorbead™ adsorbents) and Engelhard Molecular Gate® adsorption-based technology.

2. Water Removal from Natural Gas

2.1 Rationale & technologies

Water and hydrocarbons can form hydrates which may block valves and pipelines. Known for over 70 years, this has been the primary cause of plugging of transmission lines.[1]

Until today, the most popular separation technology remains absorption with liquid triethyleneglycol (TEG), followed by adsorption with solid adsorbents such as silica, molecular sieve or alumina which was introduced in the late 1950's. Other offered technologies comprise membranes, vortex tubes and even supersonic separations.

The amount of water in a gas is often described not in terms of concentration (such as mg/Nm³) but rather as a temperature ("dew point temperature") below which water will condense and form liquid droplets. This dew point temperature is also dependent on the amount of water present in a gas.

2.2 Adsorption Process Description

Water adsorbs and condenses on the surface of a silica gel – this is the same phenomenon which causes bathroom mirrors (silicate surfaces) to fog. The key to understanding the technical process is the vast inner surface of modern adsorbents: silica gel has specific surface areas of up to 850 m²/g. Example, a tablespoon of silica gel (10 g) has more surface area than a football field (105m x 70m = 7350m²).

Beyond the pure surface adsorption, a secondary mechanism, capillary condensation kicks-in when pore diameter is comparable to molecular diameter. Pores in the silica gel are asymmetrical, i.e. the further down into the gel, the narrower the pore becomes (like a volcano crater). This capillary condensation is driven by differences of partial pressure outside and inside of the pore.

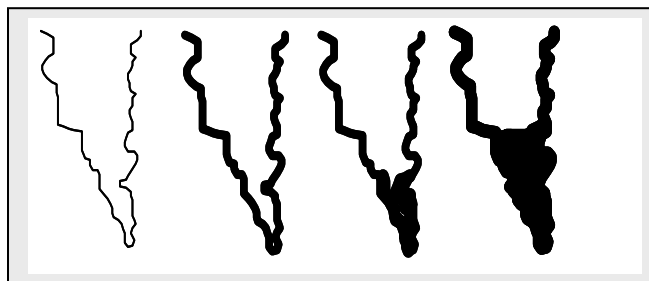


Figure 1: Schematic representation of capillary condensation.

To remove the water from the silica surface, energy is used – or if to remain in the analogy of a fogged bathroom mirror: just as the hot air stream of a hair-dryer will clear up the mirror immediately, so will a temperature increase (typically up to 250-280 °C) remove the water from the adsorbent in an industrial process. After regeneration, the adsorbent can be put to use again after cooling to ambient temperature.

High performing adsorbents are, therefore, designed to withstand the cyclical temperature increase without further damage. Good practical process design recovers as much of the regeneration heat as possible.

2.3 Silica Gel Requirements

Ideally, a superior adsorbent is characterized by:

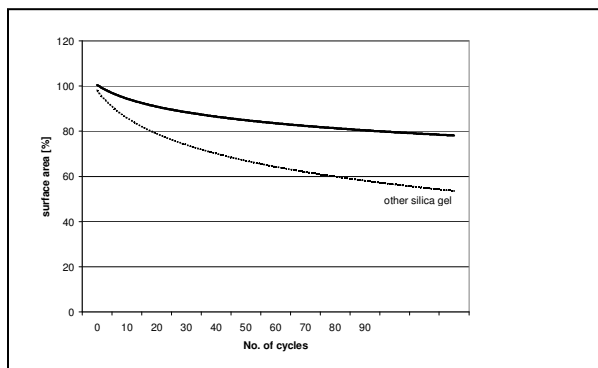
- High capacity (lowers required adsorbent volume, thus smaller vessels and smaller capital expense) – Silica gel can adsorb up to 45% of its own weight in water.
- High selectivity (no removal of other valuable components, less operating expense).
- Easy regeneration (less energy requirement to regenerate, less operating expense) – There is one major difference between silica gel and molecular sieve for removal of water from natural gas. While molecular sieve adsorbs water more strongly than silica gel, thus reaching lower dew points which are usually only required for liquefaction processes, this comes at a price. More energy is needed to overcome the stronger adsorption of water. As energy is always related to cost, the right choice of adsorbent, depending on required dew point specification, can have a significant financial impact.
- Low pressure drop – Right particle size distribution, typically this is in the 2-5 mm range.
- Long life time (less maintenance, less cost for change-out, less cost for replacement material, less loss of production).

Whereas capacities can be found from data sheets and selectivity and regeneration from process design, determining life time is usually difficult to assess. Long life-times can be expected when the adsorbent shows superior mechanical properties such as:

- Higher crush strength
- Lower attrition
- Lower dust, and
- Higher stability against aging

The mechanical requirements are typically met when using a silica gel, which is produced directly as a bead as opposed to having first a precipitation and then a granulation step. This can be done by using a drop process, where first silica sol droplets are formed, which cure (sol-gel process) to the final silica gel bead - no further granulation or particle forming step is required. Best results are achieved when using an oil-drop-process for bead formation, instead of a water- or air-drop process, as this gives the longest gelling time. With regard to aging, significant differences can be found:

Figure 2: Comparison of aging behavior of different silica gels.



Please note that when designing a unit, all factors contributing to performance over life time have to be accounted for -- surface area is only one among many other factors affecting performance.

However, life times of 4-6 years are typical with silica gel produced with an oil drop process. Life times of 10+ years have been observed quite regularly, and, in some cases, the silica gel is a life time item. Thereby, no replacement is expected during the life time of the whole unit (such as in underground storage with only a reduced number

of operating days per year).

Engelhard has over 30 years experience in these kinds of applications. They include:

- Removing water on a gas production site (achieving water dew point specifications).
- Dehydration after underground storage (UGS).
- Acid gas dehydration.
- Offshore applications (no problems with tilt or rolling of offshore platforms).

Experience has shown that it always depends on project specifics which treating technology is the most economical and that there is no inherent advantage of one technology over another.

2.4 Case Study: Comparison TEG / Silica Gel

A typical unit set-up for an adsorption unit is given in *Figure 3*, design flow rate is 2.7 – 54 MMSCF/D.[2]

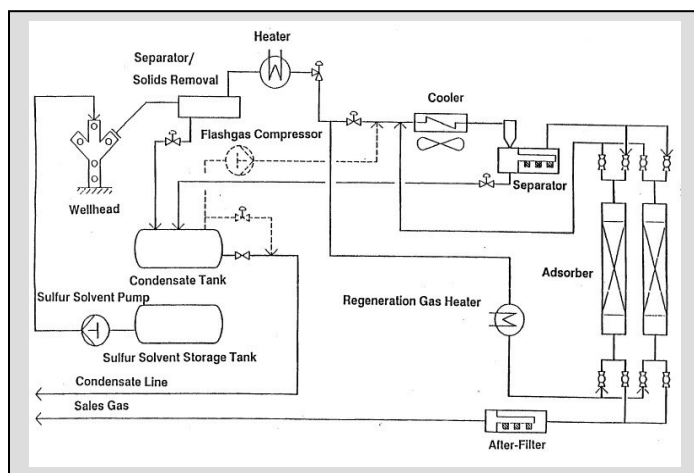


Figure 3: Flow sheet of an adsorption unit for water removal [2].

As can easily be seen, this unit comprises two adsorption towers: one in adsorption mode and the other being regenerated. Typically these units are designed as long-cycle units, one cycle taking about 12 hours. It can handle the full flow range from 2.7 – 54 MMSCF/D, while achieving the required specifications.

For comparison, please see *Figure 4* below for a glycol unit for the same set of parameters.

Both flow sheets show similar complexity and, indeed, estimated project costs are in a similar range (*Figure 5*). However as a glycol unit cannot handle the full flow range, project costs are given for selected flow rates, within this range.

It demonstrates clearly that glycol units are only having the edge when designed for very small flow rates, without having the ability to treat larger flows. For larger flow rates (> 25 MMSCF/D) an adsorption unit is more economical in this case and gives also much operating flexibility.

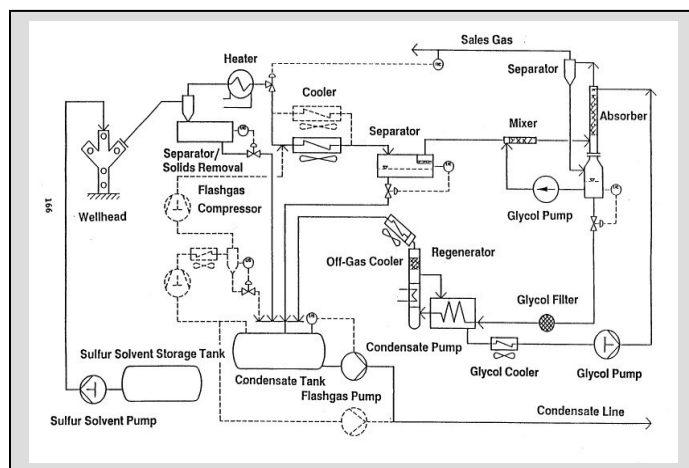
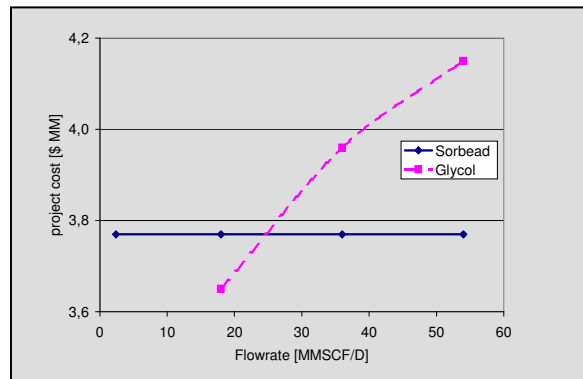


Figure 4: Flow sheet of a glycol unit [2].

Figure 5. Cost comparison between adsorption (Sorbead) and absorption (glycol) unit.



The silica gel unit is readily designed to handle a wide feed flow range and change in gas composition, as typical for an aging gas field – a major advantage of an adsorption unit::

- High turn-down rates.
- Unit can adapt immediately to new operating conditions, often by simple modifications to the cycle time.

Other advantages include:

- Instant availability (first cycle after stand-still already delivers gas on spec.)
- Ease of operation (even remote control possible)
- Low maintenance
- No energy consumption during stand-by
- Less energy demand for regeneration (71000 BTU vs. 102000 BTU in this case study)

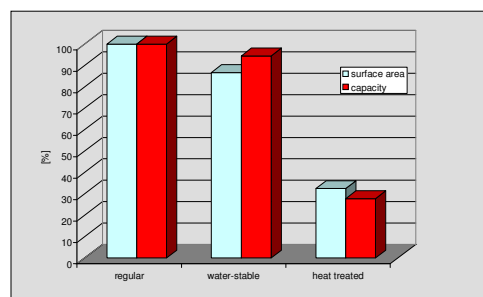
As can be seen from comparison in *Figure 5* above, adsorption can be a very competitive alternative versus traditional TEG-absorption.

2.5 Liquid Water

Whereas water can be easily adsorbed from the gas phase, liquid water droplets or slugs present an altogether different challenge:

- Hydraulic “hammer” effect.
- Breakdown of the adsorbent, due to local –microscopic– overheating. (liquid water is a very high “local” concentration of water, which leads to high local heat of adsorption and thus high local temperatures.
- Broken adsorbent can lead to higher pressure drop and eventually channeling, thus, reduced performance of the unit.

The best way to avoid this problem is to carefully design the inlet separator. Experience shows that this item is often under designed. The next best way – or as an additional safeguard – is to use a guard layer of water stable adsorbent on top of the main adsorbent bed at the feed inlet. The challenge is to have a water stable material, which has still a high adsorption capacity, because otherwise one would just increase the amount of inert material on top of the bed.



There are generally two ways to produce water-stable silica gels:

- Heat treatment: Silica gel is tempered and sintered at high temperatures to reduce vulnerability against temperature spikes – heat treatment however also destroys many micro and meso-pores, thus reducing capacity.
- Special production processes (*Figure 6*).

Figure 6: Comparison of water-stable silica gel with regular silica gel and heat treated silica gel.

This clearly demonstrates that water-stable silica gel, which is produced according to a special production process, is nearly equal to regular high-performance silica gel and vastly superior to heat-treated silica gel.

In most units, these specially produced water-stable silica gels takes-up the top 10-20% of the bed for protection purposes. This technology is becoming also more popular with molecular sieves. In many LNG units, one can find a top-layer of water-stable silica gel as a guard-bed on top of the molecular sieve. In some cases, this could demonstrably increase the life time of the molecular sieve.

3. Hydrocarbon Removal from Natural Gas

3.1 Rationale & Technologies

Not only water can cause problems, but also heavy hydrocarbons, which can fall out of the gas phase on pressure or temperature decrease. These heavy hydrocarbons can also cause plugging of downstream valves and pipes or fouling of other equipment (i.e. gas separation membranes). Terminology again does not refer directly to compositions and concentrations, but rather to the temperature (hydrocarbon dew point) at which the gas begins to condense (at specified composition and conditions).

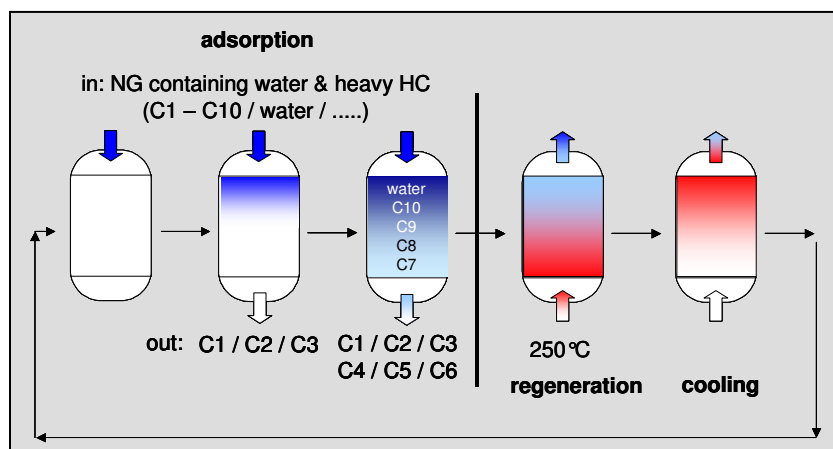
Some of the world's largest adsorption units belong to this category: Two units in the Netherlands, each treating up to 1400 MMSCF/D per single train and another unit in Russia, treating 750 MMSCF/D per train.

Basically these units are very similar to water removal units. They use silica gel as an adsorbent and are regenerated by heat. Actually because of this similarity, not only remove heavy hydrocarbons but on top of that they also remove water to the required dew points. However, there are also differences:

- Other silica gel grades required (however, always with a "topping" of water-stable silica then similar life times as in a dehydration service are expected).
- Design is for adsorption of more than one component (key consideration).
- Typically, much shorter cycle times (as short as 45-60 minutes).
- Often, three or more adsorption vessels.

Figure 7 shows schematically the adsorption process. Key to design is a clear understanding of the breakthrough behavior of individual components. As the longer the cycle runs, the heavier components are breaking through and increase the dew point. Regeneration is usually countercurrent in order to prevent any chance of condensation and deposition of water and/or very heavy components in the cooler parts of the bed during regeneration.

Figure 7: Schematic of adsorption cycle of one single adsorber.



3.2 Sordeco™ Process

To compare this adsorbent-based technology with other treating technologies; Sordeco™ was selected as a reference point. The Sordeco process is co-operatively licensed by Shell Global Solutions and Engelhard. The Sordeco process applies Engelhard's Sorbead™ adsorbent beads packed into adsorber columns. [3]

Shell has more than 15 years of experience in design and operation of hydrocarbon dew pointing facilities with Engelhard's Sorbead adsorbent, which is applied in over 200 facilities for natural gas processing worldwide.

3.3 Other Technologies

Alternative technologies for hydrocarbon dew pointing include:

- Low temperature separation (LTS): Cooling the feed gas with treated gas and expanding the gas over a Joule-Thompson valve. This results in a pressure drop and gas will cool further down while heavy hydrocarbons and water will condense out and will be separated. (Usually, an additional hydrate inhibitor is also needed – this can be glycol.) The pressure drop over a LTS unit is often in the range of 20-40 bar (the pressure drop over a Sordeco unit is in the range of 2-5 bar).
- Turbo expansion: Same basic principle, however, work released during expansion is used for a compressor – resulting pressure drop is less pronounced.
- Mechanical refrigeration – Natural gas is cooled with a refrigerant, this is usually considered when there is no permissible pressure drop or feed gas pressure is lower than sales gas pressure and the gas has to be compressed. The reasoning is that compression is costly -- compressing first and then removing water and heavy hydrocarbons afterwards by one of the methods mentioned above which is always combined with a loss in pressure - making it uneconomical.
- Lean oil absorption (mostly obsolete).

As one can see, one of the major factors influencing the choice of technology is the pressure differential between the feed gas and the pipeline requirements. This can be schematically shown, as in *Figure 8a*. While, *Figure 8b* shows the field of play for a typical Sordeco unit.[3]

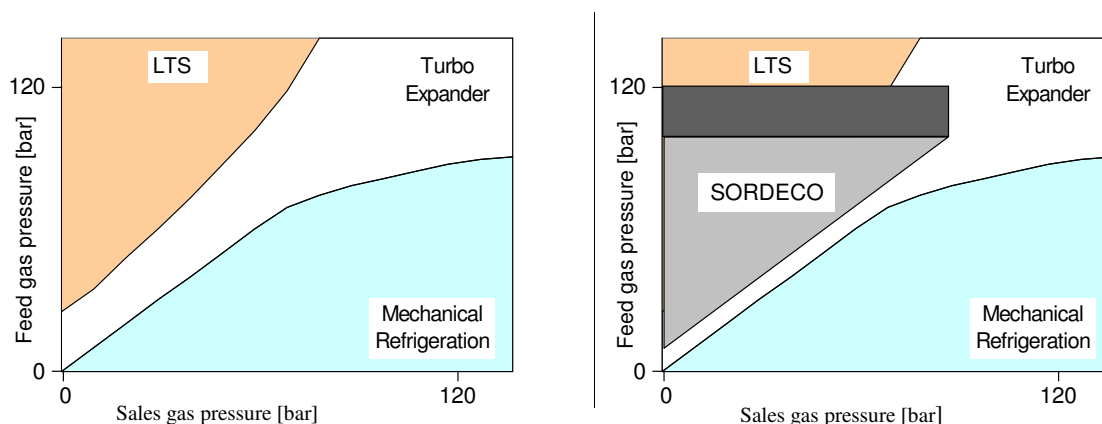


Figure 8a/b: Basic selection of dew pointing processes (with and without Sordeco).

When comparing LTS and Sordeco, beyond installed cost, there are advantages and disadvantages to both systems:

Table 1: General comparison between solid adsorbent and LTS dew pointing technologies.

SORDECO	LTS
Advantages • Low manifold pressure required • Excellent water and hydrocarbon dew point control and not sensitive to feed gas compositions • Produces on-spec gas during start-up • Operating flexibility is high • No continuous use of hydrate inhibitors required • Low pressure drop	• Fuel gas consumption is low • Low emissions of CO₂ and NO_x in the total process • Simple control system
Disadvantages • Fuel gas consumption resulting in emissions of CO₂ and NO_x • Exhausted adsorbent would need to be disposed off with an approved environmental method	• Off-spec sales gas during start-up • Glycol unit responsible for emissions such as BTEX • Process sensitive to feed gas composition • High required inlet manifold pressure

3.4 Case study: Comparison LTS / Sordeco

For a given gas composition and flow rate (=285 MMSCF/D) — Total Installed Cost (TIC) for a new plant have been estimated ($\pm 35\%$ accuracy) with respect to feed gas pressure and dew point specification. The variation of feed gas represents the normal development of the pressure of a gas reservoir, the two different dew point specifications correspond to stringent and relaxed operating conditions as shown in Figure a/b.

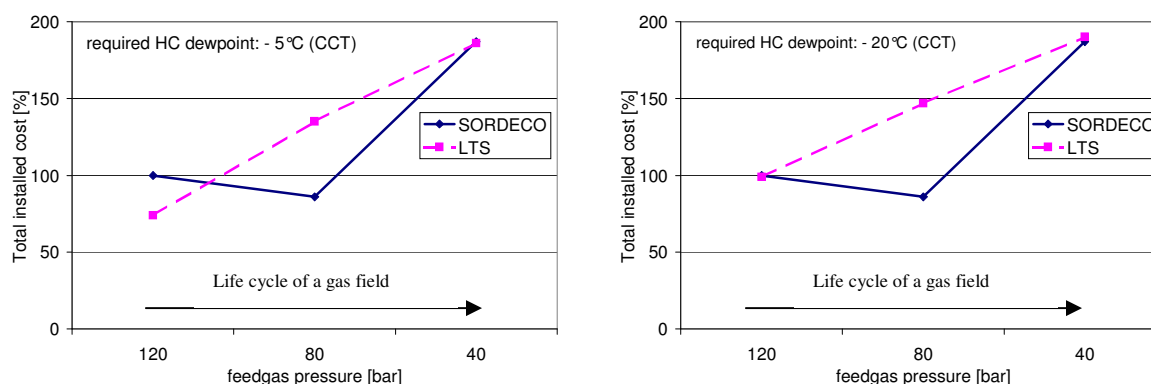


Figure 9a/b: Comparison of total installed cost (for a grassroots plant) for different feed gas pressures (pipeline pressure = 75 bar).

The results from this study can be summarized as follows:

- TIC for Sordeco is identical for both dew point specifications. Due to hydrodynamic reasons, the same amount of adsorbent has to be installed for both cases, i.e. no extra cost for achieving better dew point.

- For high pressures, LTS has an advantage if product specifications are relaxed, when having more stringent requirements both technologies are evenly matched.
- For medium feed gas pressures, Sordeco offers always a cost advantage (reason is that for LTS compression is required) – or, in other terms, with Sordeco the need to use costly compressors in the life cycle of the gas field is postponed.
- For low pressures, both technologies are quite similar due to the equalizing influence of compressor cost.

Indeed, in some cases, gas fields started out at high pressure with LTS treating units and progressed later in their life cycle to adsorbent based systems. This comparison demonstrates the wide adaptability of solid adsorbent based systems not only in technical but also in economic terms.

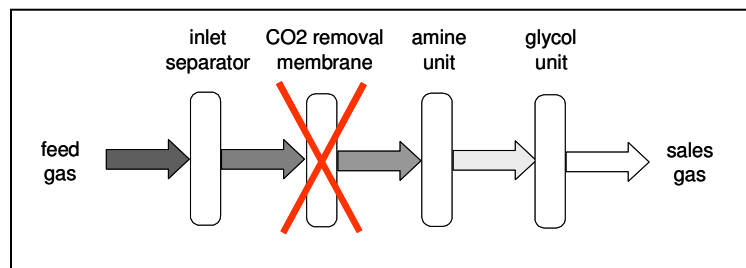
3.5 Case study: Grissik – High performance adsorption

Although cost considerations are critical, the base of any technology is the performance. The Grissik plant, located in South Sumatra, is an excellent example on how adsorption can contribute.[4]

The Challenge:

Original set-up of the plant for treating 300 MMSCF/D is shown in *Figure 10*. After only 3 months, membrane capacity decreased to 10% of original capacity. The problem was heavy hydrocarbons (C8 – C18) and aromatics (benzene to naphthalene), which were not detected during initial gas analysis.

Figure 10: Original set-up of Grissik gas plant.



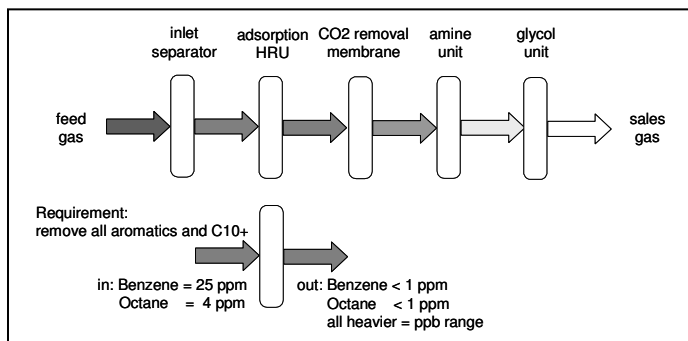
The Solution:

As advised by the membrane provider, the solution was to eliminate all aromatics and C10+. Two technologies were initially considered:

- Gas chilling (refrigeration) – Rejected due to thermodynamic reasons required specification could not be met.
- Adsorption – This was the preferred solution: 2 trains each with 230 MMSCF/D capacity (each four adsorber vessels) were implemented to treat not only the affected gas stream but also a secondary stream.

The final set-up is shown in *Figure 11*. The hydrocarbon dew point was lowered by 60°C from 30°C to – 30°C (both at approx. 77 bar).

Figure 11: Current layout of Grissik plant, including adsorption unit.



The Results:

The implementation of the adsorption HRU proved to be a great success. The unit was installed in 2000 and the membrane kept its capacity as expected. It still operates as of today and has already surpassed the expected membrane life-time of three years. A full report on this unit is expected to be published.

4. Nitrogen (N₂) Removal from Natural Gas

4.1 Rationale & Technologies

Nitrogen rejection to meet typical pipeline specifications of 4% is a challenge; however, with 11% of U.S. production and 16% of U.S. reserves contaminated with nitrogen, this natural gas source is substantial. [4]

The large majority of existing nitrogen rejection facilities use cryogenic processing. Such processes are economically viable when flows are high. The cryogenic systems generally require multiple processing steps and operator attendance. Therefore, relatively few systems have been built. Extensive pretreatment is involved and the processing steps include very often:

- Amine wash (bulk CO₂ removal)
- Water removal
- CO₂ clean up (adsorption on molecular sieves)
- Cryogenic unit
- Recompression
- And, if O₂ is present, a catalytic reaction system is required additionally

In most cases, such cryogenic facilities have been justified due to the production of helium as a by-product. Other processes also have been commercialized for nitrogen rejection, but despite substantial nitrogen contaminated reserves, less than two dozen facilities have been installed in the United States to date.

Since nitrogen is an inert, it is common to utilize low quality reserves by blending with quality gas. Since blending is not always a possibility, it is very common to simply shut-in wells where nitrogen is encountered.

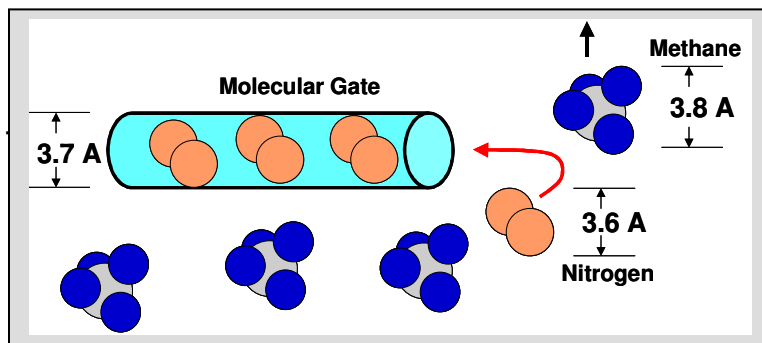
4.2 Engelhard Molecular Gate® Adsorption-Based Technology

Engelhard Corporation has developed and patented a new family of molecular sieves based on the technology of titanium silicates.[5,6,7] These materials have unique surface properties as well as the unique ability to adjust pore size openings. The pore size is precisely adjusted within an accuracy of 0.1 angstrom in the manufacturing process. This allows the production of a molecular sieve with a pore size tailored to size-selective separations.

Nitrogen and methane molecular diameters are approximately 3.6 angstroms and 3.8 angstroms, respectively. In an Engelhard Molecular Gate® adsorption-based system for upgrading nitrogen-contaminated natural gas, a pore size of 3.7 angstroms is used. This adsorbent permits the nitrogen to enter the pore and be adsorbed while excluding the methane, which passes through the fixed bed of adsorbent at essentially the same pressure as the feed. This size separation is schematically illustrated in *Figure 12* on the next page.

Molecular Gate nitrogen rejection process takes a unique approach as compared with other commercial nitrogen rejection technologies, by adsorbing nitrogen from the feed stream while producing the product sales gas at essentially feed pressure. This feature preserves the available feed pressure.

Figure 12: Schematic drawing of size selective adsorption process.



The same principle applies for CO₂ removal (molecular diameter of 3.3 Å) from natural gas with Molecular Gate adsorbents.

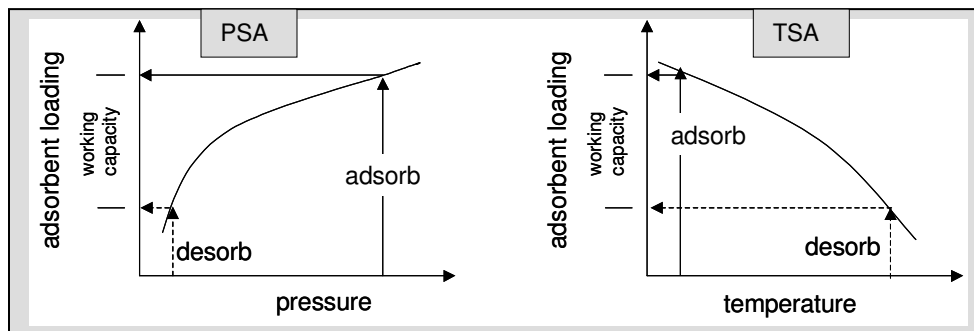
When comparing with silica gel, distinctive differences can be highlighted:

- The first semi-commercial Molecular Gate unit was erected in 2000.
- Since that time, six more new units have come on-stream (both N₂ and CO₂ removal systems) and two more projects have been awarded. Silica gel units have been around since about 40 years, and Sorbead is installed in 200+ units worldwide.
- Molecular Gate adsorption technology is marketed as a complete process plant that includes the equipment, adsorbent and control system, whereas Sorbead and Sordeco are sold separately and independently of each other and the process equipment.

But beyond these more commercial aspects and a different adsorbent and adsorption mechanism, there are fundamental technical differences in the process design:

- Silica gel beads (should) contain no binder, whereas, Molecular Gate adsorbents as a specialty molecular sieve require a binder for particle production. This binder can give rise to secondary effects (adsorption of heavy hydrocarbons).
- Silica gel units are usually regenerated by heat (Temperature Swing Adsorption - TSA), whereas, Molecular Gate adsorbents are regenerated by decreasing the pressure (Pressure Swing Adsorption - PSA). Figure 13a/b demonstrates schematically these two processes.

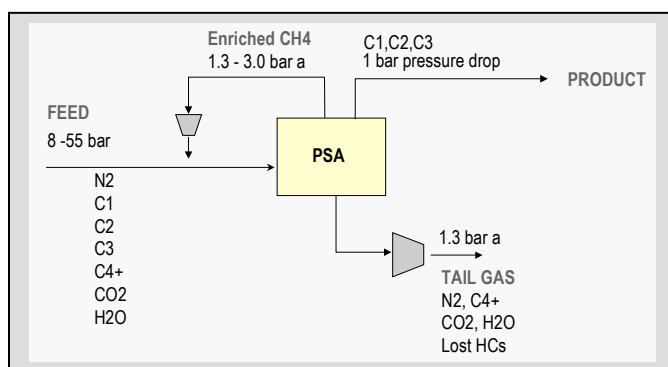
Figure 13 a/b: Adsorption and regeneration for PSA and TSA processes.



4.3 Technology & Process of Molecular Gate Adsorbents

The major equipment for a Molecular Gate unit for N₂ removal is shown schematically in Figure 14. As water is also adsorbed on the Molecular Gate adsorbent, it is good design practice to remove the water beforehand (i.e. by adsorption on a silica gel) to enhance working capacity for nitrogen adsorption, however, it can also be removed in one step as shown in Figure 14.

Figure 14: Block-flow diagram of a Molecular Gate process.



Feed gas is introduced into the Molecular Gate system at ambient temperatures and at high pressure (the feed may or may not require compression). In most cases, the optimum operating pressure is between 8-40 bar. Operation outside this range is possible.

In the process, methane, ethane and about half the propane pass through the bed of adsorbent into the product stream. The system adsorbs the residual water, all of the carbon dioxide and all of the C4+. These heavy hydrocarbons do not fit within the pore

of the adsorbent; however, they are attracted to the binder used to hold the molecular sieve crystals together and are removed with the other adsorbed components into the tail gas.

Typical methane recovery rates of 90-95% are achieved by removing a methane rich stream at low pressure, and after compression, it is routed back to the feed. If this recycle were not employed, this methane would be lost into the tail gas.

The Molecular Gate system operates unattended and can be monitored remotely. Where maintaining an inert level within a small window is critical, a product heating value analyzer can be used to adjust the operating conditions of the system. Such an analyzer allows the unit to automatically compensate for changes in the feed composition or pipeline requirements.

From a zero pressure condition, start-up can be conducted with delivery of product gas to the pipeline within 30 minutes. Control, operation and monitoring of the unit can be conducted locally and monitored through a remote station and a modem connection. The system can be designed to continue operation (at reduced performance) in the event of a failure of the recycle compressor or vacuum blower.

4.4 Comparison: Molecular Gate Adsorbents / Cryogenics

Figure 15 and Table 2 shows the respective fields of play for both Molecular Gate adsorbents and cryogenics for nitrogen removal with advantages and disadvantages for both systems.

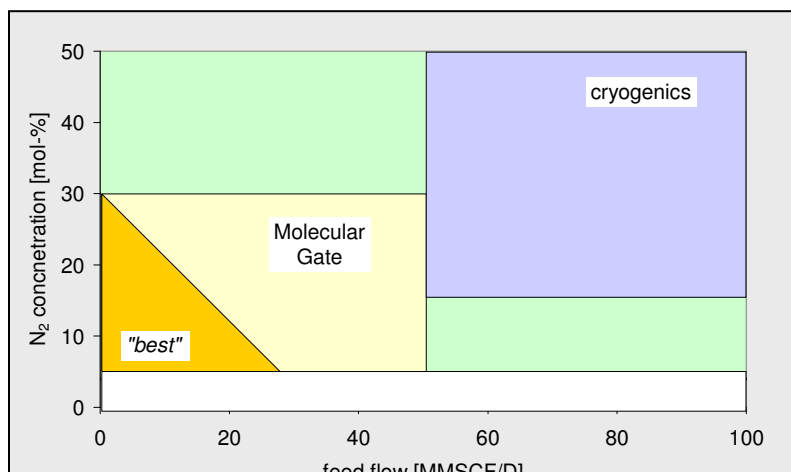


Figure 15: Typical operating conditions for Molecular Gate adsorbents and cryogenics.

Table 2: General comparison between Molecular Gate adsorption technology and cryogenics.

Molecular Gate	Cryogenics
• CO₂ removed • Medium pressure • Lower power • Mercury acceptable • Wellhead gas • Flexible operation • Tail gas is low BTU • Helium requires additional equipment	• CO₂ pretreatment • High pressure • Recompression of CH₄ • Rich feeds, NGL recovery • Feed pretreatment • Attended operation • Helium by-product

In producing pipeline quality gas, Molecular Gate systems have the characteristic that, while methane flows through the bed and is available at near feed pressure, heavy hydrocarbons are removed along with the nitrogen. This characteristic can be a benefit where product dew point control is an issue; however, the heavy components will end up in the tail gas of the unit where their BTU value can be used to drive an engine or other heat demands.

When the natural gas feed contains substantial levels of heavy components, the system can be penalized by the loss of the heavy components with the nitrogen and/or carbon dioxide impurities. These heavy hydrocarbons are enriched in concentration in the tail gas; however, they are now at a reduced pressure. In fact, they are at a lower partial pressure than the feed gas because the bulk pressure in the waste gas is low. The apparent disadvantage of the removal of heavy hydrocarbons into the low-pressure tail gas is turned to an advantage when an NGL recovery unit is added to the main Molecular Gate system – although this option is not further discussed in this paper.

Figure 16 shows estimated processing cost for removing N₂ out of a feed gas stream containing 15% N₂ down to 4% at various flow rates. Due to economy of scale, processing cost is decreasing with increasing flow rates.

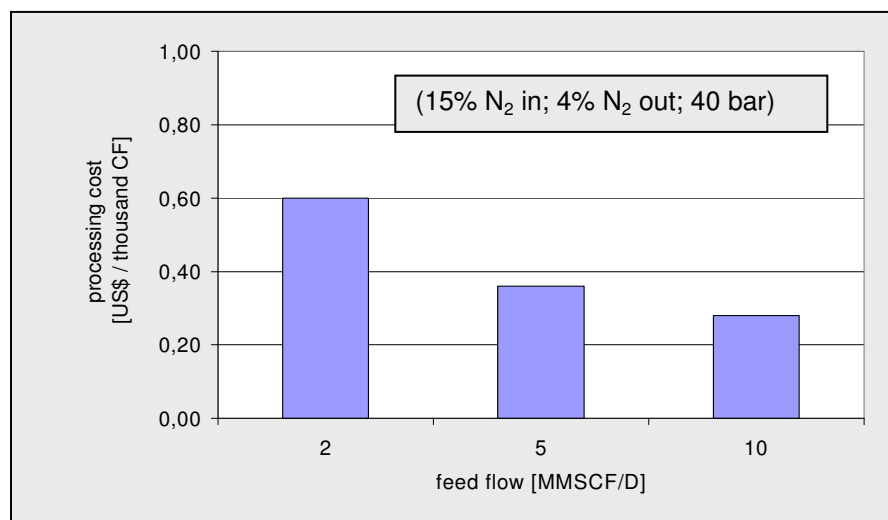


Figure 16: Capital plus operating cost for N₂ removal from natural gas – processing cost does not include feed compression / drilling / gathering and is based on amount of product generated.

4.5 Case Study: Hamilton Creek

The introduction and proven viability of any new technology is often a challenge. To overcome this hurdle, Engelhard built a small commercial unit to demonstrate the technology in Hamilton Creek located in

Southwest Colorado. This unit began operation in late 2000 and has operated for over three years with excellent results.

Located at a remote wellhead site where the feed contains approximately 18% nitrogen and less than 1% carbon dioxide, the product is routed to either of two local pipelines. To meet the local pipeline specifications, the unit has been operated with a product nitrogen content ranging between 3% and 6%.

This site is not easily accessed, and for this reason, power is provided by a rental genset unit, and a packaged unit supplies instrument air. The feed capacity of the system is about 0.2 MMSCF/D with an operating pressure that is typically 24 bar.

The operation of the system at Hamilton Creek has proven to be both effective and reliable. The pumper responsible for the wells operates the system and visits the site once per day spending about one-half hour with the unit reviewing a checklist for performance monitoring. The reliability of the system has been excellent with a 99% availability factor. This availability is under unattended conditions, where in the event the unit trips, it is not restarted until the pumper's normal visit to the well site. The system includes the ability to dial-in and monitor the system from a remote location.

Performance has been consistent with no loss in adsorbent capacity performance. The unit has met expectations and is being debottlenecked and relocated to a commercial site where it will continue to produce pipeline quality product.

5. Carbon Dioxide (CO₂) Removal from Natural Gas

5.1 Rational and Technologies

The quantity of natural gas reserves contaminated with carbon dioxide is even larger than that for nitrogen at 22% of production and 27% percent of reserves in the U.S.; however, carbon dioxide removal is much more widely practiced than nitrogen rejection. Carbon dioxide removal is also motivated by the fact that it is not simply an inert but also can be corrosive. Generally, the carbon dioxide concentration must be removed to less than 2%. The cost of removing carbon dioxide is also much lower than that for nitrogen, and, consequently, it is less common to shut-in carbon dioxide contaminated wells.[6]

Carbon dioxide must also be removed prior to low temperature processing for NGL recovery. In the United States, there are some 600 large carbon dioxide removal facilities; in most cases these facilities use amine processing.

Historically, carbon dioxide is removed through the use of amine based solvents. The systems, though widely applied, can pose operating difficulties due to the challenge of keeping the solvent clean and operating within the process constraints of the system.

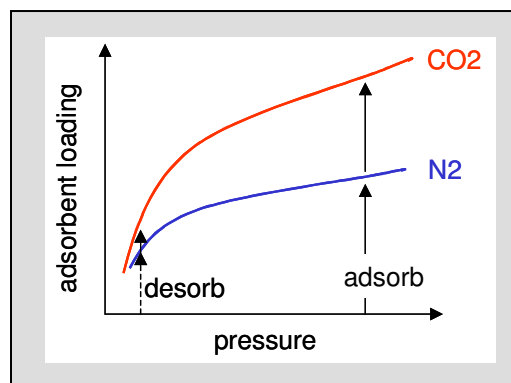
Membrane systems also have been used for carbon dioxide removal and, within certain process conditions, can be an attractive alternative. One challenge for membrane systems is reaching the low allowable carbon dioxide levels required by the pipeline system. For this reason, membrane systems are sometimes integrated with further processing.

The Molecular Gate system for carbon dioxide removal can, for certain applications, allow for CO₂ removal without the operational challenges of amine based systems or the process limitations faced by the membrane systems.

5.2 Comparison: N₂ / CO₂ Removal with Molecular Gate adsorbents

In the removal of carbon dioxide from natural gas, carbon dioxide (3.3 Å) is both a smaller molecule than methane (3.8 Å) and one that is adsorbed more strongly. The combination of pore size optimization and adsorbent attraction results in the ability to remove carbon dioxide with minimal adsorbent inventories and high methane recoveries.

Figure 17: Generalized N₂/CO₂ – isotherms for Molecular Gate adsorbents.



Since carbon dioxide is strongly adsorbed, the adsorbent properties can be tailored so that it can also remove water vapor. This eliminates the need for dehydration, as is the case with nitrogen rejection, providing an operational and cost benefit.

Essentially both types of Molecular Gate systems tend to be very similar; however, CO₂ removal systems tend to be less complex due to a simpler separation and no need for pretreatment.

5.3 Comparison: Molecular Gate Adsorbents / Amine Wash

The CO₂ removal system can be very economic – especially for lean natural gases or coal bed methane, as there are no heavy hydrocarbons, which can lost through the tail gas – although natural gas liquids recovery options are available.[7] Flow rates in the range from less than 1 MMSCF/D up to 100 MMSCF/D can be economically processed. The feed concentration can range from low levels to 50%, the product specification achieved in a single step is typically 2%, but can be as low as parts per million.

Its main advantages compared to an amine system are:

- Ease of operation
- No need for up-stream dehydration
- No amines (some are classified hazardous chemicals)
- Total installed cost very similar to traditional amine systems (dependent upon actual conditions which is more economical)

Figure 18 gives a cost estimate for CO₂ removal with Molecular Gate. As can be seen, the treating cost is much less than for N₂ rejection.

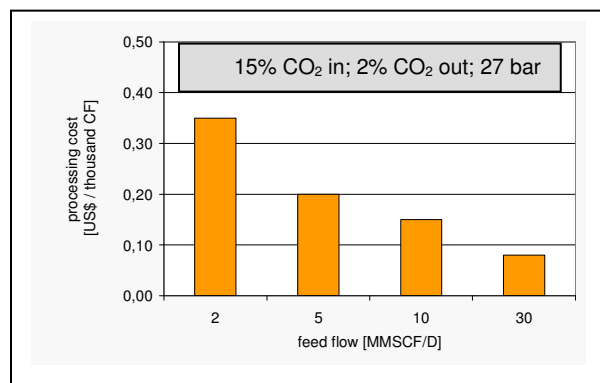


Figure 18: Capital plus operating cost for CO₂ removal from natural gas. Processing cost does not include feed compression / drilling / gathering and is based on amount of product generated.

5.4 Case Study: Tidelands

In May of 2002, the first Molecular Gate carbon dioxide removal system for the removal of carbon dioxide started up at the Tidelands Oil Production Company operated facility in Long Beach, California.[8]

The feed source for the unit is hydrocarbon rich, water-saturated, associated gas from water flood enhanced oil recovery operations. The feed CO₂ concentration varies widely and, though originally designed for 18% CO₂, it more typically operates at 30-40% while reducing the carbon dioxide level to less than 2%. Due to the source of the feed, a large quantity of heavy hydrocarbons is also present and the feed is water saturated. The unit removes carbon dioxide, heavy hydrocarbons and water producing pipeline specification gas for sale to the local natural gas utility company.

The operation and start-up of the Tidelands unit resulted in a few unexpected developments. The feed stream CO₂ level typically operates at about twice that of the design rate (37% versus 18%). While the unit is still able to operate at full capacity, some portion of this capacity was gained by the relaxation of the product specification such that up to 2% CO₂ is permitted into the product stream as compared to the design level of less than 2000 ppm.

In other respects, the start-up was uneventful and from feed-in to normal, unattended operation; the time required was a few days. It is desirable to operate the unit continuously and this has generally been the case since start-up with on-stream factors of over 99%.

6. Conclusion

Adsorption technologies in natural gas treatment form a critical part of gas processing and are here to stay and grow in importance. Furthermore, it could be demonstrated that adsorptive systems can be competitive against other technologies, in both technical and commercial terms. Emerging technologies – such as Engelhard Molecular Gate adsorbents – create even more potential. It can be summed up in two points:

- **Experience & Development:**
Silica gels have been in use for more than 40 years in natural gas processing, with more than 200 units worldwide using silica gel and also many more using molecular sieves or other adsorbents. Nevertheless, new developments and technologies are still introduced to the market that either improve existing technology such as Sordecos or allow completely new separations such as Molecular Gate adsorbents.
- **Performance & Selectivity:**
Modern adsorbents allow for astonishing purifications and separations, such as removing traces of very heavy hydrocarbons and aromatics from gas streams into the ppb region or separating nitrogen and methane by size. Although performing highly specialized tasks, these adsorbents withstand harsh process conditions. For example, being heated up to 280 °C, cooled down and heated up again for ten thousands of times or being subjected liquid water attack. This resilience and versatility of modern adsorbents only makes very large units possible, treating more than 1 bn SCF/D of gas in one single train.

About Engelhard

Engelhard Corporation is a surface and materials science company focused on technologies that dramatically improve products and processes. A Fortune 500® company, we have 6,500 employees in more than 100 locations and in 24 countries. We are a global leader in providing superior technologies for environmental, process, appearance, and performance applications.

At Engelhard, we believe it's absolutely essential to deliver solutions that provide lasting business value. Working closely with our customers and their customers is one of our fundamental value propositions. With years of experience in developing top-quality, active adsorbents for a wide variety of industries, Engelhard is ready to assist you in meeting your specific business requirements.

To learn more about Engelhard adsorbent products and services for natural gas treatment, please visit us at www.engelhard.com/fuelpurification.

7. About the Authors

Drs. Ulrich Daiminger and Waldemar Lind are Market Managers for Separation Systems at Engelhard Corporation.

Joining Engelhard in 2001, Dr. Daiminger has held various positions in separations design, process development, product management and new business development. He has been involved in the German Joint Committee (VDI and DECHEMA) on solvent extraction. Dr. Daiminger holds a Bachelor of Science degree in Chemistry and a PhD in Industrial Chemistry from the Technical University in Munich, Germany. He has also published numerous research papers as well as received six patent applications – all concerning separations and process intensification.

Dr. Waldemar Lind received his PhD in Chemistry at the Technical University in Braunschweig, Germany. Throughout his distinguished career, Dr. Lind has held several positions in Sales and Product Management at various well known biotechnology and chemical companies. His professional background also includes a 4-year stint as head of Moscow office operations managing syngas, refinery and petrochemical catalyst applications.

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