

ECONOMIC N2 REMOVAL

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ECONOMIC NITROGEN REMOVAL WITH MOLECULAR GATE™ TECHNOLOGY

Nitrogen contaminated natural gas is a worldwide issue and more than eleven percent of natural gas reserves in the USA are sub-quality due to the presence of excessive levels of nitrogen. The USA contaminated fields tend to be small producers that cannot support significant operator attention and for which low capital, easy equipment relocation, and minimal pretreatment and simple operation are critical.

The technology was developed by Engelhard corporation (now part of the BASF Group) and Guild Associates was involved from the earliest studies, first in pilot plant studies and ultimately for the supply of commercial units. In 2000, the first Molecular Gate® adsorbent-based system for the rejection of nitrogen commenced operation and, since that time, 30 systems have been fabricated for N₂ and/or CO₂ removal. In 2006 Guild was licensed to provide both the equipment and adsorbent for the Molecular Gate systems. The technology is targeted at the smaller fields and for flows from less than 0.5 MM SCFD to 30 MM SCFD or more.

The systems are designed for unattended operation, push-button start-up and modularity. They are also noted for the unequivocal ability to meet pipeline nitrogen specification regardless of the nitrogen level in the feed. This ability has proven to be a great advantage when the design feed does not match the gas composition actually seen in the field. Unlike all other nitrogen rejection technologies, Molecular Gate adsorbent removes the nitrogen from the natural gas leaving the methane rich sales gas at high pressure.

Molecular Gate adsorbent is a new type of molecular sieve that has the unique ability to adjust pore size openings within an accuracy of 0.1 angstrom. The pore size is precisely adjusted in the manufacturing process to allow the removal of N₂ and/or CO₂ while having minimal capacity for methane.

Nitrogen and methane molecular diameters are approximately 3.6 angstroms and 3.8 angstroms, respectively. In a Molecular Gate adsorbent-based system for upgrading nitrogen-contaminated natural gas, a pore size of 3.7 angstroms is used. This adsorbent permits the nitrogen (as well as carbon dioxide, hydrogen sulfide, water and oxygen) 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 1*.

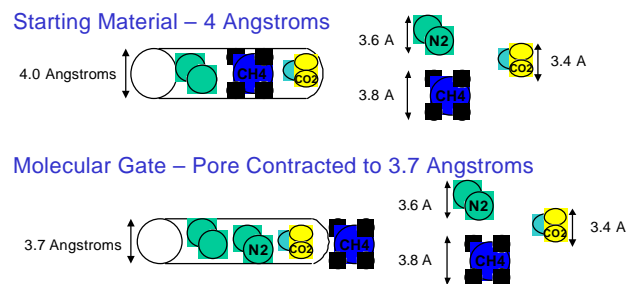
When the feed contains both nitrogen and carbon dioxide, the carbon dioxide is completely removed in a single step with the nitrogen due to the fact that CO₂ (3.4 angstroms) is an even smaller molecule than nitrogen and easily fits within the adsorbent pore. This important advantage avoids the additional cost and processing steps of a separate amine or membrane unit for CO₂ removal.

Oxygen (3.5 angstroms) is also smaller than nitrogen and is partly removed with the nitrogen (while carbon dioxide is completely removed). Water is also a small molecule that fits in the adsorbent pore and can be removed but in most cases the feed is dehydrated before being admitted into the unit.

Process Description

The adsorbent is applied in a Pressure Swing Adsorption system (PSA) wherein the system operates by “swinging” the pressure from a high-pressure feed step that adsorbs the nitrogen to a low-pressure regeneration step to remove the previously adsorbed nitrogen. Since methane does not fit within the pore of the adsorbent, it passes through the bed at the feed pressure.

Figure 1: Schematic view of Molecular Gate adsorbent pore size and relative molecule size



Pressure Swing Adsorption (PSA)

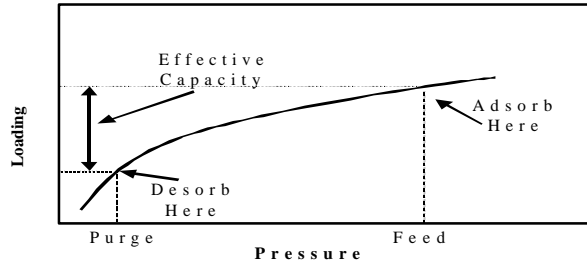


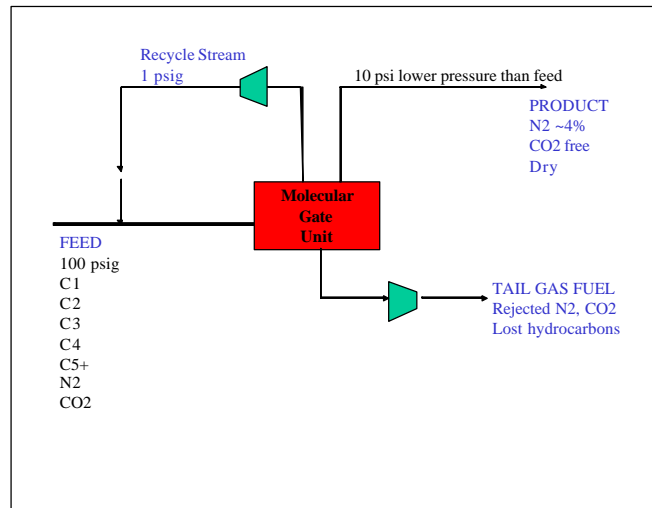
Figure 2: Generic isotherm for adsorption and desorption pressures

PSA is widely used in light gas separations with many hundreds of units in operation in the oil refining, petrochemical and air separation industries. The system is characterized by automatic and simple operation with high reliability.

Figure 3: Block flow diagram of a Molecular Gate adsorbent-based process

To maximize the working capacity of the adsorbent, a single stage of vacuum is commonly used to enhance the regeneration. The swing between the high adsorption pressure and regeneration at low pressure is completed in rapid cycles, on the order of minutes, to minimize the adsorbent inventory.

Feed gas is introduced into the system at ambient temperatures and at high pressure. This pressure is typically 100 psig.



For low-pressure wells, it is common to compress the feed to 100 psig with an oil flooded screw compressor, remove the nitrogen and deliver the methane product stream at near feed pressure for further compression to pipeline pressure.

Typical methane recovery rates of 90-95% are achieved.

Field Experience

The introduction and proof of new technology is often a challenge. To overcome the introduction hurdle, in 2000 a small commercial unit was built and operated to demonstrate the technology and operated at a remote wellhead site in Colorado for two years removing 18% nitrogen to pipeline specifications with excellent results. The initial system demonstrated an availability factor of 99%, which is quite high considering that the site was not easily accessible and the unit's operator attention was limited to a daily visit by the pumper responsible for the wells.

The demonstration unit was followed up with the ongoing successful operation of a CO₂ removal unit at Tidelands Oil Production Company in Long Beach, California. These two units formed the experience base to move the technology forward in the commercial marketplace.

As of summer 2008, a total of 30 units are operating or are in design/fabrication for nitrogen rejection and two units for CO₂ removal.

To date, the units tend to be for relatively small flows from 0.5 MM SCFD to 10 MM SCFD. The nitrogen levels treated, thus far, are as high as 40% and the CO₂ levels are as high as 38%. Most market interest is for

installations at the wellhead, although units have also been installed in gas plants downstream of the extraction of NGL liquids. A typical small Molecular Gate adsorbent-based system is shown in *Figure 4*.



Figure 4: Typical installation for a 2-4 MM SCFD Molecular Gate nitrogen rejection unit

Equipment

The equipment required for the removal of the impurities consists of adsorber vessels filled with adsorbent, a valve and piping skid placed alongside the adsorber vessels and a single stage vacuum compressor to maximize the regeneration of the adsorbent. The control system serves the purpose of switching flows between adsorber vessels as they cycle between the process steps of adsorption, depressurization, regeneration and repressurization.

In general, the system consists of three to six adsorber vessels – with four vessels being the most common design.

Since certain flows leaving the system can fluctuate, buffer tanks to smooth flows are generally required. Peripherally, compression of the feed, recycle or product can be required depending upon the available pressures and product use pressure. The system is cycled by an integrated control system and operator interface.

Operating Features

The Molecular Gate adsorbent-based system generally operates unattended. In general, small units are monitored by a daily visit to the unit by the well pumper or mechanic to keep an eye on the operation.

Start-up is at the push of a button with delivery of product gas to the pipeline within minutes. Control, operation and monitoring of the unit can be conducted locally and can be monitored through a remote station and a modem connection if desired.

The nitrogen removal system can deliver high on-stream factors in part because it eliminates the need for a separate carbon dioxide removal unit. Any CO₂ in the feed is removed by the Molecular Gate adsorbent and the product inert will be nitrogen. This ability is unique and considerably simplifies the operation. Systems for

only CO₂ removal are also offered and a CO₂ system operating with no change in performance since 2002 is shown in *Figure 5*.



Figure 5. A Molecular Gate Adsorbent-Based System for CO₂ removal

Since it has a limited number of critical items, the system also achieves a high on-stream factor. This reliability, combined with the unattended operation and servicing by the pumper, results in nitrogen rejection with minimal operations and maintenance costs.

Commercial systems are offered as shop-fabricated, modular units with maximum skid mounting of equipment for minimal installation cost that are delivered with minimal coordination required from the user. A photo of a small, nominal 0.5 MM SCFD SPEC plant is shown in figure 6. These smaller units are both sold as equipment and leased which can be attractive to determine well decline rates prior to a larger drilling program.



Figure 6. A SPEC plant used to treat smaller flows

Feed Pretreatment and Natural Gas Contaminants

There are minor pretreatment requirements for nitrogen rejection and it is generally limited to feed dehydration (CO₂ units remove water vapor when they remove the CO₂). The tail gas contains the rejected nitrogen and any unrecovered hydrocarbons.

In processing a feed that contains nitrogen and carbon dioxide, the carbon dioxide is adsorbed more strongly and is removed by the adsorbent while a portion of the nitrogen is simultaneously removed to achieve the product specification. Since carbon dioxide is commonly present in natural gas, the ability to remove both carbon dioxide and nitrogen in a single step is highly desirable.

Pretreatment to remove oxygen is generally not required since it fits within the pore and is partly removed.

Hydrogen sulfide, if in the feed, is removed as part of the low-pressure tail gas where it can require further treatment for environmental reasons. In most cases it is preferable to separately treat the feed gas for H₂S removal at high pressure prior to nitrogen removal, though systems are operating and removing as high as 4000 ppm of H₂S to pipeline specifications.

Though helium is a small molecule and easily fits within the pores of Molecular Gate adsorbent, it has little surface attraction for the adsorbent and passes through the bed with the methane product. Where the quantity of contained helium is high enough to justify the added cost, it can be recovered through the use of a downstream membrane unit to produce crude helium or further upgraded in a small PSA system to produce higher purity, higher value product.

Tail Gas Use

A Molecular Gate adsorbent-based system does not recover all the methane and loses a portion into the tail gas. In many cases, the use of the tail gas as fuel to a gas engine means there is essentially no loss of methane from the system. To simplify the system and maintain high facility reliability, it is desirable to minimize the number of gas-engines in the production train. Smaller units of a few MM SCFD will generally be designed for a single gas-engine drive genset to burn the tail gas as fuel and use electric drives for the vacuum pump and any other required compression.

Project Economics

Project economics are site-specific. When one or more exploratory wells have been drilled and subsequently shut-in, it can be more economically attractive to develop these fields compared to untested fields. In our market activities, we see most interest for flows of less than 5 MM SCFD and nitrogen concentrations of less than 30%. As noted above the smaller SPEC plant design can be used to prove the production of experimental wells prior to a larger drilling program. Units are also designed for expansion where increases of 50% or 100% can be accommodated at a cost considerably less than that of another unit.

Economics are most favorable for lower levels of nitrogen in the feed. Lower nitrogen concentrations mean higher hydrocarbon concentration and sales gas flows, less adsorbent is required, reduced methane losses and capital and operating costs are lower. In addressing the nitrogen in the feed, it is also important to recognize that the system will remove CO₂ and a portion of any oxygen in the feed without separate processing. As has been proven in the field, the unit's ability to produce pipeline quality sales gas regardless of the level of nitrogen in the feed is important should the actual field gas composition not match that of the design.

The minimal flow rate for reasonable economics can be 0.5 MM SCFD depending on existing infrastructure. Such small flows can be attractive for stand-alone projects or can permit a level of cash flow as a field is developed to provide larger flows. The system can be debottlenecked, often to double the initial capacity, by increasing the adsorbent volume.

Economy of scale are such that the processing costs per MCF decrease from 0.5 MM SCFD to 15 MM SCFD and continue to decrease as the flow rate increases up to the maximum single train capacity, which is in excess of 50 MM SCFD. *Figure 7* presents processing economics to treat a 15% nitrogen contaminated feed gas at 100 psig and with a pipeline nitrogen specification of 4%.

The economics to develop *Figure 7* assume a seven and a half-year project with capital paid out with a 10% interest loan and power costs at 8 cents per kW. It includes both the capital and operating cost of a Molecular Gate adsorbent-based system on an installed cost basis. The operating costs are for power to drive the vacuum pump (or cost of a genset if grid power is not used) plus minor operator attention and maintenance items.

Compression is not included and for low pressure wells the cost of capital and operation for compression to 100 psig for treatment followed by product compression from 90 psig to 800 psig to a transmission pipeline would cost roughly the same as for the gas treatment costs.

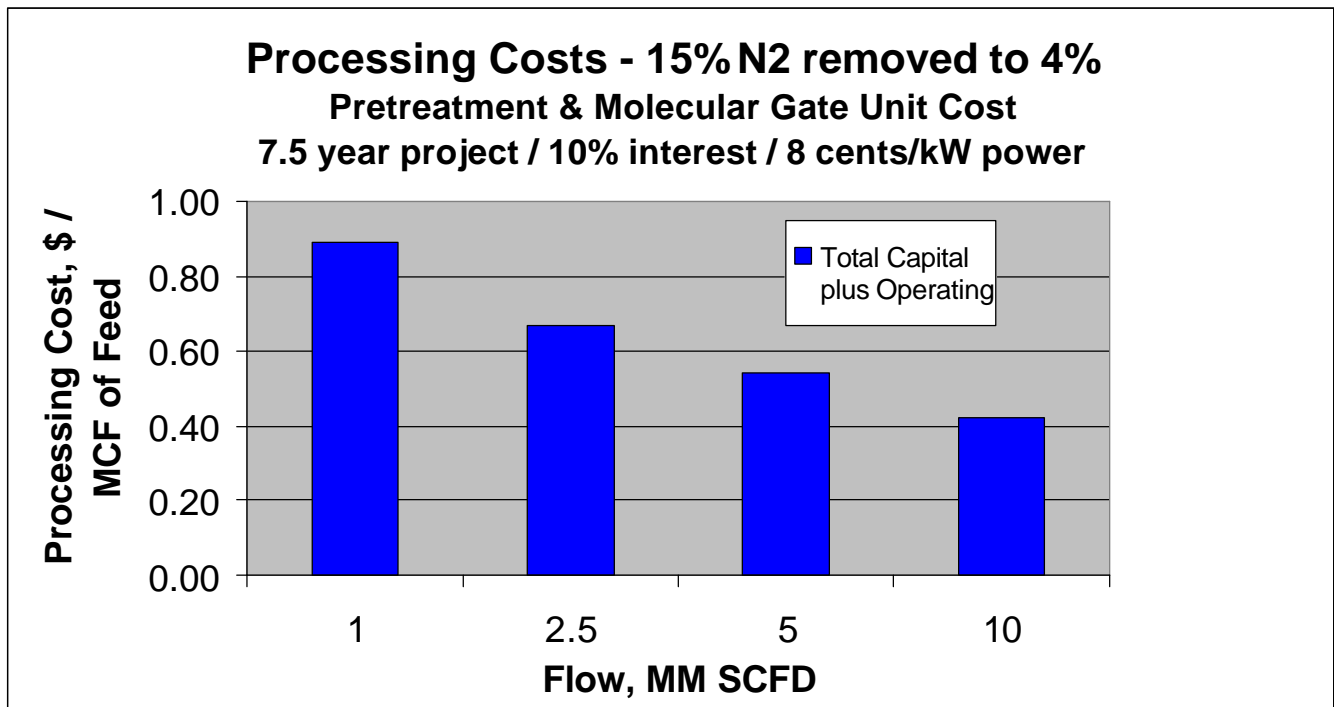


Figure 7: Feed gas processing costs, \$/MCF of contaminated feed

Project Development

A Molecular Gate adsorbent-based system can remove N_2 , CO_2 , O_2 , H_2S and water to meet pipeline specifications. Other challenges of developing a successful project include:

- *Gas ownership* needs to be established and is not always clear, especially when dealing with previously drilled fields and associated *royalty payments* to working and non-working partners.
- *State and local taxes* are not always clear and widely vary.
- The *equipment site* must be selected to maintain good relations with the plant neighbors.

- *Well leases* are generally granted on the state level and need to follow state guidelines. We have encountered instances where local jurisdiction over wells has been claimed, leading to conflict with State authorities.
- *Gathering systems* at low pressure generally use low-pressure plastic pipe to collect the gas from many wells. Since gas is produced at low-pressure, sizing and pressure drop is critical. These gathering systems will often cross the property of many individual landowners, requiring the right of way for both private and public lands.
- *Gas compression* cost can vary widely for purchased and rented equipment. The ability to use tail gas as fuel is helpful to the project economics, and the skills of the gas-engine manufacturer or rental fleet service personnel range widely. Since tail gas is “free fuel”, it is important that this be properly addressed.
- *Power* is required for any project. As a general rule, small systems use a gas engine driven genset or grid power to provide power with electric drives used on the rotating equipment. Many options exist in this regard, but directionally the number of gas engines is minimized due to their relatively low reliability.
- *Air permits* may be required for the gas engine and require proper paperwork, typically on the State level.
- *Product compression* is required where the product is routed to a high-pressure transmission pipeline. Sale to local distribution companies likely allows delivery without further compression. The use of one gas engine to drive a genset for electric loads (including the vacuum pump) plus a second gas engine driving a product compressor can be attractive for larger flows.
- *Pipeline gas sales* are more complex than one unfamiliar with the gas market would assume. For transmission pipeline sales, a pipeline tap is required which can be expensive, thus, a project site that can deliver to existing taps is preferred. The pipeline company will generally require gas composition (or heating value) and flow measurement to assure pipeline quality is delivered. These items may have to be purchased from the transmission company. For local distribution companies, odorization of the product may be required.

Summary

In applications for nitrogen rejection and carbon dioxide removal, Molecular Gate adsorbent-based technology offers an attractive route for meeting the long established needs of the natural gas industry. The 30 systems to date demonstrate the viability and economics of the breakthrough technology.

Molecular Gate systems offer an unattended, cost effective means to upgrade nitrogen contaminated natural gas sources especially for smaller flows and its widespread adoption point to continuing growth.

Guild is a licensee of Engelhard's Molecular Gate Ò Adsorbent Technology (now part of the BASF Group) and is solely responsible for all representations regarding the technology made herein.