MOLECULAR GATE® ADSORPTION SYSTEM FOR THE REMOVAL OF CARBON DIOXIDE AND / OR NITROGEN FROM COALBED AND COAL MINE METHANE

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Introduction
The recovery of natural gas (primarily methane) from coalbed deposits is an established and growing source for the U.S and accounts for almost 10% of its total natural gas production. The gas from on-purpose degassing is often pipeline quality and requires only compression and dehydration before being admitted to the pipeline grid. However, the raw gas is sometimes contaminated with nitrogen (N₂) and/or carbon dioxide (CO₂) that can make the gas inadmissible to the transportation pipeline. In general, the N₂ must be 4% or less and the CO₂ should be 2% or less.

In treating gas produced from virgin coal bed or from degassing operations where CO₂ is present, amine systems are traditionally used for its removal. Guild’s Molecular Gate® adsorption system offers an attractive alternative due to its skid-mounted equipment, low pressure and unattended operation, economic cost and high on-stream reliability.

Natural gas can also be sourced from the residual coal, after the coal has been mined. This source can be the GOB or gas remaining in abandoned coal mines. This source is almost universally contaminated, often with a combination of CO₂ and N₂. If the source is from air intrusion, the source can also be contaminated with O₂. In treating CO₂ / N₂ contaminated feeds, the Molecular Gate adsorption system removes both of the impurities along with a level of O₂ within a single processing step.

To date, 30 Molecular Gate units are underway with twelve projects for upgrading gas from abandoned coal mines. The technology consists of specialty adsorbents and advanced PSA processes that are offered as fabricated packaged equipment. Upgrading requirements, project challenges and project arrangements are discussed in this paper.

Molecular Gate Adsorbent
The Molecular Gate process for coal bed and coal mine methane takes advantage of a unique molecular sieve that has the ability to adjust pore size openings within an accuracy of 0.1 angstrom. The pore size is precisely adjusted in the manufacturing process and 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 the Molecular Gate adsorption system for upgrading nitrogen-contaminated methane, a pore size of 3.7 angstroms is used. This adsorbent permits the nitrogen and carbon dioxide 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.

Carbon dioxide is an even smaller molecule than nitrogen at 3.3 angstroms and is easier to remove than nitrogen. One major advantage of the process in upgrading nitrogen contaminated feeds is that such feeds almost always have a level of CO₂ contamination and, in the process, CO₂ is completely removed in a single step with the nitrogen removed to pipeline specifications.

Since coal bed methane is produced at low pressure (vacuum is sometimes pulled to increase production) the possibility of introducing oxygen into the system exists. Oxygen is also a small molecule at about 3.5 angstroms and fits within the pore of the adsorbent and it is partly removed.

**Process Description**

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

As can be seen in Figure 2, CO₂ adsorbs at a higher capacity than N₂ and thus is more easily removed. A system designed for N₂ removal will require more adsorbent and, thus, have a higher cost than one for CO₂-only removal.

PSA is widely used in light gas separations with thousands 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 1**  
Schematic view of the Molecular Gate pore size and relative molecule size

**Figure 2**  
Generic isotherm for adsorption and PSA pressures
Figure 3 depicts the overall flow process for a typical Molecular Gate adsorption system applied to upgrading coal bed or coal mine methane. Feed gas from the wells is compressed from near atmospheric pressure to typically 100 psig where it is introduced into the Molecular Gate adsorption system. For coal bed and coal mine methane, a screw compressor to 100 psig is typically applied.

The process generates a low-pressure recycle stream that is rich in methane and recirculated back to the suction of the feed compressor. By incorporating this recycle stream, the methane recovered as product sales gas is increased without adding additional compressors. The recycle rate is typically 10-15% of the raw feed rate.

To maximize the working capacity of the adsorbent to remove the N\textsubscript{2}, CO\textsubscript{2} and/or other impurities, a single stage of vacuum is 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 a few minutes, to minimize the adsorbent inventory.

Typical methane recovery rates of 90-95% are achieved in the process. The rejected tail gas, containing the lost hydrocarbons, may be suitable as fuel to gas engines driving gensets or compressors and making use of the otherwise lost methane is a key part of the process optimization.

Development History and Field Experience

The introduction and proof of new technology is a challenge. To overcome the introduction hurdle, a small commercial unit to demonstrate Molecular Gate’s viability was built. This unit started operation in late 2000 at the Hamilton Creek site in SW Colorado and was operated for two years with excellent results. After the demonstration period, it was relocated to a commercial site in Ohio.

In Colorado, the unit was operated on a remote natural gas wellhead site where the feed contained 18% nitrogen and less than 1% carbon dioxide. The system operated to direct the product to one of two local pipelines that accepted either 3% or 6% nitrogen. This site was not easily accessed and lacked electric power, thus, a rental genset unit was used to provide power, and a packaged unit was used to provide instrument air.

The operation of the system proved to be both effective and reliable. The pumper responsible for the wells operated the system and generally visited the site once per day for about a half hour to review a checklist for performance monitoring. The reliability of the system was very good and demonstrated a 99% availability factor.

In May of 2002, the first Molecular Gate adsorption system for the removal of carbon dioxide from associated natural gas was started up at a Tidelands Oil Production Company operated facility in California (~30% CO\textsubscript{2} removed to <2%). A photo of the unit is shown in Figure 4. The system is skid-mounted with low capital and operating costs, and provides automatic and unattended operation with high on-stream factors. A dry product is produced with no need for further dehydration. Permitting and operability concerns were the main drivers for the selection of the Molecular Gate adsorption technology at this location. It continues operation six years later with no change in performance.

The Hamilton Creek N\textsubscript{2} rejection demonstration unit and the Tidelands CO\textsubscript{2} removal unit established the experience base for the technology. Since the start-up of the Tidelands unit in 2002, 30 additional units have been awarded and are operating or in fabrication. Twelve units have been supplied for CBM or CMM upgrading.

Commercial systems are designed to operate unattended and have been built for flow rates as low as 0.5 MM SCFD to as much as 10 MM SCFD. The systems are offered as a complete unit with maximum skid mounting of equipment for minimal installation cost. A single price and warranty is provided with the unit.
Gas Production from CO₂ Contaminated Coal Bed Methane

Coal bed methane is produced from various basins in the USA, typically from shallow mines with gas produced at the surface at low pressure. Contamination with CO₂ is common and the prolific San Juan basin requires the operation of many amine plants for removal of CO₂. Other basins have some level of contamination, though less widespread, including coals from the Black Warrior, Powder River, Illinois and Appalachian basins.

While amine plants are a traditional solution for the removal of CO₂, there are drawbacks for the technology and for certain applications, Molecular Gate adsorption systems can offer an attractive alternative. In amine system, the amines solvents can degrade and cause corrosion, especially from oxygen contamination that is a concern with low wellhead pressures, with resulting downtime and operational challenges.

Amine systems generally operate at high pressure requiring compression of a wet, CO₂ rich feed. This presents challenges in the compression design and operation with corrosion and on-stream factor issues for the multi-stage compressors commonly used. The amine plant also produces a water saturated product stream that requires glycol dehydration to meet pipeline water specifications. In comparison the Molecular Gate adsorption system operates at a relatively low pressure, typically at the discharge of a screw compressor, for which corrosion is a minimal concern and the dry, low CO₂ product stream presents no concern for a product reciprocating compressor.

Gas Production from GOB and Abandoned Coal Mines

Abandoned coal mines must be evaluated for their composition and gas production. Both of these items are difficult to accurately establish, since the shut-in wells are typically at substantial pressures, as high as 40 psig. The flow rate of gas will decrease and its composition may change as the gas is withdrawn.

The gas capacity of the abandoned mine is a function of the coal characteristics, volume of remaining coal and size of the mine. We have seen wells under fairly high pressures of 20-40 psig, whose capacity would be misleading if one simply expected the initial flows from depressurizing wells to be maintained. In general, it is prudent to install upgrading equipment of a capacity that can be fully utilized while including the ability to expand capacity if the gas production proves to be greater than initially assumed. This is the typical approach for Molecular Gate adsorption system design and takes advantage of the ease and cost effectiveness by which the system can be expanded, typically to twice the initial rate.

The feed gas composition can change, as the pressure of the mine is reduced, and a larger portion of the produced gas comes from gas desorbing off the coal rather than that from the mined out area of the mine. The composition change is not well defined. And in this consideration, the ability to remove both carbon dioxide and nitrogen along with flexibility for changes in composition is critical for continual production of pipeline quality gas.

Where the gas is produced from the GOB from active mining, the flow and composition variations are larger due to changing production patterns. The Molecular Gate adsorption system is flexible to such changes and can always produce pipeline quality gas regardless of the feed level of CO₂ or N₂.
Figure 5. A small 1 MM SCFD unit designed to upgrade CMM

*Figure 5* shows a small Molecular Gate unit that was installed in the Illinois basin. This feed gas contained a few percent CO$_2$ and up to 10% N$_2$. As with most units in low-pressure applications, the feed gas was compressed to 100 psig in a gas engine driven screw compressor burning the tail gas from the process. The product gas after the Molecular Gate unit was further compressed from 90 psig to 600 psig in a two-stage electric driven, reciprocating compressor for sale into an interstate pipeline. Since both the vacuum pump and product compressor were electric driven, a gas engine driven genset (also burning tail gas as fuel) was used to provide power. Due to the use of tail gas as fuel there was no direct loss of methane from the system.

The small unit allows for the mounting of the vessels and vacuum pump on a single skid. To minimize the installation costs, the system was mounted on timbers and gravel and moved as a single unit.

**Equipment of the Molecular Gate Adsorption System**

The basic equipment required for the removal of the impurities consists of multiple adsorber vessels filled with adsorbent and a valve and piping skid that is placed alongside the adsorber vessels and serves the purpose of switching flows between adsorber vessels as they cycle between the process steps of adsorption, depressurization, regeneration and repressurization.

It is common to regenerate the system with a single stage vacuum compressor to maximize the regeneration of the adsorbent. This vacuum pump is generally electric driven and, depending on its size, can be on the main valve and piping skid or on its own separate skid for installation alongside the Molecular Gate unit in the field.

The overall system control system, often including feed and product compression, is controlled by an integrated control system that provides for push-button start-up. The control system operator interface can be supplied with the ability to remotely monitor the system via a modem connection.

Figure 6. A 2.5 MM SCFD unit designed to upgrade CMM (plus contaminated natural gas)

A photo of a larger 2.5 MM SCFD unit in the Illinois basin is shown in *Figure 6*. This unit started operation in 2002 and upgrades gas from a series of wells from abandoned coal mines and nitrogen contaminated natural gas. Since many wells feed this unit and the sources vary, the system sees a range of feed compositions. In general, the feed contains up to 6% CO$_2$ and up to 15% N$_2$ with a pipeline specification of 4% inert.

The system consists of an oil flooded screw compressor and two-stage product compressor, tail gas vacuum pump, four adsorber vessels and a valve and piping skid. Buffer tanks to smooth the fluctuations in the flows of certain streams are also provided.

Unlike the smaller 1 MM SCFD unit in Figure 5, the four adsorber vessels for this unit are mounted on a concrete pad and placed alongside the valve and piping skid. The vacuum pump is next to the skid on its own skid package.

At this site, drives are electric and tail gas is burned in gensets to meet the power needs of the site.
Operating Features
The Molecular Gate adsorption system operates unattended and can be monitored remotely. Where maintaining an inert level within a small window is critical, a product 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 15 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 deliver a high on-stream factor. For nitrogen rejection units this is, in part, because it eliminates the need for a separate carbon dioxide removal unit, has limited critical items, and continues operation in the event of the failure of certain components. This reliability, combined with the unattended operation and occasional monitoring by the pumper, results in minimal operation and maintenance costs.

Commercial Molecular Gate adsorption systems are offered as a complete unit with maximum skid mounting of equipment for minimal installation cost. The shop-fabricated, modular systems are delivered with minimal coordination required from the user.

Tail Gas Use
Because the Molecular Gate adsorption system does not recover all the methane and loses a portion into the tail gas, the use of the tail gas is a process optimization for each project. Where the coal mine methane feed gas contains relatively low levels of inerts, the tail gas from the Molecular Gate adsorption system has a sufficient heating value to provide fuel to the feed compressor and/or pipeline compressors.

The feed compressor, product compressor and vacuum pump can consume in the range of 8-12% of the methane in the feed. This fuel demand permits the balancing of the methane recovery by the Molecular Gate unit with the fuel demand (where the tail gas is burned as fuel). In this manner, there is essentially no loss of methane from the system. Burning the low heating value tail gas requires air/fuel control adjustments in the compressor. An automatic control system tailored to the application has been incorporated into several systems to allow robust operation.

Project Considerations
The items below are factors for project development:
- Gas production rate
- Gas ownership and royalty payments
- State and other taxes
- Equipment site
- Well leases and approval requirements
- Gathering system and collection of gases
- Feed and product gas compression
- Power
- Air permits
- Gas treatment – N₂, CO₂, H₂S, O₂, H₂O
- Pipeline gas sales

These considerations can be simplified into gas production, gathering, processing and sales. To generalize, many gas producers tend to drill and produce the gas, while desiring the sale of the gas at the wellhead and leaving the downstream activities to others. The remaining items can involve gathering companies for collecting the gas (often including gas sales to the pipeline) and Engelhard / Guild for the supply of the Molecular Gate adsorption system.

Commercial scenarios that can be considered include the following:
1. Gas production, gathering and sales by the leaseholder who also purchases the Molecular Gate adsorption system. The scope of supply beyond the Molecular Gate unit itself can also include feed and product gas compression, turnkey installation and remote monitoring.
2. In addition to the above, a gathering company could be brought in to collect the gas from the wells and can also take title to the gas at the wellhead along with the responsibility for gas sales. In general, the gathering company will be paid on the basis of gas collected.
3. Financing considerations where the Molecular Gate adsorption system is paid over time rather than purchased.
4. Percent of proceeds contracts where the Molecular Gate adsorption system plus compression is installed in exchange for a share of the sales gas revenue.
5. Percent of proceeds contracts can also include gathering companies to collect the gas for a share of the revenue.

The minimal flow rate for reasonable economics is approximately 0.5 MM SCFD. This flow can be attractive for stand-alone projects, or can permit a level of cash flow, as a field is
developed to provide larger flows. Systems can often be debottlenecked, typically to twice the initial flow rate, by increasing the adsorbent volume.

The Molecular Gate adsorption system economics are most favorable for lower levels of impurities in the feed. Lower impurity concentrations mean higher hydrocarbon concentrations and sales gas flows, require lower adsorbent quantities, have lower methane losses and result in lower capital and operating costs.

In CO\textsubscript{2} removal from coal bed methane, the feed and product compression mean a large fuel sink exists. Thus, feeds that are relatively low in CO\textsubscript{2}, less than about 10\%, are most attractive since the tail gas can be used as fuel and there is no loss of methane from the system. In this application, the capital cost of the Molecular Gate adsorption system will generally be similar to that of an amine plant for smaller flows, while having operational advantages. For larger flows, the Molecular Gate adsorption system offers savings in the 20\% range as compared to amine plus glycol systems.

For N\textsubscript{2} removal from GOB or abandoned coal mines the economics can be favorable even at small flows of 0.5 MM SCFD where the nitrogen is less than about 30\%. In addressing the nitrogen in the feed, it is also important to recognize that the system will remove CO\textsubscript{2} and a portion of any oxygen in the feed without separate processing.

**Summary**

In addition to the growth of interest in coal bed methane, gas production from GOB gas and coal mine methane is growing. The need for the removal of nitrogen, carbon dioxide, oxygen and water, along with a large fuel demand using tail gas as fuel, is also on the rise. These dynamics present an ideal fit for the skid-mounted, expandable, unattended operation of the Molecular Gate adsorption system.