NITROGEN REMOVAL FROM NATURAL GAS WITH THE MOLECULAR GATE ä ADSORPTION PROCESS

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ABSTRACT

Since the introduction of the Molecular Gate process at the 2002 GPA annual conference thirty units have been constructed for the removal of nitrogen and/or carbon dioxide from natural gas making the technology the leading process for the nitrogen rejection. The technology removes nitrogen from contaminated feeds while methane flows through the bed of adsorbent to sales at feed pressure. This adsorption of nitrogen is unique and scalable such that it offers the economical processing of smaller flow rates with design rates as low as 0.5 MM SCFD along with growing experience for larger flow rates with the largest operating system at 10 MM SCFD. This paper provides an overview of the technology, pre-treatment requirements and presents field unit experience for several operating plants. Processing costs for nitrogen rejection are also presented.

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INTRODUCTION

Market and Technology Overview

Since the introduction of the Molecular Gate process at the 2002 GPA annual conference thirty units have been constructed for the removal of nitrogen and/or carbon dioxide from natural gas making the technology the leading process for the nitrogen rejection. The market need for nitrogen rejection is well recognized with approximately 15% of U.S. natural gas reserves containing excess nitrogen; however, what is commonly missing in such broad statements is that these reserves tend to be for smaller flow rates and for reserves that are not well proven. With pipeline requirements typically at 4% nitrogen, nitrogen rejection is costly and places an added expense on the usual challenges of developing a natural gas project.

Since the published volume of nitrogen contaminated reserves is large and improved processing desirable many companies have invested to develop technologies targeted at improving the state of the art. Technologies used to date include (1) cryogenic processing which fractionates methane from nitrogen after liquification at low temperatures and with methane delivered at reduced pressure (2) methane adsorption onto activated carbon (while nitrogen is less adsorbed) with subsequent methane desorption at low pressure as sales gas (3) oil solvent wash systems which absorb methane into a lean oil at low, but not cryogenic temperatures, with subsequent low pressure flashing of the methane as sales gas and (4) membrane processing where methane permeates from high pressure to low pressure for delivery as low pressure sales gas. While these technologies all have been employed they share the trait that the methane product is delivered at a pressure much lower than the feed, hence the methane is removed from the residual nitrogen which remains at relatively high pressure.

The Molecular Gate process is unique in its ability in that it removes the nitrogen from the methane by adsorbing the nitrogen on a molecular sieve while the methane passes through the fixed bed of adsorbent as sales gas at near feed pressure.

The optimum feed pressure is 100 psig which fits well with the current reserves which tend to be tight sands, shale formations and other low pressure sources. In a typical application feed gas is compressed from low pressure to 100 psig using an oil flooded screw compressor and with sales gas produced at 90 psig. By employing vacuum regeneration and a small recycle stream typical methane recovery rates of 90-93% are achieved. A typical flow scheme is presented in Figure 1.

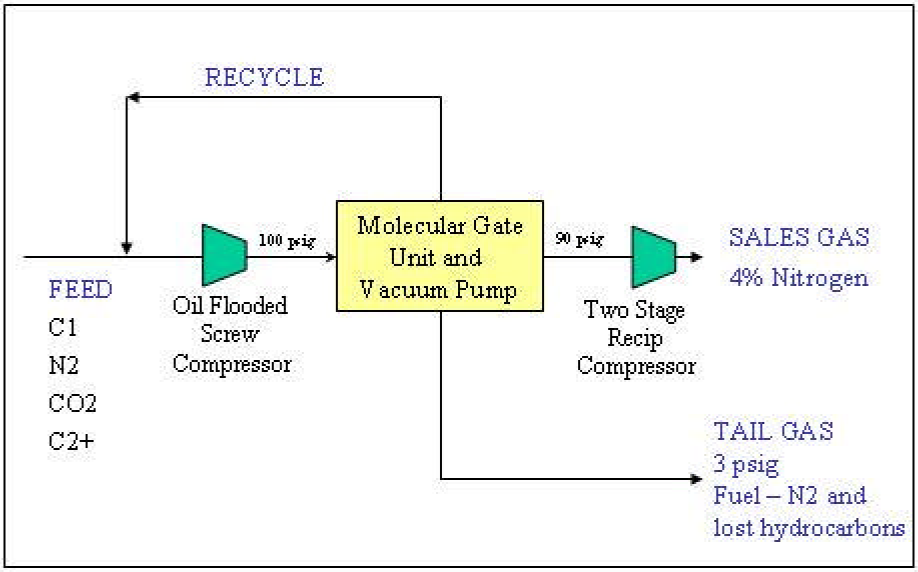

Figure 1: Process Flow Sheet

Development, Experience and Equipment

The introduction and proof of new technology is always a challenge. To overcome the introduction hurdle, in 2000 a small commercial unit was built and operated to demonstrate the technology at a remote wellhead site in Colorado. This first system was operated 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 carbon dioxide 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 early 2009, a total of 30 units are operating or are in design/fabrication. 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% (carbon dioxide levels treated 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 natural gas liquids. A typical Molecular Gate unit is shown in Figure 2.

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

The unit shown in Figure 2 is a recent installation and upgrades a feed of 2 MM SCFD with nitrogen at 40% (plus carbon dioxide at 1%) removed to a pipeline required inert level of less than 5%. The equipment required for the removal of the impurities consists of adsorber vessels filled with adsorbent (these are the four vertical vessels shown in Figure 2), a valve and piping skid placed alongside the adsorber vessels and a single stage vacuum compressor to maximize the regeneration of the adsorbent (not shown). 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. Generally three to six adsorber vessels are applied with the equipment delivered with maximum skid mounting of equipment for minimal installation cost.

Since certain flows leaving the system can fluctuate, buffer tanks to smooth flows are provided. Peripherally, compression of the feed, recycle or product can be required depending upon the available pressures and product use pressure.

The Molecular Gate system operates unattended and can be monitored remotely. Where maintaining an inert level within a small window is critical, a product analyzer signal is used to automatically 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 as well as through a remote station via a modem or internet connection. The system delivers a high on-stream factor in part because it eliminates the need for a separate carbon dioxide removal unit, has limited critical items, and can continue operation in the event of the failure of certain components. This reliability, combined with the unattended operation and a daily check by the well pumper, results in nitrogen rejection with minimal operations and maintenance costs.

Key features of this system are:

- Simplicity of operation
- Minimal maintenance
- No recurrent costs, it works without consuming any adsorbent materials
- High methane recovery
- Contaminants are removed in a single step

Process Description

The technology is based upon the use of a titanium silicate molecular sieve, for which the pore sizes are established during the manufacturing process. This ability to adjust the pore sizes is unique and the pore size is precisely adjusted to allow the removal of nitrogen and/or carbon dioxide while having minimal capacity for methane.

Nitrogen and methane molecular diameters are approximately 3.6 angstroms and 3.8 angstroms, respectively and 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 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 3*.

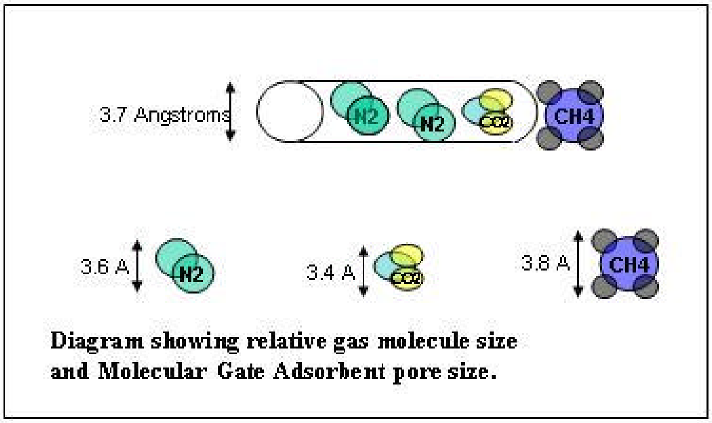

Figure 3: Schematic of size separation within the Molecular Gate Adsorbent.

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. The relative capacity of the adsorbent for typical gases is presented in *Figure 4*.

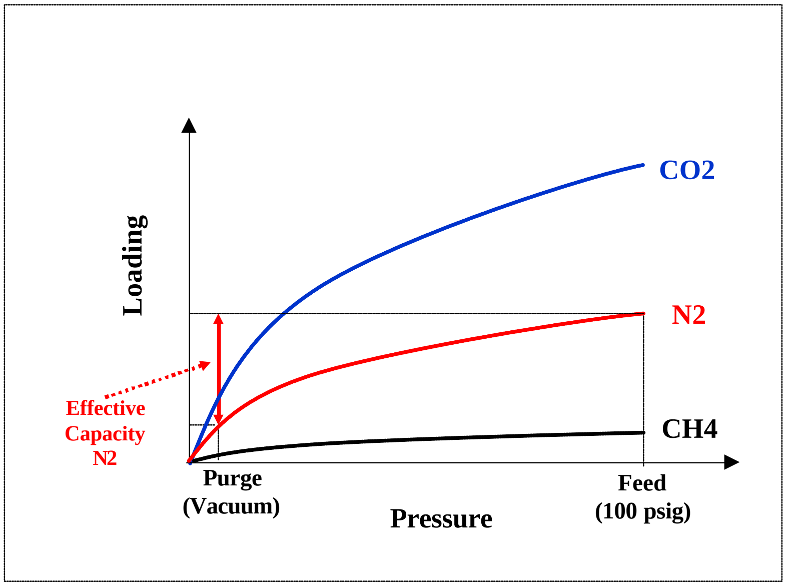

Figure 4: Relative Adsorption of Gas Components

Figure 4 indicates that carbon dioxide is more strongly adsorbed than is nitrogen. For this reason when the feed contains both nitrogen and carbon dioxide, the carbon dioxide is completely removed in a single step while the nitrogen is removed to typical pipeline specifications. As a general rule feed streams containing carbon dioxide concentration that are as high as the concentration of the nitrogen can be processed (for example 10% carbon dioxide and 10% nitrogen treated to nil carbon dioxide and 4% nitrogen. This is due to the fact that carbon dioxide (3.4 angstroms) is an even smaller molecule than nitrogen and easily fits within the adsorbent pore and also has a higher affinity for the adsorbent surface.

This ability to remove carbon dioxide without a separate processing step is an important advantage for the Molecular Gate technology and avoids the additional cost and processing steps of a separate amine or membrane unit for carbon dioxide removal.

The fact that the carbon dioxide is near completely removed is also an advantage for pretreatment prior to LNG plants where two Molecular Gate systems have feed streams containing both carbon dioxide and nitrogen and where the carbon dioxide is removed to less than 50 ppm.

Figure 4 also indicates that the adsorption isotherm shows curvature at the low pressure range with improved effective nitrogen capacity as the purge pressure is reduced. For this reason a vacuum pump 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.

Feed Pretreatment, Water Vapor and Heavy Hydrocarbons

There are minor pretreatment requirements for nitrogen rejection and it is generally limited to feed dehydration since water adsorbs strongly (units designed to remove carbon dioxide also remove water vapor when they remove the carbon dioxide). As with all molecular sieve systems liquid carryover is not permitted and coalescing filters are used for liquid water removal. Since feed flow is upward and the feed is dehydrated, liquid carryover is not an issue in practice.

High pressure wells can be glycol dehydrated but low pressure wells will often employ a TSA dryer prior to the Molecular Gate unit. Where this is done the recycle stream is used for regeneration and the water leaves the system as a condensed liquid. This integration is shown schematically in Figure 5.

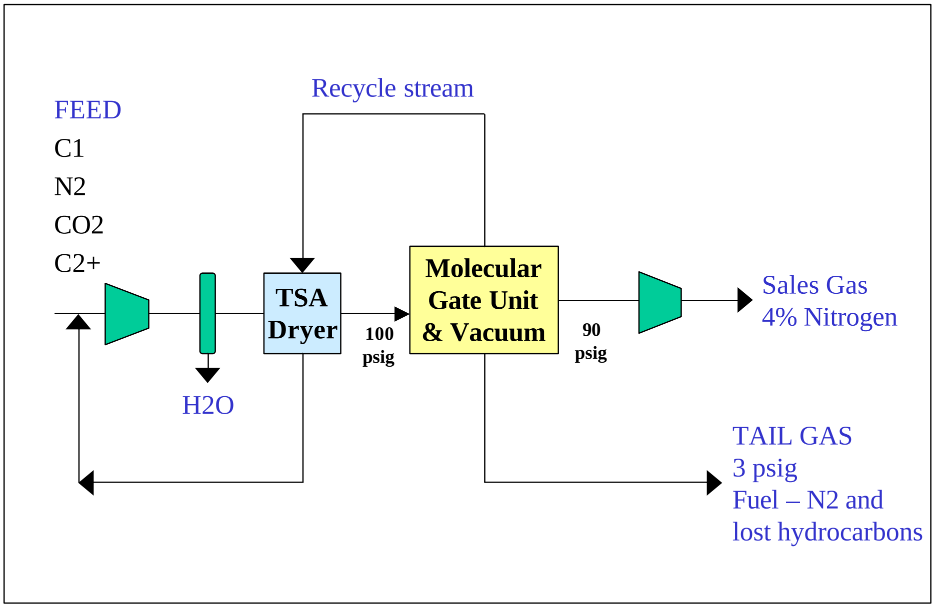

Figure 5: Integrated Dehydration Prior to the Molecular Gate Unit

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. To date hydrogen sulfide levels as high as 4000 ppm have been removed.

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 downstream membrane or PSA units to produce crude helium or further upgraded in a small PSA system to produce higher purity, higher value product.

Heavier hydrocarbons do not behave in the process as might be initially expected. Methane and ethane are both recovered at high recovery rates to sales gas since they are only minimally adsorbed. However, propane and especially C4+ hydrocarbons, while not fitting within the pores of the adsorbent, have an affinity for the binder and surface of the molecular sieve leading to their co-adsorption on the adsorbent surface. The removal of heavy hydrocarbons at the same time as nitrogen and carbon dioxide is an advantage when treating rich gas since the hydrocarbon dew points are met in a single step. However, the adsorption of the heavies means the potential revenue they represent is not captured.

Molecular Gate units have been placed into service where heavy hydrocarbons are extracted before feeding the nitrogen rejection unit and also where heavy hydrocarbons are captured from the tail gas. The tail gas is rejected at low pressure (3-10 psig) but it is enriched in heavy hydrocarbon concentration by a factor of 3 to 6 times as compared to the feed stream concentration. In our experience, in treating the relatively small flows targeted by the Molecular Gate technology the added equipment for the recovery of heavy hydrocarbons can be is economically difficult to justify and is most attractive for larger flows or richer feed streams.

Since the facility requires considerable power to drive compressors and vacuum pumps a more common approach is to use the rejected tail gas as fuel to a genset (or gas driven compressor) to provide power to the facility. Since the tail gas is effectively "free" fuel such genset will typically have a simple return of less than one year as compared to the cost of grid power.

Project Development

The successful exploration and production of conventional natural gas wells requires overcoming a wide range of challenges and nitrogen contamination adds a level of complexity not seen with higher purity wells. In most cases conventional wells can be brought to the market with gas processing limited to compression and dehydration, both of which can be leased on a short term basis. Even where carbon dioxide removal or dew point control is required the equipment is readily available. This allows the wells to be produced based upon exploratory drilling and for accurate decline curves to be established leading to highly accurate drilling programs and "right sizing" of the associated gas processing equipment.

Historically, nitrogen contaminated wells do not have such a luxury since the nitrogen in the feed keeps the gas from being accepted by the pipeline and thus nitrogen rejection drilling plans have been implemented based on extrapolated results from short-term gas flow tests. In Guild's experience such extrapolations can not only be erroneous, the inherent risk of such extrapolation can keep nitrogen contaminated gas projects from progressing. Thus, projects with positive exploratory tests and short term flow results can be abandoned and shut-in.

To help address such limitations Guild developed and offers a "SPEC Plant" which is a fixed size, standard design plant with a nominal capacity of 0.5 MM SCFD when upgrading a feed of 15% nitrogen to 4%. Guild has built seven of these plants and a photo of one is shown in Figure 6.

Figure 6: A SPEC plant used to treat smaller flows

The SPEC plant is offered on rental basis (typically 6-months) during which the unit allows the exploratory wells to be produced and accurate production and decline curves developed. Pending the results of the field work the unit can be replaced with a more appropriate size system to match the field's capacity and future drilling plans, or purchased with a portion of the rental fee credited against the purchase.

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 lower than that of an additional 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 inventory, reduced methane losses and lower capital and operating costs. In addressing the nitrogen in the feed, it is also important to recognize that the system will remove carbon dioxide 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 is typically 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 economy of scale is 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 depending on the feed nitrogen level, can be as large as 50 MM SCFD. *Figure 7* presents processing economics to treat 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 kWH. It includes both the capital and operating cost of a Molecular Gate adsorbent-based system on an installed cost basis. The included 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.

In Figure 7, 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.

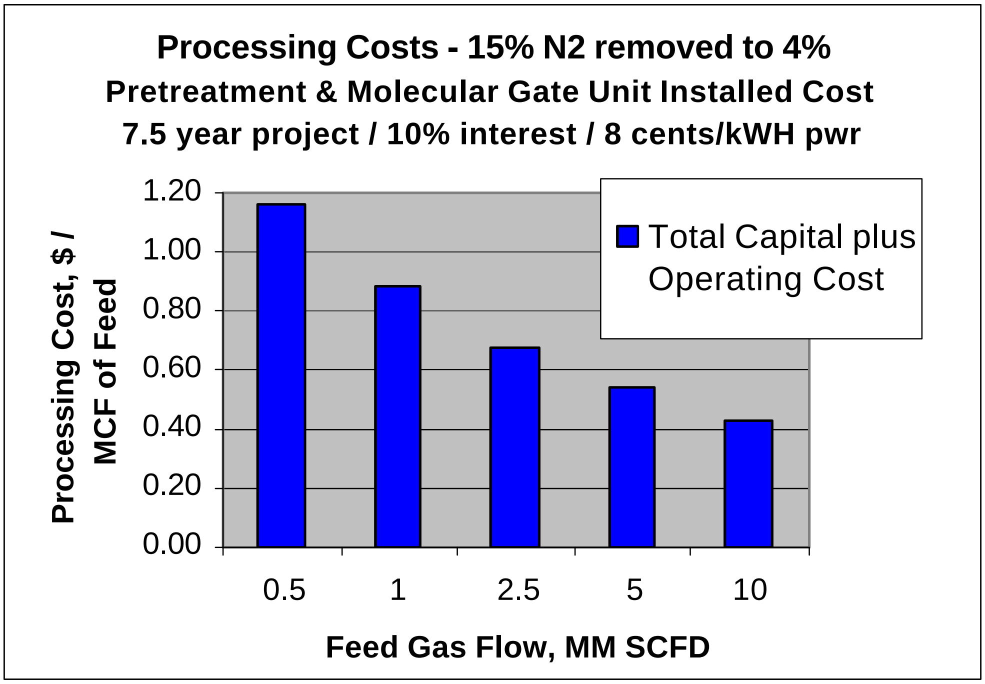

Figure 7: Feed gas processing costs, $/MCF of contaminated feed

Project Development

While the Molecular Gate adsorbent-based system can remove impurities 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 often 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.

- *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. Since tail gas is "free fuel", consideration of its use in a genset or gas-driven compressor is important since cost savings can result. 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 generally allows delivery without further product compression.

- *Pipeline gas sales* can be complex. 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 the 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 GateÒ Adsorbent Technology (now part of the BASF Group) and is solely responsible for all representations regarding the technology made herein.

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