Nitrogen contaminated natural gas is a worldwide issue and more than 11% of natural gas reserves in the USA are sub-quality due to the presence of excessive levels of nitrogen. In the USA, contaminated fields tend to be small producers that cannot support significant operator attention and for which low capital, equipment relocatability, minimal pretreatment and simple operation are critical.

In 2000, the first Molecular Gate® adsorbent based system for the rejection of nitrogen commenced operation and, since that time, eight additional units are underway (seven for nitrogen rejection and two for carbon dioxide removal). The technology is targeted at the smaller fields and for flows from less than 1 MMSCFD to 30 MMSCFD or more.

The systems are designed for unattended operation, push button startup and modularity. They are also noted for the unequivocal ability to meet pipeline nitrogen specification regardless of the nitrogen level in the feed. Unlike all other nitrogen rejection technologies, the Molecular Gate adsorbent removes the nitrogen from natural gas rather than removing the methane from the nitrogen that can lead to nitrogen contaminated product in excess of pipeline specifications.

Interest in the technology has increased steadily and continued growth is projected.

The 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 Å. The pore size is precisely adjusted in the manufacturing process to allow the production of a molecular sieve with a pore size tailored to size selective separations.

Nitrogen and methane molecular diameters are approximately 3.6 Å and 3.8 Å, respectively. In a Molecular Gate adsorbent based system for upgrading nitrogen contaminated natural gas, a pore size of 3.7 Å 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 Å) 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 unit for CO₂ removal.

Oxygen (3.5 Å) is also smaller than nitrogen and is removed at about the same rate as nitrogen (while carbon dioxide is completely removed). Water is also a small molecule that fits in the adsorbent pore and can be removed.

**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 2 illustrates adsorbent capacity versus pressure.

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 characterised by automatic and simple operation with high reliability.
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Field experience

The introduction and proof of new technology is often a

challenge. To overcome this hurdle, a small commercial

unit was built to demonstrate the technology. In late 2000,

it began operation at a remote wellhead site in Colorado

and operated for two years removing 18% nitrogen to

pipeline specifications with excellent results. The system

has demonstrated an availability factor of about 99%. This

is quite high considering that the site was not easily acces-

sible and the unit’s operator attention was limited to a daily

visit by the pumper responsible for the wells. It was

recently relocated to a commercial site in Ohio where it

continues in service producing pipeline gas. At its current

location in Ohio, the feed is 24% nitrogen with a pipeline

specification of 3%.

The demonstration unit was followed up with the suc-

cessful 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 July 2004, a

total of nine units are operating or are in design/fabrica-

tion, including seven units for nitrogen rejection and two

units for CO₂ removal.

To date, the units tend to be for relatively small flows,

from 1 MMSCFD to 10 MMSCFD. Thus far the nitrogen

levels treated are as high as 24% and the CO₂ levels are

as high as 38%. The most interest is for installations at the

wellhead, although units have also been installed in gas

plants downstream of the extraction of NGL liquids. A typ-

ical small Molecular Gate adsorbent based system is

shown in Figure 4.

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 maximise the regen-

eration of the adsorbent. The control system serves the

purpose of switching flows between adsorber vessels as

they cycle between the process steps of adsorption,

depressurisation, regeneration and repressurisation.

In general, the system consists of four to seven adsor-

ber vessels, with four vessels being the most common

design. Since certain flows leaving the system can fluctu-

ate, buffer tanks to smooth flows are generally required.

Peripheral, 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 in-

tegrated control system and operator interface.

Operating features

The Molecular Gate adsorbent based systems generally

operate 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.

Startup is at the push of a button with delivery of prod-

uct 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

onstream 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 remov-

ing CO₂ only are also offered and one such system is

shown in Figure 5.

Since it has a limited number of critical items, the sys-

tem also achieves a high onstream factor. This reliability

combined with the unattended operation and servicing by

the well 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 is delivered with minimal

coordination required from the user. A photo of a valve and

piping skid for a 3 MMSCFD unit is shown in Figure 6.

Pretreatment and contaminants

There are minor pretreatment requirements for nitrogen

rejection. The tail gas contains the rejected nitrogen, CO₂

and any unrecovered hydrocarbons as well as any water

from the feed. Since tail gas is typically used as fuel, feed

stream dehydration with either a glycol unit or a two bed

adsorption dryer is common to eliminate concern with

liquid water carryover and to remove winterisation require-

ments.
ments to burn wet fuel. In either case, only bulk water removal is required.

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 removed at about the same rate as nitrogen. For example, a feed with 20% nitrogen requires about an 85% removal rate to meet a 4% pipeline specification. If oxygen were present in the feed, then about 85% of the oxygen would be removed with the nitrogen.

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 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. has worked closely with gas engine manufacturers to optimise the burning of this low heating value stream. 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 minimise the number of gas engines in the production train. Smaller units of a few MMSCFD 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.

For larger units, two gas engines are often considered, one for a feed/product compressor (when required) and another for a gas drive genset to provide power to all other consumers.

**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, most interest is for flows of less than 5 MMSCFD and nitrogen concentrations of less than 30%.

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, methane losses are lower, and capital and operating costs are lower. The economics can be favorable even at small flows up to about 30% nitrogen. In addressing the nitrogen in the feed, it is also important to recognise that the system will remove CO₂ and a portion of any oxygen in the feed without separate processing.

The minimal flow rate for reasonable economics can be less than 1 MMSCFD 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. A simplified system for a smaller flow of 0.5 MMSCFD is being fabricated.

Economy of scale are such that the processing costs per MCF decrease rapidly from 1 MMSCFD to 15 MMSCFD and continue to decrease as the flow rate increases up to the maximum single train capacity, which is in excess of 50 MMSCFD. Figure 7 presents processing economics to treat a 15% nitrogen contaminated feed gas at 100 - 200 psig and with a pipeline nitrogen specification of 4%.

The economics to develop Figure 7 assume a five year project and include both the capital and operating cost of a Molecular Gate adsorbent based system on an installed cost basis. The operating costs are about 6 - 8 US¢/MCF and are included in the chart. 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.

Not included in the chart is an allowance for the product compressor if such compression is required. Assuming a pipeline pressure of 700 psig, compression from 100 - 200 psig would add 3 - 6 US¢/MCF to the chart above.

**Project development**

A Molecular Gate adsorbent based system can remove N₂,
CO₂, O₂, H₂S 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 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 important, and the skills of the gas engine manufacturer or rental fleet service personnel range widely. Since tail gas is ‘free fuel’, it is critical that this be properly addressed.
- Power is required for any project. As a general rule, small systems use a gas engine driven genset 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 minimised 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 may be 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 is common.
- Pipeline gas sales are far 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 can also cost more than one would assume and may have to be purchased from the transmission company. For local distribution companies, odorisation of the product may be required.

**Summary**

In applications for nitrogen rejection and carbon dioxide removal, Molecular Gate adsorbent based technology offers a new route for meeting the long established needs of the natural gas industry. The successful field systems operations clearly demonstrate the viability and economics of the breakthrough technology. Molecular Gate adsorbent based systems offer an unattended, cost effective means to upgrade nitrogen contaminated natural gas sources especially for smaller flows. Recent adoption of the technology and current market interest point to continuing growth.