

NITROGEN-REJECTING MEMBRANES TO INCREASE GAS HEATING VALUE AND RECOVER PIPELINE NATURAL GAS: A SIMPLE WELLHEAD PROCESS APPROACH

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ABSTRACT

The Gas Research Institute (GRI) has estimated that approximately 17% of the natural gas reserves in the United States cannot be used because of high nitrogen content. Besides naturally occurring N₂, even in normal gas production processes, in many cases during well workups N₂ gas is used to fracture and increase production. Significant amount of N₂ –rich vent gases that cannot be piped are produced at the wellhead and need to be vented for several days. This represent an environment issue as well as a significant product loss.

At present, the only proven technology available to upgrade this gas to pipeline specification is cryogenic separation. However, cryogenic plants are complex, require numerous moving parts and have high capital and operating costs. Furthermore, these plants must process a relatively high volume of gas before they are economical, typically in the range of 50 to 500 million standard cubic feet per day. As a result, smaller gas fields cannot be economically treated.

Membrane Technology and Research, Inc. (MTR) has developed a membrane-based separation process to remove excess nitrogen from natural gas. The process is particularly suitable for small fields, with production rates up to 10 to 15 million standard cubic feet per day. The MTR process is also skid-mounted and movable from one location to another. This makes this process very suitable for well head processing of gas produced during venting after a well work-up.

This paper describes the membranes and processes used, provide data from tests, and discuss commercial installations as case studies.

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A recent Gas Research Institute study showed that about 17% of known U.S. natural gas reserves are sub-quality due to high nitrogen content (1). Naturally-occurring nitrogen is the most common cause of high nitrogen content in natural gas, but in addition, nitrogen content can increase to unacceptable levels even in normal gas production processes. For example, in many cases during well work-ups, nitrogen gas is used to fracture and increase production. Significant amounts of nitrogen-rich vent gases that cannot be piped are produced at the wellhead and need to be vented for several days until the gas quality is at a level which can be used. This represents an environmental issue as well as significant product loss. The transient nature of the high nitrogen content gas released during well work-ups is very well suited to membrane processing. In this application for example, feed gas nitrogen content can be as high as 50 mole% at the start of the work-up and will decline to 6-10 mole % in the due course of time. Figure 1 represents the typical nitrogen content and flow rate in a high rate nitrogen- rich foam fractured horizontal well.

Until recently, the only technology available to upgrade nitrogen-rich natural gas to pipeline specification has been cryogenic technology. However, cryogenic plants are complex, require numerous moving parts and have high capital and operating costs. Furthermore, these plants must process a relatively high volume of gas before they can be run economically, typically in the range of 50 to 500 million standard cubic feet per day. Also cryogenic plants are designed very specifically for fixed inlet gas composition and cannot be used when the inlet conditions vary widely over a short period of time.

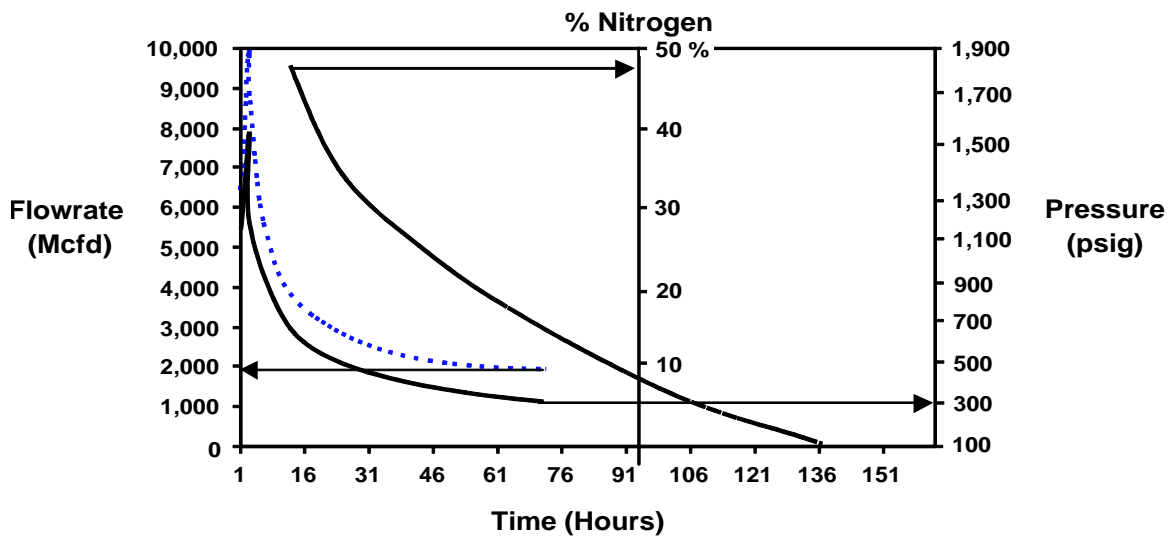


Figure 1. Nitrogen content and blow down flow rate in high rate nitrogen rich foam fractured horizontal well.

In the mid-1980s, membrane systems for the removal of carbon dioxide from gas were first introduced to the natural gas processing industry. These membranes separate gases primarily by virtue of molecular size, and permeate carbon dioxide 10-15 times faster than methane. Unfortunately, the difference in size between methane and nitrogen is very small (kinetic diameter $\text{CH}_4 = 3.8 \text{ \AA}$; $\text{N}_2 = 3.64 \text{ \AA}$), so size-selective membranes were not able to achieve economically useful separations. About five years ago, MTR developed membranes that perform separations by virtue of differences in the solubility of the two gases in the membrane. Methane, being more condensable than nitrogen, is about seven-fold more soluble in certain polymers. This difference in solubility has been used to produce membranes that are three- to fourfold more permeable to methane than nitrogen.

Selection of Membrane Materials [2]

The ability of a membrane to permeate gases is measured by its permeability, P , defined as the rate that a gas permeates a membrane ($\text{cm}^3(\text{STP})\text{cm}^2.\text{s}$) of standard thickness (1 cm) under a standard driving force (a pressure differential of 1 cmHg). Permeability of gases is most commonly measured in Barrer, defined as $10^{-10} \text{ cm}^3 (\text{STP})\text{cm}/\text{cm}^2.\text{s}.\text{cmHg}$ and named after R.M. Barrer, a pioneer in gas permeability measurements.

The membranes used industrially to separate gases are dense polymeric films that contain no pores. The permeating gas molecules dissolve in the polymer film as in a liquid and then diffuse through the membrane down a gradient in concentration created by the pressure difference across the membrane. Gas permeabilities, P , can be expressed as the product of two terms

$$P = D_i K_i \quad (1)$$

The diffusion coefficient, D_i , reflects the mobility of the individual molecules in the membrane material; the gas sorption coefficient, K_i , reflects the number of molecules dissolved in the material.

The most basic factor determining the ability of a membrane to separate two gases, i and j , can be expressed as the ratio of the gas permeabilities, α_{ij} , called the membrane selectivity

$$\alpha_{ij} = [D_i/D_j][K_i/K_j] \quad (2)$$

The ratio D_i/D_j is the ratio of the diffusion coefficients of the two gases and can be viewed as the mobility selectivity, reflecting the different sizes of the two molecules. The ratio K_i/K_j is the ratio of the sorption coefficients of the two gases and can be viewed as the sorption or solubility selectivity, reflecting the relative condensabilities of the two gases.

In all polymer materials, the diffusion coefficient of a gas decreases with increasing molecular size, because large molecules interact with more segments of the polymer chain than do small molecules. Hence, the mobility selectivity always favors the passage of small molecules over large ones. Another important factor affecting overall membrane selectivity is the sorption or solubility selectivity. The sorption coefficient of gases and vapors, which is a measure of the energy required for the permeant to be sorbed by the polymer, increases with increasing condensability of the permeant. This dependence on condensability means that the sorption coefficient also increases with molecular diameter because large molecules are normally more condensable than smaller ones.

In the case of high-nitrogen-content natural gas, nitrogen is smaller but less condensable than methane, so membranes can be made that preferentially permeate *nitrogen* by relying on the mobility selectivity term or that preferentially permeate *methane* by relying on the solubility selectivity term.

In our work, we have chosen to use hydrophobic rubbery polymers with small diffusion selectivity terms and solubility selectivity terms close to the theoretical maximum of 6 to 7. Under these conditions, we obtained membranes with a selectivity of three to four. Some data obtained in the laboratory and then at a pilot plant installed at a Butcher Energy gas field in Ohio are shown in Figure 2. Membrane selectivity increases somewhat at lower temperatures because of changes in the relative solubility of methane and nitrogen.

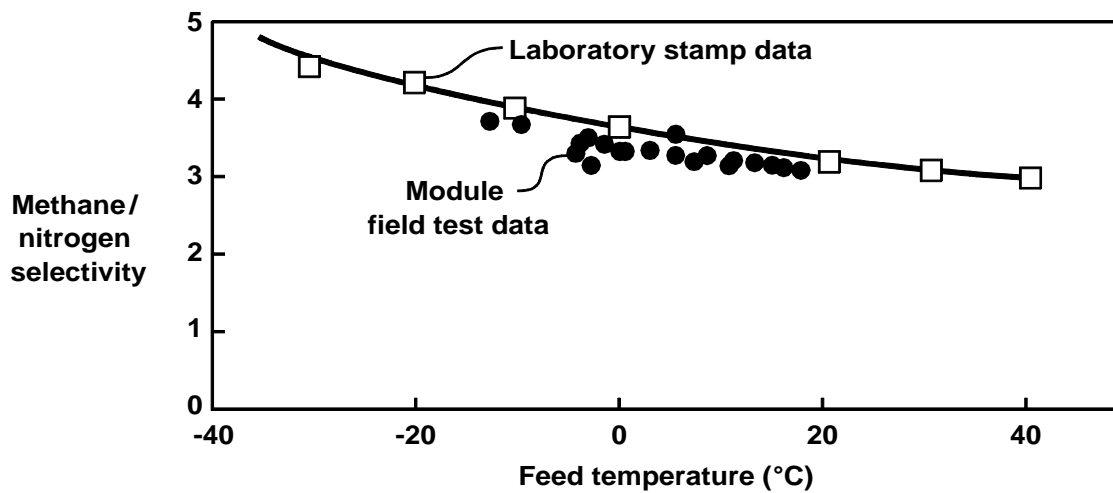


Figure 2. Methane/nitrogen selectivity as a function of gas temperature in laboratory membrane stamp tests and module tests performed over a six-month period at Butcher Energy's Ohio gas field.

Membrane and Module Preparation

For a variety of reasons, membranes used to separate nitrogen from natural gas typically require the use of composite membrane structures. First of all, the optimum materials for methane-permeable membranes are made of rubbery polymers that are not mechanically strong. Furthermore, to obtain high permeation rates, the selective membrane must be very thin, typically between 0.5 and 5.0 μm thick. Finally, the membrane must be able to comfortably support a pressure differential of 500 to 1,500 psi. These contradictory needs are met by forming multilayer, composite membranes of the type shown in Figure 2. The nonwoven polyester paper provides the mechanical strength required. The surface of this material is too coarse and porous to be directly coated with the ultra thin selective layer, so the paper is first coated with a microporous polymer layer. The surface of this microporous layer has pores 0.01 to 0.1 μm in diameter, so these pores are easily bridged when they are coated with the thin selective layer.

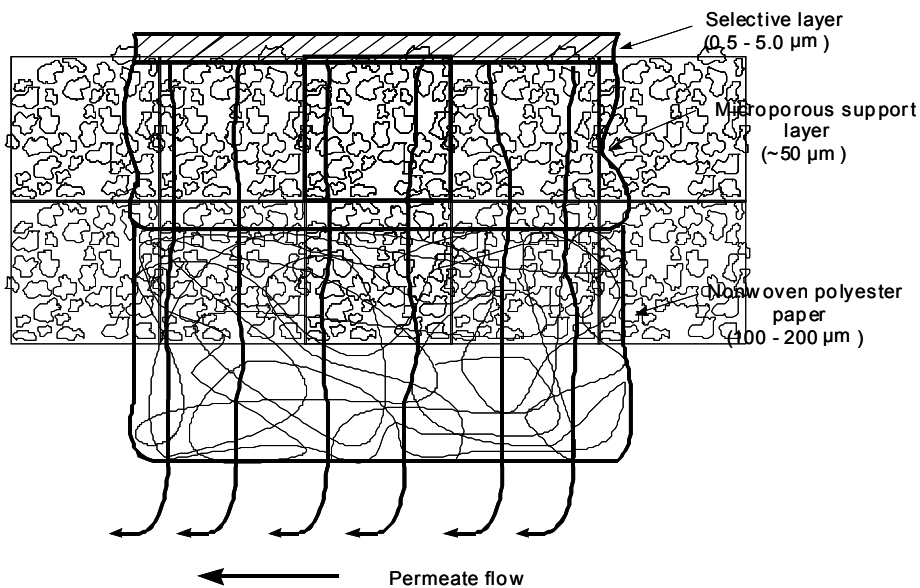


Figure 3. Schematic diagram of a multilayer composite membrane (not to scale).

Even though membranes of the type shown in Figure 3 have extremely thin selective layers, many square meters of membrane are required to separate a useful amount of gas. The units into which large areas of membrane are packaged are called membrane modules. In this nitrogen separation process, we chose to use spiral-wound membrane modules of the type illustrated in the exploded view shown in Figure 4.

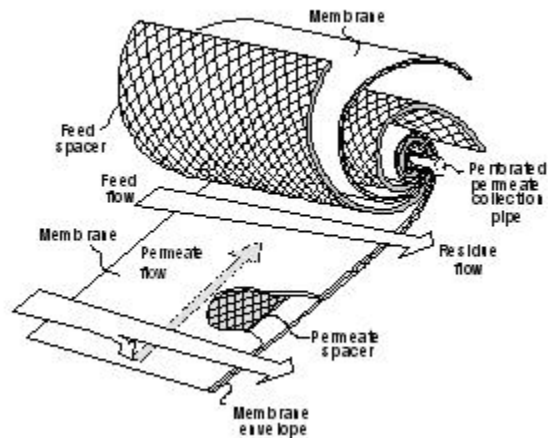


Figure 4. Exploded view of a spiral-wound membrane module. The wound module is contained in a tubular pressure vessel. High pressure, nitrogen-contaminated gas passes across the membrane surface. Methane and other hydrocarbons preferentially permeate the membrane, producing a nitrogen-depleted permeate. The residue gas is enriched in nitrogen.

Spiral wound modules are manufactured on an industrial scale and are standardized in sizes at 8" and 12" diameter modules. A complete separation plant may use from 10 to several hundred modules, depending on the size of the gas stream to be treated.

Process Design

The complexity and cost of the membrane process increases with the nitrogen content of the gas, especially if the product gas contains low mol% nitrogen. If the gas contains less than 6 mol% nitrogen, a single bank of modules can be used to produce the separation required. A typical process is shown in Figure 5(a). Pressurized feed gas passes across the surface of the membrane: the permeate, depleted in nitrogen, is re-pressurized while the residue is used as fuel. The process achieves higher than 90% methane recovery in the product gas and even higher Btu recovery since the membrane permeates essentially all of the ethane, propane and higher hydrocarbons from the residue gas. The product gas consists of nitrogen, methane and very little else.

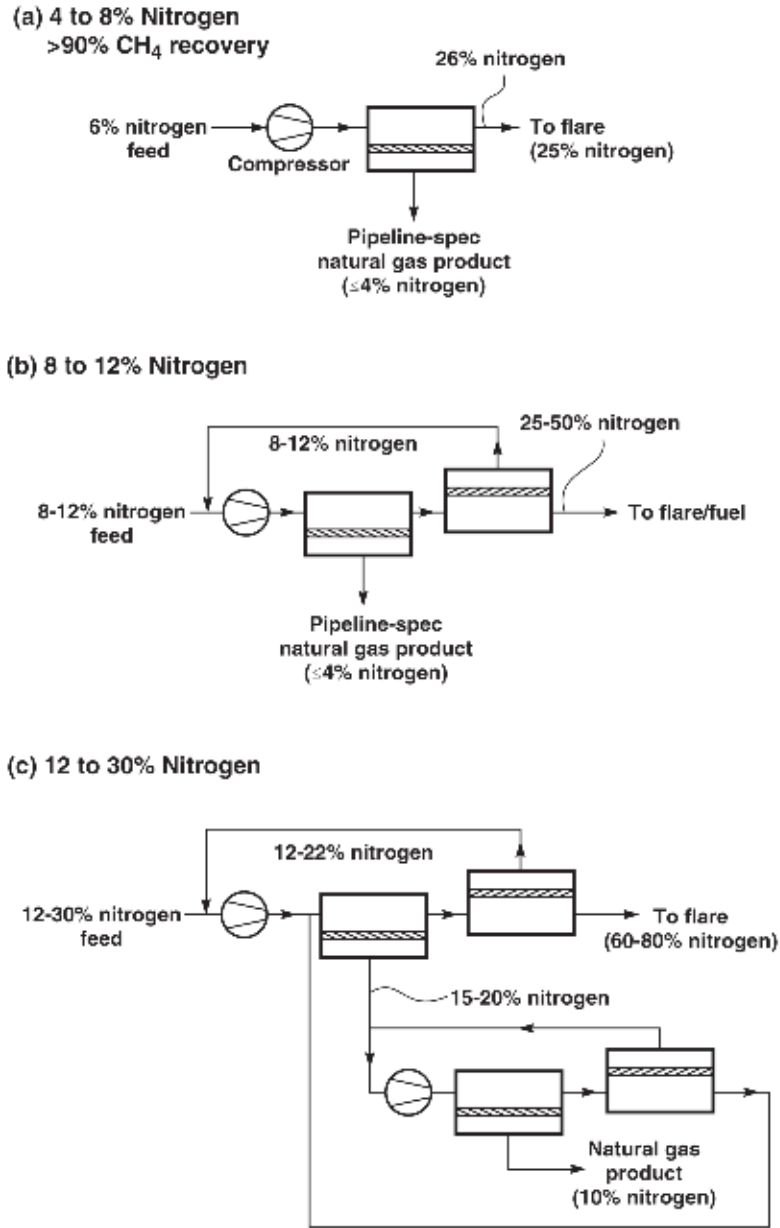


Figure 5. Membrane-based process designs for nitrogen removal from natural gas streams of varying nitrogen content.

MTR's first proof-of-concept system was designed to treat this type of gas. The gas was being used to power a fuel cell, but contained up to 6% nitrogen. High nitrogen was a problem because it produced small amounts of ammonia in the fuel cell reformer, which then degraded the fuel cell electrolyte. The customer purchased the membrane unit to reduce the nitrogen concentration to 3% in the permeate. The high-nitrogen residue gas was used as boiler fuel. This simple system has been in operation for two years and has demonstrated the overall reliability of the membranes. A photograph of the system at the fabricator's shop is shown in Figure 6.



Figure 6. Photograph of nitrogen removal membrane system that reduces nitrogen content of a fuel cell line stream from 6 mole% to 3 mole%.

If the natural gas stream being treated contains more than about 8% nitrogen, it is no longer possible (with today's membranes) to produce gas with $\leq 4\%$ nitrogen and good hydrocarbon recovery in the product gas in a single-stage membrane process. For feed gas containing 8-12% nitrogen, the type of design shown in Figure 5(b) would be used. As in the Figure 5(a) design, the gas is passed across the first set of membrane modules to produce a permeate product gas containing $\leq 4\%$ nitrogen. The nitrogen-rich residue then passes to a second set of modules, which produces a residue gas containing 25-50% nitrogen and a nitrogen-depleted permeate gas containing 6-10% nitrogen. The permeate gas contains too much nitrogen to be mixed with the product gas, so it is recycled and mixed with the incoming feed gas. A residue stream containing 25-50% nitrogen gas can be used as compressor fuel. As for the previous lower nitrogen content approach the process for treating 8-12% nitrogen streams achieves about 90% methane recovery in the product gas and typically close to 93-94% Btu recovery because of preferential permeation of the higher hydrocarbons.

Gas containing 12-30% nitrogen would be treated by a process of the type shown in Figure 5(c). The nitrogen content of the feed gas is too high for gas with $\leq 4\%$ nitrogen to be produced in a single membrane unit, so two membrane separation units stages are linked. The first unit produces a residue stream containing 60-80% nitrogen to be flared and a low-pressure gas stream containing 12-22% nitrogen. This low-pressure stream is fed to a second membrane unit, which produces gas with $\leq 10\%$ nitrogen content that can be blended with appropriate pipeline-quality natural gas to achieve the specified nitrogen content for an overall pipeline product gas. A residue gas from the second membrane unit (typically containing about 20% nitrogen) is recirculated to the first membrane process. Compressor fuel gas is obtained by fractionating a portion of the residue gas.

If the gas contains more than 30% nitrogen, processing with membranes to produce pipeline quality gas is usually not economically feasible. However, using the membrane process to fractionate a high nitrogen gas into a 10-20% nitrogen fuel gas and a 70-80% nitrogen gas to be flared or re-injected should be considered.

Economic Evaluation of the Membrane for Processing Nitrogen-Rich Blow Gas Produced in Nitrogen Foam Fracturing

Two cases have been considered: 1) for a high-volume horizontal well and 2) for a vertical well.

Nitrogen foam fracturing generates wellhead gas with nitrogen content varying over time from as high as 54 mol% to as low as 5-12 mol%. Our economic evaluation is based on transient-state nitrogen content. The reason to evaluate the economics on a transient basis is because as nitrogen content falls, the overall MMBtu recovery level increases and therefore net revenue also increases.

Right after fracturing and holding the well with nitrogen foam, the well pressure is reduced. The initial gas is predominantly nitrogen and over time, as the well is blown down, methane content starts to increase. Up to 3-8 days of blowdown are required to reduce the nitrogen content to levels where the gas can be piped for sale. This represents a transient condition on the wellhead with respect to nitrogen content, flow and pressure. During this period, however, a large amount of natural gas is also lost with the nitrogen. If the natural gas in the stream could be recovered effectively, it would be efficient not only for its economic value but the emission of the greenhouse gases would also be reduced. To date, no easy solutions have been available for processing this transient stream to provide pipeline-quality gas. However, with the recent availability of nitrogen separation membrane technology, this application is now feasible. Not only are membranes good in delivering suitable product under transient conditions of changing nitrogen content and so forth, but membrane systems are compact and lightweight. They can be mounted on flat bed trailers to produce the mobility required to bring the technology to any wellhead that can be reached by truck. Furthermore, this mobility means that membrane units can be moved from site to site to cover a broad area of wells that are being fractured sequentially.

The performance, capital and operating costs of the membrane systems illustrated in Figure 5(b) & (c) are shown in Table 3. The economic analysis of these membrane systems show simple payback times of less than a year at the current natural gas price of US \$ 8.00 per MMBtu. MTR's nitrogen removal membrane systems require only a simple filter coalescer upstream to remove aerosols and particulates, which significantly reduces the pretreatment capital and operating expenditure required, when compared to other technologies. Typical membrane cartridge life is from 3-5 years of continuous operation.

The economics are obviously more attractive with US\$8 per MMBtu natural gas prices, reducing the payback time to 9 months from 18 months for US\$4 per MMBtu.

Table 3. Performance, Capital, and Operating Cost of Membrane Systems With Horizontal and Vertical Well Nitrogen Removal Membranes.

	Vertical Well High-Nitrogen Blowdown Processing	Horizontal Well High-Nitrogen Blowdown Processing
System Characteristics		
Feed Gas (MMSCFD)	0.5	3.5
Inlet Nitrogen Feed Gas (mole%)	15-8	31-12
Product Gas Nitrogen Content(mole%)	<4	<10
System Design Pressure(psig)	310	500
Capital Cost (\$ thousand)		
Membrane System Price(Including Membrane Cartridges, Pressure vessels, Inlet Filter Coalescer, skid frame, Flat bed trailer) (US \$)	350	650
Total Capital Cost	350	650
Operating Cost(per year)		
Compression Leasing, 20% of Total compression (310 psig @ US \$ 600/hp & 500 psig @ US \$ 900/hp)	35	220
Labor and Maintenance at 10% of Capital Cost	35	65
Capital and Depreciation at 20% of Capital Cost	70	130
Annualized Membrane Replacement Cost(@3-5 year life)	<u>25</u>	<u>100</u>
Total Operating Cost	165	515
Net Revenue @ \$ 8/MMBTU		
Simple Payback Period	600 9 months	3550 6 months
Net Revenue @ \$ 4/MMBTU		
Simple Payback Period	300 18 months	1775 13 months

Field Experience

MTR, together with ABB-Randall Gas Technologies, have been developing the process described in this article for the past four years. The first pilot-scale module test system was operated at a Butcher Energy high-nitrogen gas field for almost six months in 2000-2001. Later, a commercial proof-of-concept system was installed to fractionate a small gas stream containing up to 6% nitrogen into 3% nitrogen gas to be used in a fuel cell, and high-nitrogen residue gas to be used as boiler fuel. This unit has been operating without attention in a virtually maintenance-free mode for the past three years. In April 2004, the first full-scale demonstration system using the technology was installed at a North Texas Exploration well in North Texas. A photograph of the membrane skid during installation is shown in Figure 8.



Figure 8. Photograph of the first full-scale commercial system under installation for North Texas Exploration in 2004.

Conclusion

MTR has completed development, testing and demonstration of new membranes for nitrogen/methane separation. Commercial installations are now in place producing pipeline-quality gas for clients. MTR has been offering these systems for commercial installations with full guarantees and warranties since 2003.

Due to the specific requirements of the applications discussed in this paper, MTR believes our solution fulfills the various needs of producers for wellhead nitrogen/methane separation, including mobile units, transient feed gas conditions, simplicity of design and automatic unmanned operation. MTR's membrane process provides not only significant

economic benefits of recovering natural gas, but also greatly reduces on-site methane emissions to the air. This provides a win-win solution for the gas producer and for the environment.

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