Nitrogen Removal from Natural Gas

Quarterly Report
September 1 - November 30, 1996

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Work Performed Under Contract No.: DE-AC21-95MC32199

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
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December 17, 1996

Dr. Harold Shoemaker
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Re: Contract No. DE-AC21-95MC32199, Phase II
"Nitrogen Removal From Natural Gas"
Quarterly Progress Report Number 1
Period: September-November, 1996

Dear Dr. Shoemaker:

This is the first quarterly progress report from Membrane Technology and Research, Inc., to the U.S. Department of Energy under Phase II of Contract No. DE-AC21-95MC32199, entitled "Nitrogen Removal From Natural Gas." This report covers the months of September to November, 1996.

BACKGROUND

According to a 1991 Energy Information Administration estimate, U.S. reserves of natural gas are about 165 trillion cubic feet (TCF). To meet the long-term demand for natural gas, these reserves will have to be tapped. However, Gas Research Institute (GRI) studies reveal that 14% (or about 19 TCF) of known reserves in the United States are subquality due to high nitrogen content. Nitrogen-contaminated natural gas has a low Btu value and must be upgraded by removing the nitrogen.

In response to the problem, the Department of Energy is seeking innovative, efficient nitrogen-removal methods. Membrane processes have been considered for natural gas denitrogenation. The challenge, not yet overcome, is to develop membranes with the required methane/nitrogen separation characteristics. Our calculations show that a methane-permeate

membrane with a methane/nitrogen selectivity of 4 to 6 would make a membrane denitrogenation process viable.

Phase I of this project showed that this target selectivity can be achieved, and that the economics of processes based on this selectivity would be competitive. Gas permeation measurements with membranes prepared from two rubbery polymers and a superglassy polymer showed that two of these materials had the target selectivity of 4 to 6 when operated at temperatures below -20°C. An economic analysis showed that a process based on these membranes is competitive with other technologies for small streams containing less than 10% nitrogen. Hybrid designs combining membranes with other technologies are suitable for high-flow, high-nitrogen-content streams.

The Phase I work demonstrated the potential usefulness of using methane-permeable membranes for the denitrogenation of natural gas. The objective of Phase II is to determine which of the two candidate membranes is the most suitable for scale up to membrane modules for laboratory tests followed by field tests of the process.

Because the design and construction of the low-temperature full-recirculation test apparatus required for the Phase I tests took longer than anticipated, work for Phase I Tasks 3 and 4 was not all completed. This work is being completed in Phase II.

Task 3. Prepare Laboratory-Scale Modules

A silicone rubber module was prepared for these tests. The composite membrane comprised a 20- μm layer of silicone rubber on a polyetherimide (PEI) high-pressure microporous support layer. This module, which contains approximately 8,000 cm^2 of membrane area, has been tested in other projects and has performed well.

Before starting the tests with this module, we performed a set of pure gas tests to determine the separation performance of the membrane. The results of these tests are shown in Table 1.

Table 1. Results of Initial Pure Gas Tests for Laboratory-Scale Silicone Rubber Test Module

Feed Gas	Permeation Flux [$10^{-6}\text{cm}^3(\text{STP})/\text{cm}^2\cdot\text{s}\cdot\text{cmHg}$]	Gas/Nitrogen Selectivity [-]
Nitrogen	6.7	—
Oxygen	14.3	2.1
Carbon Dioxide	78.0	11.6

The module pure gas performance matched that expected from the membrane properties. This module will be used in future tests to determine the methane/nitrogen selectivity as a function of temperature. Initial results of these tests are reported in Task 4.

We also plan to perform experiments with a poly(trimethylsilyl propyne) [PTMSP] membrane. The development and testing of this membrane will occur in the next two to three months and will be reported under Task 7.

This task is 100% complete.

Task 4. Evaluate Laboratory-Scale Modules

The 10-scfm high-pressure test system, shown in Figure 1, has been modified for the preliminary low-feed-temperature tests. A shell-in-tube heat exchanger was installed in the feed stream just before the module. A small chiller rated to -20°C will feed an ethylene glycol cooling fluid to the shell side of the heat exchanger.

Figure 1. Schematic diagram of the high-pressure test system.

This system will be used to test the silicone rubber module described in Task 3. Our initial experiments will focus on determining membrane separation performance for methane and nitrogen as a function of temperature and feed pressure. The results will be compared to those obtained using membrane stamps in Phase 1 of the project.

To perform experiments at low temperatures, we had to develop an appropriate method of cooling the feed stream in our module test system. We have designed and tested a system in which the feed gas is cooled by a ethylene glycol mixture fed from an external chiller; the lowest temperature achieved was about -10°C . To reach lower temperatures, we modified this system by

adding a liquid-nitrogen-cooled double-pipe heat exchanger in the exit line of the external chiller to further decrease the temperature of the ethylene glycol solution. In preliminary tests we were able to obtain temperatures as low as -40°C. We will use this method in our module test system under various conditions of feed gas flow rate and pressure to verify that such low temperatures are achievable in the system.

Experiments performed with the silicone rubber module referred to in Task 3 yielded encouraging results. Table 2 shows the results of the tests performed with 10% nitrogen/90% methane at different feed temperatures and pressure of 400 psig.

Table 2. Results of Tests on Silicone Rubber Membrane Module Using 10% Nitrogen/90% Methane Gas Mixture at a Feed Pressure of 400 psig.

Feed Temperature (°C)	Pressure-Normalized Flux (10 ⁻⁶ cm ³ (STP)/cm ² ·s·cmHg)		Methane/Nitrogen Selectivity (-)
	Nitrogen	Methane	
20	9.0	26.6	2.9
10	8.3	25.4	3.1
0	7.3	23.2	3.2
-8	6.6	22	3.3

The following trends can be seen from the results in Table 2:

- 1) As the feed temperature is reduced, the pressure-normalized fluxes of both nitrogen and methane decrease.
- 2) The nitrogen pressure-normalized flux decreases more than the methane pressure-normalized flux, which leads to the increased methane/nitrogen module selectivity as the feed temperature is reduced.

These trends duplicate those observed in the stamp test experiments performed in Phase I of the project.

To determine the effect of temperature on the permeability in a membrane, a pseudo-Arrhenius type relationship as shown in equation (1) can be used.

$$P = P_0 \exp \frac{E_p}{RT} \quad (1)$$

where R is the gas constant, P is the pressure normalized permeation flux, E_p is the heat of permeation and T is the temperature in Kelvin.

When used in the equation, the data show that the nitrogen heat of permeation is 1,738 cal/gmol and the methane heat of permeation is 1,084 cal/gmol. The heat of permeation of methane is lower than that of nitrogen, and both are endothermic. This implies that, as the temperature is decreased, the permeation fluxes of both methane and nitrogen decrease. Typically, the heats of permeation of higher hydrocarbons (such as butane, pentane, hexane etc.) are negative, indicating that the permeation process is exothermic. For such components, lowering the feed temperature increases the permeation flux.

This task is 60% complete.

Task 7. Prepare Optimized Composite Membranes

We have already prepared optimized silicone rubber membranes for this project. We have also started to manufacture PTMSP membranes, but these have not yet been optimized. To optimize the thickness of the membrane, we needed to first optimize the chemical synthesis of PTMSP to control the molecular weight of the resulting polymer. This has been partially accomplished. We will then manufacture new membranes from this polymer, for tests in module form in the next two months.

This task is 25% complete.

Task 8. Prepare Bench-Scale Modules

No activity on this task during the reporting period.

This task is 10% complete.

Task 9. Modify Existing Test Skid

The test skid to be used for the future field test was relocated to our facility from our storage area. The system was pressure tested up to 1,200 psig. We also tested the mass flow-meters installed in the system and made appropriate adjustments. The system is currently being used for another DOE project field test. Once it is returned, it will be modified for the performance of the nitrogen tests.

This task is 15% complete.

Task 10. Evaluate Modules in Test Skid in Laboratory/Write Manuals

A manual for the test system has been written and several flow tests have been performed.

This task is 10% complete.

Task 11. Finalize Field Site/Prepare NEPA Documents

Some progress on this task has been made in the last two months. We received a lead regarding an application for upgrading low-Btu natural gas in the Appalachia region in Ohio. A brief description of the problem and our proposed solution is discussed below.

As we discussed in our Phase I final report, it is highly likely that potential applications exist for the denitrogenation of natural gas in which the product specifications are not necessarily pipeline specifications (i.e. 4 mol% maximum inerts content). In many cases, especially with smaller operators, it is quite possible that the requirements may be based on Btu value or some other specification such as the Wobbe number (defined as the ratio of the heating value to the square root of gas specific gravity). One such application (with possible implications for many natural gas wells in the Appalachia region) was reported to us by Mr. John Hawbaker from Petro Drilling Corporation.

Petro Drilling has a gas well in which the nitrogen concentration is 9.8 mol%. This concentration is too high for the pipeline, and the gas barely meets the heating value specifications. However, if this nitrogen concentration can be lowered to between 6.5 and 7 mol%, the gas will be salable to the pipeline. The feed gas is available at a pressure ranging from 1,300 to 600 psig, and the product gas is required at 200 psig. Since MTR's membranes permeate methane preferentially, the permeate stream, which is at lower pressure, can be fed directly to the pipeline without recompression. Also, the higher allowable concentration of nitrogen in the product gas makes a higher recovery of hydrocarbons possible.

An interesting feature of this application is that the wellhead pressure decreases rapidly as a function of time due to a low permeability of the formation. The operator expects that the pressure will decrease from about 1,300 to less than 1,000 psig within a day or so if the flow rate is about 0.5 MMSCFD. However, their flow tests show that the pressure will build back up to about 1,300 psig in a few hours, once the well is shut down.

To accommodate this mode of operation, we designed a membrane system with four spiral-wound elements using a silicone rubber membrane. The expected performance of this system as a function of pressure is shown in Table 3.

Table 3. Expected Separation Performance of a Membrane System Comprising Four 8-inch Elements as a Function of Feed (Reservoir) Pressure.

Feed Pressure (psia)	Feed to Membrane System (MMscfd)	Product Gas to Pipeline (MMscfd)	Heating Value of Product Gas (Btu/scf)	Wobbe Index (Btu/scf)
1,350	0.87	0.75	1,017	1,261
1,250	0.80	0.68	1,017	1,260
1,000	0.61	0.52	1,019	1,262
850	0.50	0.42	1,022	1,264
600	0.32	0.25	1,030	1,268

The data in Table 3 show that, as the reservoir pressure decreases as a function of time, the product amount of gas produced from the membrane system (matching the specification of 6.5% nitrogen) decreases. However, over the whole range of pressures, the membrane system can meet both the heating value and Wobbe index specifications. The pipeline requires the heating index to be a minimum of 1,000 Btu/scf and the Wobbe index to be a minimum of 1,222. In these calculations, a methane/nitrogen selectivity of 3 was assumed.

These data have been reviewed by the Petro Drilling personnel and also by the pipeline company. They have expressed interest in performing a field test with our membrane system to confirm that these specifications are met in the field. We have offered to provide a membrane system for the field test. Currently, we are working on the details of the arrangement.

This task is 25% complete.

Task 12. Install Test Skid at Field Site/Perform Preliminary Module Evaluation Tests

No activity on this task during the reporting period.

This task is 0% complete.

Task 13. Prepare Prototype Field Modules

During the reporting period, we successfully rolled four more 8-inch modules. We are continuing to streamline the manufacturing process so that we can optimize our success rate and minimize the time required for preparing and rolling each module.

This task is 20% complete.

Task 14. Perform Long-Term Tests at Field Site

No activity on this task during the reporting period.

This task is 0% complete.

Task 15. Survey End Users/Analyze Applications

We have initiated contacts with a number of end-users for this application. Analysis of the application from Petro Drilling Corporation was discussed in detail under Task 11. We will continue to build a data base of applications as the project continues.

This task is 10% complete.

Task 16. Perform Technical and Economic Analysis

Initial technical and economic analysis on the Petro Drilling Corporation application has been completed. We have submitted a budgetary quotation for a membrane system comprising four 8-inch spiral-wound membrane elements. The price of the membrane system was received favorably by the operator. We are currently working on details for performing a field test.

This task is 5% complete.

Task 17. Manage Program/Prepare Reports

The Phase II portion of the project is progressing according to our plan. The cost and milestone reports to the end of November are attached.

This task is 9% complete.

OVERALL PROJECT STATUS

We have started low-temperature module testing to evaluate the methane/nitrogen selectivity of membrane modules. The necessary modifications to the module test system are almost completed, and we are expecting to obtain data at temperatures as low as -40°C during the next two months. We have started to make contacts with end-users of the technology, and we are currently working out details for a potential field test at a gas well in Ohio.

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