Low-Quality Natural Gas
Sulfur Removal/Recovery System

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Introduction

Natural gas provides more than one-fifth of all the primary energy used in the United States. Much raw gas is "subquality", that is, it exceeds the pipeline specifications for nitrogen, carbon dioxide, and/or hydrogen sulfide content, and much of this low-quality natural gas cannot be produced economically with present processing technology.

Against this background, a number of industry-wide trends are affecting the natural gas industry. Despite the current low price of natural gas, long-term demand is expected to outstrip supply, requiring new gas fields to be developed. Several important consequences will result. First, gas fields not being used because of low-quality products will have to be tapped. In the future, the proportion of the gas supply that must be treated to remove impurities prior to delivery to the pipeline will increase substantially.[1,2] The extent of treatment required to bring the gas up to specification will also increase. Gas Research Institute studies have shown that a substantial capital investment in facilities is likely to occur over the next decade. The estimated overall investment for all gas processing facilities up to the year 2000 alone is approximately $1.2 Billion, of which acid gas removal and sulfur recovery are a significant part in terms of invested capital.[3] This large market size and the known shortcomings of conventional processing techniques will encourage development and commercialization of newer technologies such as membrane processes.

Second, much of today's gas production is from large, readily accessible fields. As new reserves are exploited, more gas will be produced from smaller fields in remote or off-shore locations. The result is an increasing need for technology able to treat small-scale gas streams.

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Third, 80% of raw gas that is over specification in carbon dioxide also contains hydrogen sulfide.[2] About 13% of presently known and predicted reserves are prone to hydrogen sulfide contamination.[1] As subquality fields are exploited, the need for better, cheaper hydrogen sulfide removal and sulfur recovery processes will increasing.

Finally, atmospheric discharge of sulfur compounds, either by venting or flaring, now commonly used, will be increasingly regulated for environmental reasons.[4]

Objectives

The U.S. Department of Energy (DOE) has recognized these trends and has identified a specific need to develop new technology for the economical removal and recovery/disposal of sulfur from sulfur-contaminated natural gas (sour gas) in an environmentally acceptable manner. DOE is seeking advanced technologies that can meet the pipeline specification of no more than 4 ppm hydrogen sulfide, while minimizing methane loss and satisfying environmental regulations. DOE has also stressed a particular need for processes applicable to small-scale plants.

MTR is developing membrane modules with exceptional hydrogen sulfide separating properties. The membrane can be used to remove hydrogen sulfide and water from natural gas streams, producing pipeline-quality natural gas and a concentrated hydrogen sulfide-containing permeate. This permeate stream would be sent to a Redox sulfur recovery process.

The specific objectives of the project are:

1. Verify existing membrane stamp data with laboratory-scale membrane modules at MTR.

2. Determine the optimum operating conditions for the membrane process and compare the membrane technology with competing technologies.

3. Perform testing with commercial-scale membrane modules at a field site.

Approach and Technology Description

The membrane separation system for removing hydrogen sulfide from natural gas under development by MTR is based on a family of polymers that can be formed into membranes with remarkable hydrogen sulfide separating properties. This membrane is different from those already used in natural gas processing, which are used for carbon dioxide removal.

Membrane systems can be scaled up or down to handle larger or smaller gas flows. In addition, they can be adapted to a wide range of hydrogen sulfide concentrations and to handle gas flows that vary over time. This versatility also represents a powerful advantage over other technologies. Membrane systems are light in weight compared with amine plants, have no moving parts, require little supporting equipment, do not need regenerating, and require essentially no maintenance. These attributes make them ideal for use in remote locations and in small-scale applications and give them attractive technical and operational advantages over amine plants.

Depending on the reserves, the productivity of the gas field decreases with time. Upon exhaustion of the reserves in a particular formation, it would be desirable to move the treatment plant to another location. This is virtually impossible for conventional processes. However, since membrane systems are skid-mounted, it is relatively simple to move them from one location to another. This feature of membrane processes may be especially useful to operators exploring smaller fields within a formation, by reducing the cost of gathering systems and/or by allowing the use of the same system at different locations without incurring a large investment in new installations.

Based on these attributes, it appears reasonable to suppose that membranes will be applicable and will have advantages in the following situations:

1. The gas is contaminated with hydrogen sulfide, but is at or near specification in carbon dioxide content (2-5%). It may not be economically attractive to use an amine plant in such a situation.

2. The gas field is in a remote location, where operational simplicity and reliability is of paramount importance.

3. The field is relatively small, producing less than 50 MMscfd.

4. An off-shore gas production platform is to be constructed.

It should be noted that the environments identified in 1-4 above as particularly appropriate for membrane systems match very closely with the environments in which reserves are not now exploited because of inadequate technology. If a membrane system with adequate hydrogen sulfide separating capabilities can be demonstrated, government and the private sector will have at their disposal a technology that will make utilization of low-quality natural gas possible.

A number of workers have examined membrane materials for hydrogen sulfide removal from natural gas in the past.[5,6] Some materials with hydrogen sulfide/methane selectivities in the range 20-30 have been found. In our opinion, these selectivities are not adequate to make a hydrogen sulfide removal process with membranes attractive. Our calculations show that a membrane selectivity of greater than 50 is required.

In a previous DOE program (DE-AC-87PC79856), we identified a class of polymers based on polyamide-polyether copolymers available as Pebax®, Atochem Inc., Glen Rock, NJ, that exhibit remarkable permeability and selectivity when tested with natural gas mixtures.[6] The polymers, which consist of linear chains of rigid polyamide blocks and flexible polyether blocks, demonstrated hydrogen sulfide/membrane selectivities as high as 80 in membrane stamp permeation experiments.

Results

In Phase I of the project, an extensive experimental study was performed to assess the performance of our membranes under various feed conditions. Composite membranes made from four different polymers were evaluated to determine their hydrogen sulfide/methane and carbon dioxide/methane selectivity. Two polymers were then selected for a further parametric study. The effects of the following variables were studied: the feed compositions of hydrogen sulfide and carbon dioxide, the presence of water vapor in the feed gas, and the feed gas temperature. Experiments were performed over the pressure range 400-1,000 psig. The parametric study showed that the membranes exhibit a hydrogen sulfide/methane selectivity in the range 40-70 and a carbon dioxide/methane selectivity in the range 14-16. These selectivities are maintained at pressures as high as 1,000 psig and with water vapor present in the feed gas. The methane flux of these membranes is comparable to that of commercially available cellulose acetate membranes, whereas the hydrogen sulfide/methane selectivity is two to three times higher.

In Phase II, membrane production was scaled up to commercial-scale rolls, and spiral-wound modules were manufactured from these membranes. The spiral-wound modules were tested in our 10-scfm full-recirculation test system at pressures ranging from 400 to 1200 psig with a wide variety of multicomponent gas mixtures. The hydrogen sulfide/methane module selectivity ranged from 40 to 50, and there was some evidence of concentration polarization in the modules.

We have also performed technical and process evaluations to identify the niche for membranes in the processing of sour natural gas. We have concluded that membrane processes show the greatest promise for the bulk separation of hydrogen sulfide from large flow streams, in combination with an amine or similar absorption process downstream of the membrane. We have also determined that the ideal membrane process design will involve recirculation of the permeate stream into an additional stage to concentrate the hydrogen sulfide to a level that it can be fed directly into a Claus plant to fix the sulfur. Meetings and conversations with a number of major oil and gas producing companies, including Shell Exploration and Production, Chevron, and Phillips Petroleum to discuss the application have been very positive. Shell has provided us with a test site in Texas where field testing has just started.

Benefits and Economic Analysis

For the relatively small flow rate applications in which DOE is particularly interested, we have concluded that a single-stage membrane system combined with a SulfaTreat process as the polishing step will be the most economically viable option. To define the effects of various feed conditions, we performed a preliminary economic analysis on an extensive set of process designs based on this combination. The results of this analysis are discussed below.

A schematic diagram of the membrane/SulfaTreat hybrid process is shown in Figure 1. The membrane processing step removes the bulk of the acid gases, typically up to about 90%. The residual gas from the membrane system is then sent to a SulfaTreat system, in which the gas is contacted with a proprietary solid based on iron chemistry. The residual hydrogen sulfide is removed in the SulfaTreat tower to reach pipeline specifications. In the overall process, the membrane system has to meet the pipeline specifications for carbon dioxide, since the SulfaTreat process is not able to remove any carbon dioxide. The gas discharged from the SulfaTreat process would meet pipeline specifications for both carbon dioxide and hydrogen sulfide. Further treatment to remove natural gas liquids and/or water may be required before the gas is routed to the pipeline.

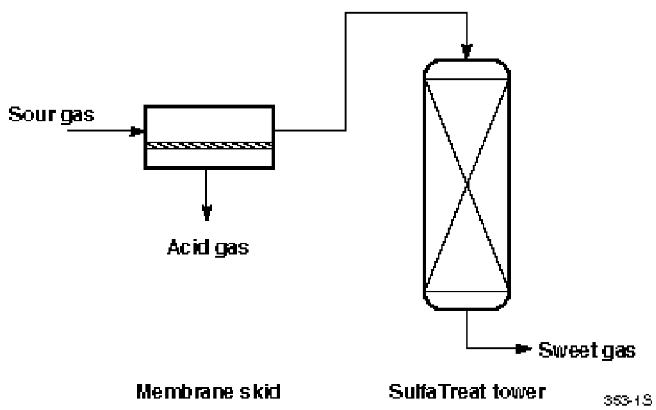

Figure 1. Schematic diagram of the membrane/SulfaTreat® hybrid process. SulfaTreat is a registered trademark of the SulfaTreat Company (Chesterfield, MO).

The hybrid membrane/SulfaTreat process was compared with amine-based adsorption. An amine absorption process consists of a scrubbing column for chemically absorbing acid gases into an amine solution, and a regeneration column for stripping the acid gas from the amine solution at high temperature before it is recycled. The cost of the amine process depends on the recirculation rate of the amine solution, which in turn depends on the acid gas content in the feed, and feed throughput.

The following conclusions were drawn from the benefits analysis.

1. At lower feed rates, the processing cost for the membrane hybrid process is lower than that for the amine process for all compositions of acid gases. At feed flow rates greater than 5 MMscfd, the difference between the amine absorption process and the membranes process is only marginal, the amine process being more expensive at the higher acid gas concentrations.

2. For the membrane process, the processing cost increases with increasing total acid gas in the feed stream. The reason for this is twofold. First, the total capital cost increases with increasing acid gas in the feed stream; therefore, the capital-related component in the processing cost also increases. Second, as feed acid gas content increases, the total methane loss to meet pipeline specifications increases, resulting in an increased processing cost.

3. The processing cost of the amine process increases substantially with an increase in the total acid gas in the feed stream, due to increasing operating expenses. Higher acid gas content increases the solvent requirement, which in turn increases the solvent recirculation rate in the amine train and leads to increased energy costs associated with the regeneration system. Thus, the processing cost at higher acid gas content for the amine process is significantly higher than for the membrane process.

   We conclude that membrane processes are suitable for lower feed rates over almost the entire range of acid gas content in the feed stream, and are also economical at higher flow rates for feeds with higher acid gas. Our calculations also indicate that amine processes and membrane processes are suitable for two different ranges of acid gas content. Membrane processes are most suitable for bulk separation of acid gases, and can perform this separation at a low operating cost, whereas amine processes are well suited for meeting pipeline specifications and for treating gas with a low acid gas content.

4. The membrane/SulfaTreat process has an advantage over amine adsorption at high acid gas concentrations even at gas flow rates over 50 MMscfd. This suggests that a membrane/amine hybrid process (probably without a SulfaTreat step) is preferred at high flow rates (> 50 MMscfd) and high acid gas concentrations (> 10%). In this hybrid process, the membrane system would remove the bulk of the acid gas and the amine process would achieve the pipeline specifications.

Future Activities

To confirm the design data used in our technical evaluations, real-life performance data are required. A two-module, fully instrumented test skid was constructed and is presently being field tested in Texas. The feed gas at this facility is at 800 psig and contains 2-3 mol% hydrogen sulfide. We plan to test the membrane modules at pressures in the range 300-800 psig and at flow rates between 100 and 200 scfm. The results of the field test will be available by the end of March, 1997, and a final report will be prepared in June 1997.

Acknowledgment

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