NG-6.3 Horizontal Drilling in Shallow Reservoirs

CONTRACT INFORMATION

| Contract Number | DE-AC21-91MC28240 | | | | | | | |
|--|--|--|--|--|--|--|--|--|
| Contractor | Belden & Blake Corporation 7555 Freedom Avenue N.W. North Canton, OH 44720 (216) 499-1660 | | | | | | | |
| Contractor Project Manager | William F. Murray, Jr. | | | | | | | |
| Principal Investigators | William F. Murray, Jr. Leo A. Schrider John V. McCallister Ray L. Mazza | | | | | | | |
| METC Project Manager | Albert B. Yost, II | | | | | | | |
| Period of Performance | September 30, 1991 to June 30, 1994 | | | | | | | |
| Schedule and Milestones | Program Schedule | | | | | | | |
| Q1 Q2 NEPA Work Plan Drilling Operation Stimulation Operations Testing and Analysis Final Report | Q3 Q4 ONDJFMAMJ | | | | | | | |

OBJECTIVES

The objectives of this joint horizontal drilling effort by the U.S. DOE and Belden & Blake in the complex, low permeability Clinton Sandstone will focus on the following objectives: (1) apply horizontal drilling technology in hard, abrasive, and tight Clinton Sandstone; (2) evaluate effects of multiple hydraulic fracturing in a low permeability horizontal wellbore; (3) assess economic viability of horizontal drilling in the Clinton and similar tight gas sands.

BACKGROUND INFORMATION

Belden & Blake and the U.S. DOE will cofund a horizontal well to be drilled in the Clinton Sandstone as part of the DOE's multi well program titled "Horizontal Drilling in Shallow Geologic Complex Reservoirs." This well will be located in Mahoning County, Ohio in an area which has demonstrated above average Clinton gas production (**Fig. 1**). To the best of our knowledge, this will be the first horizontal well drilled to the Clinton Sand formation in Ohio.

Clinton Sand Summary

The Clinton Sandstone is comprised of three members (Stray, Red, and White) and is considered a tight gas sand with sand thickness ranging from 5 to 120 feet, average porosities ranging from 6 to 8 percent, and average permeability usually 0.1 md or less. Belden & Blake has drilled approximately 2,0C0 vertical Clinton wells since 1942 with average reserves per well ranging from 50 MMCF to 500 MMCF (depending on field location) with a productive well life between 20 to 25 years. Since many of the remaining Clinton Sand drilling sites are of poorer reservoir quality, they may not be developed unless technology such as horizontal drilling can be successfully demonstrated.

High-Angle Well

In an effort to enhance recoverable reserves in the Clinton Sandstone, Belden & Blake drilled a high-angle (72°) well in the Clinton in 1989. No pilot testing was done to determine optimum well path azimuth, but

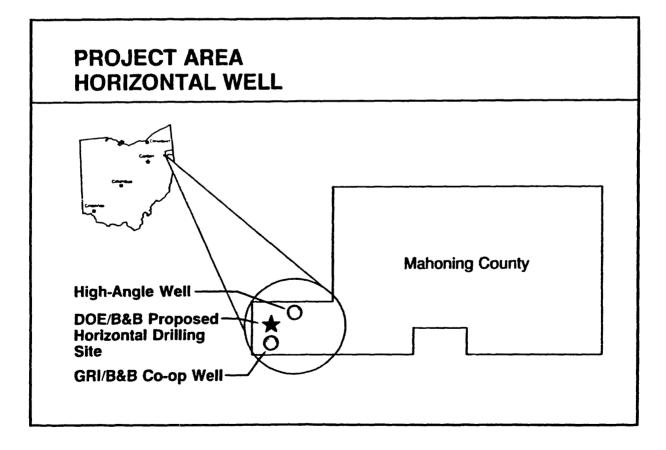


Fig. 1

S19°E was selected based on previous published data indicating Clinton induced fracture orientations of N60°E. This well was located in Mahoning County, Ohio in the adjacent area of the proposed horizontal well (Fig. 1).

This well was drilled vertically on air to the kick-off point at 4,250 feet. The angle-build portion of the hole was drilled as planned with a mud motor and brine polymer with an average build rate of 8.5°/100 feet. Rate of penetration during the build portion of the hole averaged 11 feet per hour. Once the Clinton Sand was penetrated, drilling was hampered by slow penetration rates (2 to 3 feet per hour), short bit life, and severe hole deterioration in the Rochester Shale just above the Packer Shell. After four bit trips in the Clinton with only 200 feet of penetration in the pay, the drill string became stuck. After working the pipe approximately 18 hours, the drill string was finally freed. A decision was made to TD the well at this point due to risk of sticking the drill string again and potentially loosing the hole. The well was later fractured and put into production in January, 1990. Reserves for the high-angle well appear to be approximately 25 percent below the average of the 10 closest offset wells. This may be attributed to partial bit penetration in the pay and less than optimum stimulations since only the upper Clinton Sands were exposed (Fig. 2). A post-project evaluation performed by Belden & Blake resulted in the following recommendations for future highangle/horizontal wells: (1) induced and natural fracture orientations must be determined to assure proper azimuth direction; (2) drilling bit selection must be carefully scrutinized to improve Clinton penetration rates and bit life; (3) an intermediate casing string must be set below the Rochester Shale to eliminate severe hole deterioration; and (4) hydraulic fracture design

is more complex than vertical wells and must incorporate latest technical advancements.

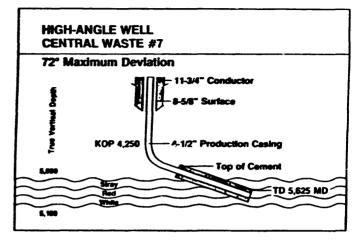


Fig. 2

Vertical Co-op Well

Upon receiving a Contract Award from the U.S. DOE to drill a horizontal well in the Clinton Sand, Belden & Blake and the Gas Research Institute drilled and completed a vertical co-op well in November/December 1991. This well was also located in Mahoning County adjacent to the proposed DOE horizontal site (Fig. 1). Other participants that were involved in the project were CER Corporation, Halliburton Energy Services, and Hunter Geophysical. The objectives of the vertical co-op well were to: (1) select proper azimuth to drill the DOE horizontal well based on induced and natural fracture orientation: (2) determine in-situ stress profile to assist in the hydraulic fracture design; and (3) determine frequency and orientation of natural fractures that may affect gas production.

Several methods were utilized to determine the induced fracture orientation including overcoring after mini-frac, Halliburton's CAST imaging tool, Halliburton's Anelastic Strain Recovery technique (ASR), and Hunter

Geophysical's tiltmeters. Attempts to use The Total - Halliburton Extensiometer Tool (THE TOOL) were unsuccessful. Maximum horizontal stress directions of the induced fracture utilizing the above techniques ranged from N30°E to N75°E with the highest frequency being in the N55-60°E direction. These findings are compatible with the results from earlier studies. Plumb and Cox (1987) determined maximum horizontal stress directions from borehole elongations of N58°E, N42°E, and N60°E in Ohio counties of Hocking, Ashtabula, and Athens respectively. Zoback and Zoback (1989) indicated that in situ stress measurements have orientations of approximately N60°E in the State of Ohio.

Natural fracture orientations were measured from the oriented core and also Halliburton's CAST imaging tool. The natural fracture orientations from those methods ranged from N55°E to N126°E with N70°E being the most predominant. **Figure 3** provides a summary of the various orientations for the induced and natural fractures.

Three open hole stress tests were performed in the vertical co-op well. Location of the stress tests include the Jlinton pay zone, Packer Shell above the Clinton, and Queenston Shale below the Clinton. A stress profile was determined from the three stress

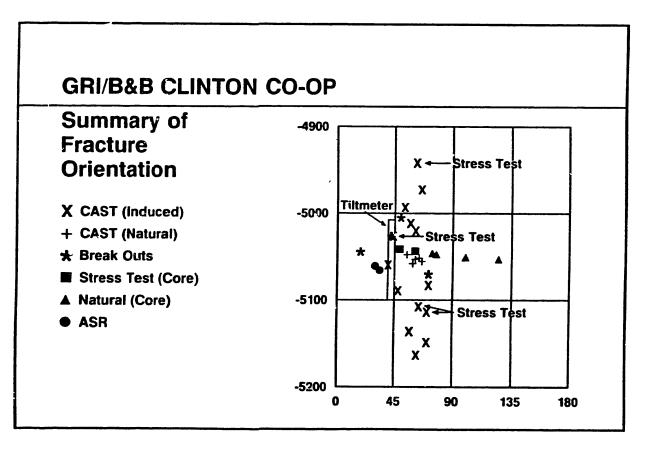


Fig. 3

tests along with log derived stresses which indicates a vertical stress contrast of 500 to 700 psi between the Clinton and vertical strata. Moceling of the main hydraulic fracturing treatment of the vertical co-op well illustrated that adequate fracture containment was achieved.

Conclusions resulting from the GRI/B&B vertical co-op well indicate that the DOE/B&B horizontal well should be drilled S25°E to optimize the induced and natural fracture orientations. Also, the stress profile derived in the co-op well illustrated that the Packer Shell and Queenston Shale are adequate barriers to contain hydraulic fractures in the Clinton Sand.

PROJECT DESCRIPTION

Proposed Location

The horizontal well which Belden & Blake and the U.S. DOE propose to drill is the Central Waste #14 (Permit #2576) and is located in Section 17 of Smith Township, Mahoning County. This well will be centered approximately 2,000 feet southwest of the high-angle well (Central Waste #7 - Permit #2351) approximately and 2.000 feet northeast of the GRI/B&B vertical co-op well (Central Waste #12 - Permit #2477). The target formation is the Red member of Clinton Sandstone which lies below the Stray and above the White (Fig. 4). The Red member

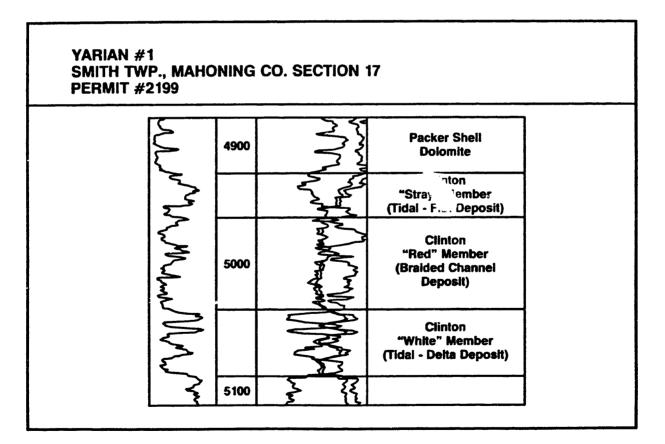


Fig. 4

is considered to be the best producing member of the Clinton in the project area. According to geologic cross sections, the Red Clinton should have a gross thickness of approximately 65 feet along the proposed drill path.

As **Figure 5** represents, the planned horizontal well is in an area of good Clinton production with reserves for the vertical wells being in the 200 MMCF range.

Drilling Plan

The surface drilling location will be set back approximately 350 feet from target to allow a maximum distance of approximately 2,000 feet in the Red Clinton target (Fig. 6).

The drilling plan is to air drill down to the kick-off point (4,373 feet TVD) with an 11 inch An 11 and 10-5/8 inch hole will be hole. drilled from the KOP along a true bearing of S31°E with a mud motor and clear brine at a build rate of 8.8°/100 feet. This angle-build section will be drilled to the top of the Stray Clinton (approximately 4.985 feet MD) with an inclination of approximately 70 degrees. An 8-5/8 inch intermediate casing string will be set and cemented back to approximately 4,100 feet to prevent hole deterioration in the shales. The remainder of the angle-build section will utilize an air motor and EMWD to drill a 7-7/8 inch hole to a terminal angle of 89.8° and a measured depth of 5,448 feet in the Red Clinton. At this point, the remainder of the

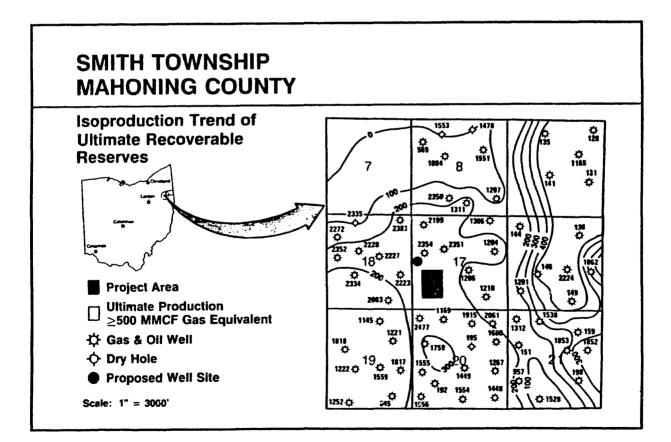


Fig. 5

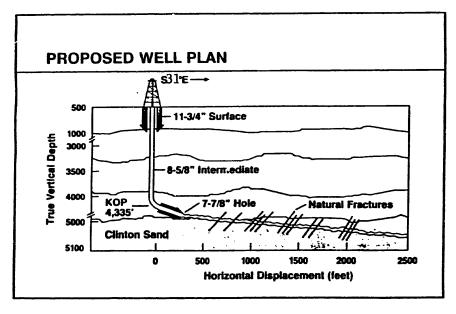


Fig. 6

lateral will be drilled with an air motor sliding and rotating as required along S31E true bearing holding 89.8 degrees with a measured depth at TD of 7,344 feet. If necessary, a rotating BHA (without motor) may be used depending on cost and downhole drilling considerations.

Logging Program

The proposed logging program for this horizontal drilling project will focus on gas detection and natural fracture location along the Clinton lateral. A mudlogger will be used during the drilling operations for gas detection and also lithology descriptions. Open hole logging will consist only of a drill pipe conveyed video camera log in an effort to visually evaluate natural fractures and gas entry. The ability to locate natural gas shows and natural fractures in the Clinton lateral will be a key in the completion design.

Completion Rationale

The completion design will strongly depend upon the ability to evaluate the natural gas shows as described above. However, the completion rationale at this time will focus initially on evaluating the open hole. If natural flow rates are acceptable, the well would be put into a production test mode. If natural flow rates are unacceptable, open hole treatments may be attempted. Ultimately, 4-1/2 inch casing could be set and cemented if the open hole treatments did not provide acceptable gas production. At that time. multiple stimulation stages would be performed and evaluated with radioactive tracer surveys.

Well Test Analysis

Well test analysis will include pre-frac buildup and post-frac drawdown/buildup tests as needed. Also, extended production tests will be designed and implemented as required.

FUTURE WORK

The well is scheduled to spud October 18, 1993 with an estimated date of kickoff of October 25, 1993. The well should be TD'd approximately November 19, 1993. The rig will be released and the openhole will be tested for approximately two weeks. At that time, a stimulation plan will be prepared and submitted.

REFERENCES

CER Corporation, 1992: "Geological, Petrophysical and Engineering Analysis of the Clinton Sandstone, Belden & Blake Corporation Central Waste #12," GRI Topical Report No. 92/0177 Prepared Under Contract No. 5091-212-2242, March.

NG-6.4 Measaurement-While-Drilling (MWD) Development for Air Drilling

CONTRACT INFORMATION

| Contract Number: | DE-AC21-88MC25105 |
|-----------------------------|--|
| Contractor: | Geoscience Electronics Corporation 725-A Lakefield Road Westlake Village, CA 91361 |
| Contractor Project Manager: | William H. Harrison |
| Principal Investigators: | William H. Harrison Llewellyn A. Rubin |
| METC Project Manager: | Albert B. Yost II |
| Period of Performance: | Sept. 30, 1988 to December 31, 1993 |

SCHEDULE AND MILESTONES

PHASE IV Program Schedule (FY 1994)

| | 0 | N | D | J | F | М | A | М | J | J | A | S | |
|---------------------------------------|---|---|---|---|---|---|---|---|---|---|---|---|--|
| System Rehabilitation Final Report | | | | | | | | | | | | | |
| - | | | | | | | | | | | | | |

OBJECTIVES

This program is being conducted under cost-sharing contract No. DE-AC21-88MC25105 with the U.S. Department of Energy, Morgantown Energy Technology Center (METC).

The program is entitled "MEASUREMENT-WHILE-DRILLING (MWD) DEVELOPMENT FOR AIR DRILLING," and is being performed by Geoscience Electronics Corporation, (GEC), in Westlake Village, California.

The objective of this program is to tool-harden and make commercially available an existing wireless MWD tool to reliably operate in an air, airmist, or air-foam environment during Appalachian Basin oil and gas directional drilling operations in conjunction with downhole motors and/or (other) bottom-hole assemblies. The application of this technology is required for drilling high angle (holes) and horizontal well drilling in lowpressure, water sensitive, tight gas formations that require air, air-mist, and foam drilling fluids. The basic approach to accomplishing this objective was to modify GEC's existing electromagnetic (e-m) "CABLELESS"" MWD tool to improve its reliability in air drilling by increasing its tolerance to higher vibration and shock levels (hardening). Another important aim of the program is to provide for continuing availability of the resultant tool for use on DOE-sponsored, and other, air-drilling programs.

The hardened MWD tool is required to meet the following minimum requirements:

o System MTBF, 50-hours.

o Maximum depth (TVD) of 10,000 feet.

o Battery life in excess of the tool MTBF.

o Operational in rotary drilling and downhole motor scenarios.

o Operate in hole diameters from 6-1/4 to 10-5/8 inch.

o Data transmission rate of 1 bit/second, minimum.

o Operating temperature
125°C, maximum.

o Directional data provided on azimuth, inclination, and tool face.

o Operate in typical air flow rates of 1,500 to 3,000 CFM, and mist or foam rates from 10 to 30 barrels per hour.

A system implementation concept is shown in Figure 1.

BACKGROUND INFORMATION

Two-way communications, between sensors and other devices at the bottom of, or along, bore holes and the surface, have traditionally been performed by wirelines and stored-data technology. Telemetry (up-link) and command (down-link) functions have more recently been performed by use of real-time, mud-based methods.

As more and more horizontal, slant-horizontal, arc, and other high-angle boreholes are drilled (some with air), the need for nonwireline and non-mud-based communications becomes more important because of the difficulty of inserting tools and logs in the absence of a large gravitational force component, and the inability of mud-based systems to operate in air or for that matter in the absence of flow. The oilfield logging industry has developed tubing-conveyed-logging tools, but these too lack the flexibility required, because they still require a wireline. Even with side-entry subs, these tools are too costly or difficult to use in some cases.

Air-drilling of directional wells is on the rise for a number of reasons, and wireline steering tools and mud-based MWD tools are proving to be less than effective.

In recent years, new wireless electromagnetic-based real-time borehole communications techniques have been developed with capabilities for supporting relatively-low data rates (compared with wire line) adequate for some applications. These are in commercial use in Measurement-While-Drilling (MWD) systems. Others are finding

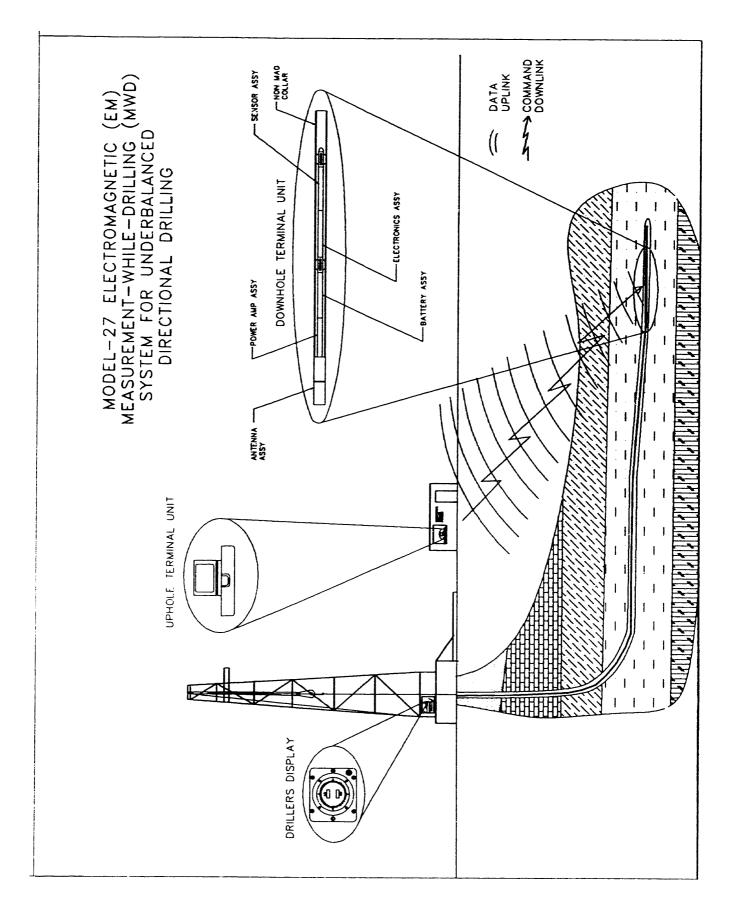


FIGURE 1. System Implementation Concept

their way into non-drilling use in connection with oil and gas reservoir evaluation and completion work. While most of the work has been done in larger boreholes, some systems are being built into drill-strings as small as 2.5 inches (6.35 cm) OD.

Wireless electromagnetic borehole communications technology holds out hope for providing reliable, two-way, high-data-rate data and command links in wellbores; regardless of hole size and angle, mud or air, flow and noflow, cased or open hole.

Historically, the modern borehole communications concept was first realized using an electromagnetic method, the wireline. The wireline presented cablehandling problems in drilling. However, it did better in many cases than competitive methods of the time. When mud-pulse-telemetry Measurement-While Drilling (MWD) was introduced, it seemed reasonable to trade away the unused high data rate of the wireline for the convenience of the "wire-less" mud-pulse tool.

Progress in the drilling industry has slowly put pressure on the MWD-services industry to improve reliability.

In the last few years, the need for reliable, low cost, directional drilling services in air drilling scenarios has become widely recognized. Attempts at using directional drilling systems that were designed to operate in mud have resulted in less than satisfactory performance when operated in air. The severe shock and vibration environment of air operation compared to mud operation immediately extracted a heavy toll in reduced reliability.

Mud pulse MWD tools, in general, perform marginally, at best, when operated on air and are not at all viable.

Even though some wireline steering tools have been made to operate reliably in air, the logistics limitations and cost of operating with a wireline are frequently unacceptable.

PRESENT PROGRAM STATUS (Phase IV)

The Phase IV effort was authorized on September 30, 1991, and consisted of the following task plan:

TASK 4-1 -- DESIGN REVIEW

Evaluated the status of the Model 27 MWD System design and convened a meeting with COTR and consultants to review and recommend design changes and other system improvements.

TASK 4-2 -- REPAIR/REPLACE EXISTING MODEL 27 EQUIPMENT

This task covered primarily the rehab of the Model 27 after Field Test #5. The work resulted in having two complete Model 27 . strings available.

• TASK 4-3 -- TRANSDUCER RE-DESIGN, FAB OF TWO UNITS, TEST OF ONE

This task took into account the guidance from the Task 4-1 Design Review, and involved an expert consultant in details of the design. Laboratory testing of one prototype was conducted in early May, after which the second unit was completed. This task also included the re-certification of the 7-1/2-inch transducers, if required under Task 4-5.

TASK 4-4 -- RE-DESIGN AND FABRICA-TION OF TWO ADVANCED UPHOLE TERMI-NAL UNITS

This work was primarily concerned with adapting GEC's design of its new PC-based AUTU to work with the Model 27, provide for field reprogramming, and on-site data management capabilities. Special attention was paid to the need for flexibility of programs, and consistency of formats with other MWD systems.

The Barrier Safety Box (lightning protection) recommended by the Design Review was designed and fabricated under this task.

TASK 4-5 -- CONDUCT UP TO FOUR FIELD TESTS

GEC's Appalachian Consultant and GEC personnel canvased available operators to make arrangements for field tests. This also included being alert to the possibility of finding a wellbore that could serve as a dedicated test facility for some or all of the field tests.

TASK 4-6 -- DESIGN AND IMPLEMENT SYSTEM IMPROVEMENTS

This task primarily was concerned with the replacement of Interconnect Harnesses and the O-Ring Sealing that were cited in the Design Review Minutes. Additionally it included work required to perform elevated-temperature environmental testing of the existing downhole units. TASK 4-7 -- DESIGN AND BUILD A DRILLER'S DISPLAY UNIT

In accordance with the guidance contained in the Design Review Minutes, one Driller's Display was designed and fabricated using a rugged commercial unit as the basis.

TASK 4-8 -- FINAL REPORT

This task covers preparation of the Final Report in conformance with the Contractual requirements

FIELD TEST #6

Field Test Number 6 (FT #6), using Geoscience's Model 27 MWD system, was performed in Fuel Resources' well, J. F. Turner #5, in Barbour County, WV between 11 October and 15 October, 1992.

The primary purpose of FT #6 was to: a) evaluate the reliability of the revised and reworked Model 27 Systems, b) further evaluate the effectivity of the system changes made to accommodate the dry-air-drilling of very dry formations, and c) evaluate the performance of software revisions suggested at the Phase IV Preliminary Design Review, held in January, 1992.

Model 27 Downhole Subsystem SN-02, using a 5-axis directional sensor unit, was installed in the drill string on Sunday, October 11 at an MD of 1262. It was removed on October 15, from TD at 5220 feet, at 14:30 for a total inholtime of 99.0 hours. During that time, there were 88.9 rotating -hours accumulated. No failures occurred during the 99.0 hours in hole, however, the downhole batteries were exhausted after 77.8 hours of operation and the system ceased sending surveys.

Survey information was acquired from an MD of 1262 to 4495 feet (battery exhaustion). A preliminary analysis of the survey data showed a Latitude and Departure of 30 feet north and 128 feet west, respectively, at a depth of 4495 feet.

Occasional signal-reception problems occurred. These manifested as check-sum errors caused by electrical noise corrupting the received data or as weak or absent signals, suggesting a high contact resistance between the BHA and the formation. Multiple surveys (1 to 5) were taken immediately after a new joint was connected and the bit placed on bottom with 10-20Klbf-load on the bit, without rotation. If the survey was not successfully received (check-sum error), then it was commanded be sent again, when it was generally successfully received. Often, the survey was commanded and successfully received after drilling had re-commenced. However, the gravity data was erroneous, due to the centripetal acceleration caused by the rotating drillstring.

The multiple surveys exercised the system extensively, and a maximum number of transmissions were made. This also consumed battery power which resulted in the batteries being exhausted prematurely. Further, the downhole transmitter was operated at higher than needed power at times, further exacerbating the battery problem. Under normal operations, multiple surveys would be infrequent and the lowest transmitter power would be used. The test is deemed quite successful overall. High-signallevel transmissions and good survey data were received under ideal downhole conditions. System changes to be made, will assure reliable survey data from deep holes under all conditions.

Model 27 Reliability

The reliability of the revised and reworked Model 27 Systems seemingly has improved radically since FT #5 in December, 1980. Prior to Field Test #6, the longest MTTF (Mean-Time-To-Failure) was just over 20 hours. In FT #6, over 78 hours of drilling time was accumulated without a failure. After battery exhaustion, the unit did not fail. Upon retrieval and replacement of batteries, it was determined to be working. Hence one could argue that the MTTF was 88.9 hours. Although it would be presumptuous to imply an MTBF from this one sample, it does indicate a substantial reliability improvement. We attribute this both to the system modifications accomplished in the past two years, plus the intensive laboratory stress testing accomplished during the period June-August, 1992.

Dry-Air-Drilling of Dry Formations

The effectivity of the system changes made to accommodate the dry-air-drilling of very dry formations was further evaluated in Field Test #6. The setting was perfect, in that the formations represent the driest, and nothing was added to the drilling air. By having the driller place the bit on bottom with about 10-20 kpsi on the bit, GEC was able to receive transmissions at virtually

every joint. In some cases however, we needed to repeat the process up to five times to receive a useful survey transmission. In most cases, after drilling recommenced, transmissions were received quite reliably, although the gravitational-based data (from accelerometers) was generally useless. GEC believes that the mechanism involved is that in drvair-drilling of dry formations, the small amount of water present in the rock matrix is blown away by the air flow prior to setting the bit on bottom, while after drilling begins again, new surfaces are constantly opened containing some pore water. The conducting media required between the lower electrode and the formation (normally provided by the mud in mud drilling) is almost entirely provided by the bit contact with the pore water in the uncut formation, in the case of dry-air drilling of dry formations.

GEC did not experience equipment failures, and hence we were able to evaluate the effectiveness of the system modifications made to accommodate the dry-hole, dryair conditions.

Software Performance

The performance of software revisions suggested at the Phase IV Preliminary Design Review, held in January, 1992, was evaluated. The ability to perform revisions in the survey parameters without losing any prior data, and the provisions for downloading the data to disc were both successfully demonstrated. In addition, plotting of Latitude and Departure versus depth was demonstrated. The inclination data from which the wellbore trajectory is comput ed, agreed closely with the single-shot data available.

Conclusions

This test was about as perfect as possible, with the exception of the husbanding of the battery life. GEC experienced difficulty early on, in receiving signals due to poor BHA/formationcontact, and made the decision to operate at high power and low frequency (low data rate), all of which ate up the batteries at a high rate. Additionally, in many cases it took up to five surveys at each joint, whereas one should have been adequate. GEC expects the future to be able to accommodate any bit run up to 7000 or more feet without experiencing battery exhaustion.

When downhole contact between the BHA and formation was optimum, as it was during rotation, high signal levels were experienced. Survey data acquired at the connections, when the BHA was totally at rest, is excellent. GEC intends modifying the system to optimize operations consistent with these disparate factors.

A Mean-Time-To-Failure (MTTF) of 89.9 hours appears reasonable from the data. It is not possible to infer an MTBF figure from this test. It is quite obvious, however, that the system reliability performance has been significantly improved since FT #5 was performed almost two years earlier.

Based on the above results, GEC concludes that it is certainly feasible to attain 100 hours MTBF, for the Model 27, in any and all situations, and hence to provide a reliable MWD for air-drilling.

FIELD TEST NO. 7

The subject test on the Geoscience Electronics Corporation's Model 27 Air-Drilling MWD system, was performed in 3-C Oil Co's Robin's Trust well, in Pratt County, Kansas, between 1 June and 8 June, 1993.

GEC was told that the Model 27 tool would be in the drillstring on Wednesday evening, June 2, and hence the GEC personnel arrived at the site the evening of June 1, and set up.

As of Saturday, June 5, the tool had not gone downhole, due to several operator-related delays in preparing for re-entry after cementing the casing.

Upon site arrival, it was discovered that all of the Downhole Instrumentation Units had arrived with smashed cases. After setting up the equipment, it was found that Sensor Unit 02 had two inoperative accelerometers. This new unit had just been completed by Tensor, and this was its first field deployment. A claim for damages was immediately filed with the freight forwarder, and the defective unit was returned to Tensor for repair.

Model 27 Downhole Subsystem SN-01, using a Tensor 6-axis directional sensor unit, was installed in the drill string at 1300 on June 6. It was removed at 1900, on June 7, for a total inhole time of 30 hours. During that time, there were 5.33 rotating hours (2.5 sliding, 2.83 rotating) accumulated, behind an air-powered mud motor. Zero failures occurred during the downhole operation. Survey information was re ceived starting at a depth of 4832 feet and continuing to a depth of 4877 feet. A preliminary analysis of the survey data indicates good correlation with comparative data available at the site.

Generally, the received signals from depth were quite adequate to have completed the bore. Some problems in downlinking occurred, which were traced to poor electrical contact between the drillstring and the BOP (casing).

On June 6, a circuit breaker feeding power to the trailer, This had also happened blew. earlier, and inspection at the time indicated a severe problem in the lighting plant. The representative of Eagle Drilling promised to have it repaired. Power was restored after the event on the 6th, but 220 volts was inadvertently fed to our 115-volt line. Several failures resulted, including the main UTU, and video display. The test proceeded, using the backup UTU.

The decision to terminate the test, short of wellbore comple tion, was reached jointly in consultation with the operator. It was concluded that the Model 27 MWD was not operationally adequate, and the operator could do better with a commercial steering tool or mud-pulse MWD. The operator expressed willingness to allow GEC to stay on as a piggy-back. From GEC's viewpoint, this meant losing the \$50K partial indemnification for LIH, and the revenues. Also, GEC may again have found the Model 27 to be in mud, and involved in an operation with lots of hole sticking, and slow drilling, resulting in poor cost-effi ciency in conducting tests.

In light of all of the above, the threat of an unrecoverable loss-in-hole, the diminished capability due to all the transit and site mishaps, and the commitment to go to Canada for underbalanced drilling tests in late June, it was decided to terminate early.

Conclusions

The preliminary conclusions drawn from this test are:

GEC is not in a position to fully support a commercial, later, the Downhole Unit will revenue service activity due to lack of hot spares. In particular the lack of backup sensor units is a severe limitation.

While GEC did correctly 0 estimate the uplink field strength, there was trouble with the downlink due to an effect, not observed in prior tests. Hence GEC concludes that learning continues, especially those that seem to be site-and equipment-specific.

No downhole failures occurred 0 to the Model 27 equipment, even though the tool was in a build curve, behind a high-torque motor on air, and experienced a 4.5°change-in-12-feet dogleg while rotating.

3-C Oil welcomed participation in their next Kansas well, but insists on more adequate backups. GEC needs to start a building program to to include at least one additional sensor unit.

Recommendations

0

The problem of receiving signals while at rest, with about 10-20 kpsi on the bit, compared with the situation while drilling has been examined. GEC has decided on a system software modification that will circumvent this problem. One additional operating mode will be provided, as follows:

Upon a special downlink command, the Downhole Unit while at rest, will read the sensors and store the data.

0 At a predetermined interval transmit a survey message using the stored data.

In this way, the system will be capable of reading the directional sensors while the BHA is quiescent, and the survey point will be almost at the same location as a single shot would be. The transmission of the data will take place while drilling, wherein the best results have been attained.

The occurrence of wells-ofopportunity, suitable for performance of meaningful tests, are diminished. Hence GEC needs to make the most of any opportunities.

FUTURE WORK

The Contract is set to expire on 12/31/93, and unless extended, will mark the end of the air drilling tests. The System has been undergoing field testing in other underbalanced drilling scenarios, mostly in Canada, and in particular, SE Saskatchewan.

Field Tests #8 and #9 are planned for November/December. A site for FT #8 has been found, but not as yet confirmed, as of this writing.

REFERENCES

Rubin, L. A., and Harrison, W.H., "Downhole Telemetry Apparatus and Method," US Letters Patent No. 4,691,203, issued 9/1/87.

Rubin, L. and Harrison, W., "Wireless Electromagnetic Borehole Communications, A State-Of-The-Art Review," Proceedings, Measurement While Drilling Symposium, Louisiana State University, 2/26-27/90. Harrison, W., Mazza, R., Rubin, L. and Yost, A., "Air-Drilling, Electromagnetic, MWD System Development," Proceedings of the 1990 IADC/SPE Drilling Conference, 2/27/90-3/2/90, (SPE #19970)

Rubin, L., and Harrison, W., "Measurement-While-Drilling (MWD) Development for Air-Drilling, Proceedings of the Natural Gas R&D Contractors Review Meeting, U.S. Department of Energy, DOE/METC-92/6125 (DE92001278), May 5-6, 1993.

NG-6.5 Steerable Percussion Air Drilling System

CONTRACT INFORMATION

| Contract Number | DE-AC21-92MC28182 | | | | | | | | | | |
|----------------------------|---|-------------------|------|--|--|--|--|--|--|--|--|
| Contractor | Smith International, Inc. 16740 Hardy Street P.O. Box 60068 Houston, TX 77205-0068 (713) 443-3370 | | | | | | | | | | |
| Contractor Project Manager | Huy D. Bui | | | | | | | | | | |
| Principal Investigators | Huy D. Bui Michael S. Oliver Michael A. Gray | Michael S. Oliver | | | | | | | | | |
| METC Project Manager | Albert B. Yost if | Albert B. Yost if | | | | | | | | | |
| Period of Performance | October 01, 1992 to December 31, 1994 | | | | | | | | | | |
| Schedule and Milestones | | | | | | | | | | | |
| FY | 93 Program Schedule | FY94 | FY95 | | | | | | | | |
| 0 | NDJFMAMJJA | SONDQ2Q3Q | 4 Q1 | | | | | | | | |
| Nepa & Work Plan | _ | | | | | | | | | | |
| Design | | | | | | | | | | | |
| Lab Testing | | | | | | | | | | | |
| Straight Hole Testing | | | | | | | | | | | |
| Directional Field Testing | | | | | | | | | | | |
| System Field Testing | | | | | | | | | | | |
| Air MWD Feasibility Study | | | | | | | | | | | |
| Final Report | | | _ | | | | | | | | |

BACKGROUND INFORMATION

The advantages of air drilling over conventional mud drilling have been documented in numerous publications: improved penetration rate, reduced mud costs, negligible formation damages and immediate indication of zone productivity (ref. 1). The application of diamond enhanced inserts to percussion bits has resulted in longer drilled footage, significantly lowered cost per foot (ref. 2 and 3) and penetration rates twice as fast as extremely high weight-on-bit rotary air drilling (ref. 4).

Percussion air drilling, unfortunately can only be used when the following conditions do not exist (ref. 5):

- Known areas of large ground water flows
- High formation and pore pressure which needs to be contained by the mud hydrostatic pressure
- Presence of sour gas
- Weak formations which require mud in the hole to prevent sloughing

Directional drilling, however, is very much limited to mud as the drilling fluid. Attempts to drill directionally with air using tricone rock bits and downhole PDM motors have not been very successful. The absence of drilling mud required to lubricate the rotor/stator and bearing assemblies has caused premature failures of downhole PDM motors and resulted in expensive maintenance and drilling costs. Furthermore, the high rates of penetration provided by percussion air drilling make PDM air drilling become less attractive.

Conventional percussion air drilling tools, commonly known as downhole hammers, on the other hand, depend on the rotation of the entire drill string to provide a means to rotate and index the percussion bit. This dependence is made necessary due to the lack of a downhole air motor to complement the percussive actions delivered by the downhole hammer. Downhole turbine or PDM motors, being designed to produce high torque and RPM required to disintegrate rocks by fatigue or abrasion methods, are not compatible with air hammers. Without a downhole means to rotate the bit, direction control of the well bore is very limited if not impossible.

Since June 1991, Smith International has been actively working on the design of an airpowered drilling tool which is coherently able to impact as well as to rotate the bit, i.e., a drilling machine which performs functions of both a downhole hammer and a downhole motor. Two prototypes of such a rotational hammer have undergone field testing since early 1992. These prototypes, designed and built around existing hardware due to limited budget, were used to prove the rotational mechanism concept by drilling a number of surface holes at 40 to 50 foot intervals in Kentucky and West Virginia.

OBJECTIVES

The cost-sharing contract between the U.S. Department of Energy and Smith International provides the funding to further develop this concept into two complete steerable percussion air drilling system prototypes, each integrated with a navigation tool (wireline steering tool), a bend sub, stabilizing devices, and to conduct laboratory and field testing necessary to prepare the system for commercial realization. Such a system would make available for the first time the ability to penetrate earthen formations by the percussion method, using compressed air as the drilling fluid, and at the same time allow the directional control and steering of the drill bit. While the drill string is not rotating (slide mode), one can orient to build angle in the desired direction at a predictable rate. This build rate can be in the range of 1-20 degrees per one hundred feet and proceeds until the

desired inclination or direction has been obtained. The drill pipe is then set in rotation, nullifying the effect of the bend angle, and causes the assembly to drill straight. The sliding procedure can be repeated as often as corrections for hole's inclination or direction are needed.

PROJECT DESCRIPTION

I. Design and Fabrication

The above referenced contract calls for the design and fabrication of the following components:

1 - Rotational Hammer: Two downhole hammers with built-in rotational mechanism:

Hammer OD: 6 3/4" to 6 7/8" Hammer Length: 5 to 7 feet Rotational Speed: 20 to 30 RPM Output torque: 1,000 ft-lbs max.

2 - Percussion Bits: Up to 14 Diamond Enhanced bits required to conduct field tests, as described in the Future Work section, either 7 7/8", 8 1/2" or 8 3/4"

3- Bend Subs: Either fixed or adjustable angle bend subs, from 1/2 degree to 3 degrees

4 - Stabilizers: Near-bits and other stabilizers required in the bottom hole assemblies

5 - Running gear for wire-line steering tool: Two sets of the running gear modified to provide shock protection for the steering tool. The downhole probe is retrievable but is semirigidly attached to an anchor sub via elastomer shock isolators. A section of the wireline connects the probe assembly to a wet-stab connector located in the vertical section of the hole. A sinker bar assembly mating with this wet-stab connector and having its top end connected to the wireline is the only part that needs to trip out and in of the hole when a pipe is added to the drill string.

II. Laboratory and Field Testing

Part of Smith International's contribution to the project is a laboratory flow loop equipped with a test fixture capable of testing the hammer at different inclinations and a data acquisition system with instrumentation required to measure the striking frequency, impact energy, output torque and pressure rises and falls in different chambers. The field testing program to be conducted next year is discussed in details in the Future Work section.

RESULTS

As of October 15, updates of the works performed are as follows:

1 - Design and build a test fixture equipped with a 1200 CFM air compressor capable of testing the hammer operation at open or close positions and at different weights-on-bit.

2 - The instrumentation and data acquisition system is currently capable of capturing the pressure profiles at different chambers and determining the striking frequency, impact velocity, and shock level. The torque sensor will be added in December.

3 - Complete the design of the new rotational hammer. A laboratory prototype is being manufactured and will be ready for laboratory testing in November. Findings from these tests will be used to modify the design of the field version. Two field prototypes are to be built, laboratory tested and ready for field tests in early 1994.

FUTURE WORK

The first two field tests, limited to straight hole drilling, will take place in the first quarter of next year. The objectives of these tests are to develop an understanding of the rates of penetration, mean-time and footage drilled between failures and to identify wear patterns and problem areas.

The following two field tests are scheduled in the second quarter and involve drilling directional shallow holes. The objective is to test the tool's "steerability", i.e., the ability to build or drop angle and to drill straight with the same bottom hole assembly. The effects of bend angle and stabilizer design and placement on the build rate will be studied by modifying the Bottom Hole Assembly Program (BHAP) which was developed for conventional drilling, to better represent the behavior of a hammer bottom hole assembly. Prediction of the build rate and the BHA behavior will be verified in these field tests. Single or multi shot magnetic survey tools and/or wireline steering tool will be used to confirm the hole inclination and direction.

The third and fourth quarter will involve the drilling of three horizontal wells in the U.S. continent. Different stabilizer designs such as integrated blade, either 4 or 5 or full cover spiral, or roller stabilizer will be tested. The tool's capability to reach out horizontally and the magnitude of additional air volume required to clean the horizontal hole while the drill string is not rotating will also be experimented with. The modified wireline steering tool will be used for navigational purposes.

A wireless directional MWD tool that can transmit data in air would greatly improve the system's efficiency. The development of such an MWD tool would take several years and is certainly beyond the scope of this project. However, the study into the feasibility of transmitting microwave energy through the hollow drill string, which acts as a wave guide, or electromagnetic waves through the earth formation as telemetry means is being discussed as parts of the contract.

REFERENCES

- Whitley, M.C., England, W.P., "Air Drilling Operations Improved by Percussion Bit -Hammer Tool Tandem", SPE/IADC 13429 presented at the SPE/IADC Drilling Conference New Orleans, LA, March 6-8, 1985.
- Reinsvold, C.H., Clement, J., Oliver, M., Witt, C. and Crockett, J., "Diamond-Enhanced Hammer Bits Reduce Cost per Foot in the Arkoma and Appalachian Basins", SPE/IADC 17185 presented at the SPE/IADC Drilling Conference, Dallas, TX, February 28-March 2, 1988.
- Weller, T.F., Baum, G.A., Muncy, W.H., "Diamond-Enhanced Hammer Bits Reduce Costs-per-Foot and Directional Problems in Southwestern Pennsylvania Oriskany Wells", SPE/IADC 19335 presented at the SPE Eastern Regional Meeting, Morgantown, WV, October 24-27, 1989.
- Pratt, C.A., "Modifications to and Experience with Percussion Air Drilling", SPE/IADC 16166, presented at the SPE/IADC Drilling Conference, New Orleans, LA, March 15-18, 1987.
- Sheffield, J.S., Sitzman, J.J., "Air Drilling Practices in the Midcontinent and Rocky Mountain Areas", SPE/IADC 13490, presented at the SPE/IADC Drilling Conference, New Orleans, LA, March 6-8, 1985.

Session NG -- Natural Gas Technology

Session NG-7

Natural Gas Atlases and Data Management

NG-7.1 Development of the Natural Gas Systems Analysis Model (GSAM)

CONTRACT INFORMATION

| Contract Number: | | | | | | | DE-AC21-92MC28138 | | | | | | | |
|--|------|---|---|---------|------|-----|---|-------|------|---|---|---|---|--|
| Contractor: | | | | | | | ICF Resources Incorporated 9300 Lee Highway Fairfax, VA 22031 (703) 934-3000 | | | | | | | |
| Contractor Project Manager: | | | | | | | Mich | ael G | odec | | | | | |
| Principal Investigators: | | | | | | | Mark Haas William Pepper Judah Rose | | | | | | | |
| METC Project Manager: | | | | | | | Anthony M. Zammerilli | | | | | | | |
| Period Of Performance | e: | | | | | | June 22, 1992 - June 21, 1995 | | | | | | | |
| | | | | FY 9. | 3 PR | OGR | AM S | CHEI | DULE | 1 | | | | |
| | S | 0 | N | D | J | F | М | A | М | J | J | A | S | |
| Technology Review Model Review GSAM Design Prototype Developmer | | | | ••••••• | | | | | | | | | | |

OBJECTIVES

The objective of this research is to create a comprehensive, non-proprietary, microcomputer model of the North American natural gas system. The model is to explicitly evaluate key components of the natural gas system, including resource base, exploration and development, extraction technology performance and costs, transportation and storage, and end use. It will be used to evaluate alternative METC Natural Gas R&D strategies and to estimate the impact of federal energy and environmental policy initiatives on domestic natural gas potential. The three-year project timetable has been accelerated to provide a working prototype model by December 1993.

BACKGROUND INFORMATION

Recent dramatic changes in natural gas markets have significant implications for the scope and direction of DOE's upstream as well as downstream natural gas R&D. Open access transportation changes the way gas is bought and sold. The end of the gas deliverability surplus requires increased reserve development above recent levels. Increased gas demand for power generation and other new uses changes the overall demand picture in terms of volumes, locations and seasonality.

DOE's Natural Gas Strategic Plan requires that its R&D activities be evaluated for their ability to provide

adequate supplies of reasonably priced gas. Potential R&D projects are to be evaluated using a full fuel cycle, benefit-cost approach to estimate likely market impact as well as technical success. To assure R&D projects are evaluated on a comparable basis, METC has undertaken the development of a comprehensive natural gas technology evaluation framework. Existing energy systems models lack the level of detail required to estimate the impact of specific upstream natural gas technologies across the known range of geological settings and likely market conditions.

Gas Systems Analysis Model (GSAM) research during FY 1993 developed and implemented this comprehensive, consistent natural gas system evaluation framework. Rather than a isolated research activity, however, GSAM represents the integration of many prior and ongoing natural gas research efforts. When complete, it will incorporate the most current resource base description, reservoir modeling, technology characterization and other geologic and engineering aspects developed through recent METC and industry gas R&D programs.

PROJECT DESCRIPTION

GSAM is being developed in two phases. Phase I includes the review of existing natural gas extraction technologies, a review of current upstream natural gas computer models and the development of a comprehensive natural systems evaluation gas framework. Phase I concludes with the development, testing and peer review of a working prototype GSAM model and reservoir database, originally scheduled for December 1993. Phase I model development and partial validation of some system components will be completed on schedule. Full system validation and peer review, however, cannot be completed until a reservoir database becomes available (expected by Spring 1994).

Phase II encompasses preliminary use of GSAM to support METC R&D strategy development and estimate impacts of federal policy initiatives on the domestic gas industry. METC will set Phase II priorities and direct selected GSAM modeling enhancements, to be concluded in June 1995. At that time ICF Resources will install GSAM at METC and train METC staff.

Design Philosophy

GSAM models the upstream natural gas system at the level at which operators make investment and technology selection decisions — the individual reservoir. Each component of the upstream evaluation methodology accommodates this level of detail:

- The *resource base* is characterized as individual reservoirs with average effective reservoir properties and, for known reservoirs, complete drilling and production histories.
- *Technology* is characterized in terms of the explicit physical parameters that affect gas contact, flow rates and ultimate recovery, and the costs associated with applying a group of technologies in specified reservoir settings.
 - *Production modeling* accounts for unique interactions of geology, technology and reservoir operating practices that influence gas recovery rate and ultimate recovery.
 - *Project economics* are analyzed on an industrystandard, discounted cash flow, pro forma basis for both full and incremental project evaluation.
 - Decisionmaking incorporates the inherent uncertainties and inefficiencies in resource characterization, technology performance and gas markets.

Analysis of downstream issues such as gas demand, transmission, storage, imports, additional gas sources, pipeline capacity additions and interfuel competition are aggregated to the regional level.

Model Structure

GSAM is segmented into separate Upstream and Downstream Modules linked by an Integrating Module (Figure 1). Modules may be run independently or as an integrated system. For upstream issues, this structure provides the flexibility to examine extraction

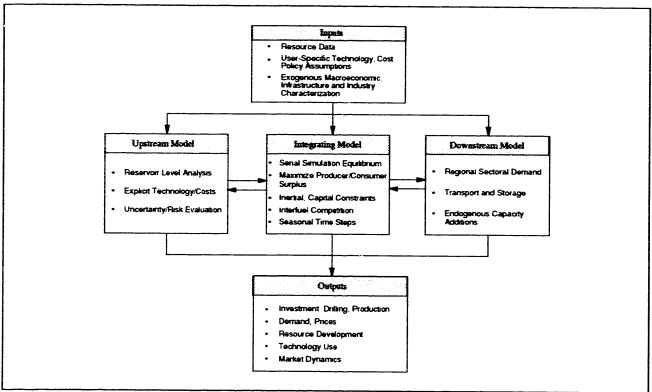


Figure 1 - GSAM Schematic

technology performance or economics of a reservoir, region, resource type or for the entire North American gas market.

Upstream Module

The Upstream Module estimates gas recovery and costs at the level of individual reservoirs. We briefly describe below the key aspects of resource base characterization, reservoir performance modeling, technology characterization, reservoir development, economic evaluation, exploration, treatment of uncertainty, estimation of other gas supplies and the role of technology transfer.

Resource Base Characterization

GSAM will incorporate a reservoir database of about 5,000 fully characterized producing reservoirs. Reservoir data will be primarily derived from the Gas Information System (GASIS), currently under development by METC, and other sources. GSAM users may also provide their own reservoir data. Although the validity and internal consistency of data for each reservoir will have been confirmed in the GASIS development process, GSAM will contain a complete set of default algorithms to assign values for missing or inconsistent reservoir properties.

GSAM evaluates three types of reservoirs: producing, discovered nonproducing, and undiscovered. All reservoirs will be described geologically in a common database format, although the characterization of each will depend on available data. In many cases, reservoir level defaults will be generated by transforming data from higher or lower levels of aggregation, all of which will be documented. (Figure 2).

Producing reservoirs' ultimate recovery or flow rate may be increased by application of improved technology. Accurate characterization of reservoir properties and current depletion status are necessary to accurately estimate this potential using GSAM's reservoir models. GSAM and GASIS developers will work together to history match selected producing

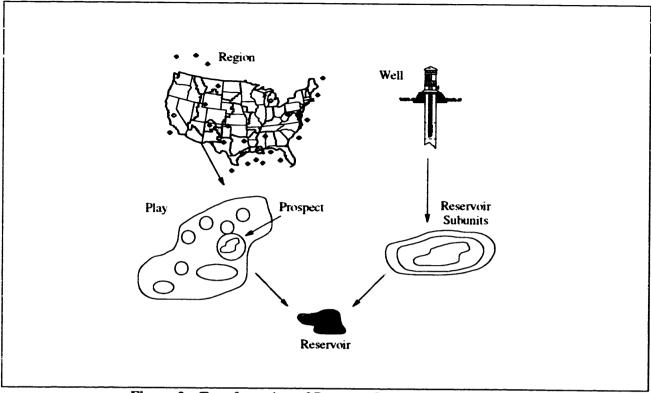


Figure 2 - Transformation of Resource Data to Reservoir Level

reservoirs to verify internal consistency between reservoir properties and production history.

Discovered, nonproducing reservoirs primarily represent reservoirs recently discovered but uneconomic to develop on a sunk-cost basis. Because they are a potentially large source of low-cost, near-term reserve additions, accurate estimates of their number, size and characteristics are critical.

Undiscovered resources are defined in GSAM as typical reservoirs by field size within geological plays. Since known reservoirs to be described in GASIS are likely to adequately represent the range of geological settings that constitute reservoirs yet to be found, they provide acceptable analogs to characterize undiscovered resources. GSAM research in Phase II will enhance the current method to characterize these typical play and size-class specific reservoirs.

Including typical undiscovered reservoirs will add the equivalent of another 5,000 reservoirs to be evaluated. A prospect-play resource appraisal technique will be used to generate undiscovered resource field size distributions from play-specific distributions of known fields, once validated reservoir level data are available.

GSAM makes two additional changes in gas resource base characterization that should improve the ability to evaluate issues such as reserve growth on a more consistent basis. First, all reservoirs will be described on a resource-in-place basis, similar to the procedure for oil. The lack of volumetric reservoir data for gas reservoirs has precluded this characterization in the past. This more realistically accommodates resource accumulation theory and eliminates the need to use implicit technology and economic factors that affect recovery and size classification. With greater consistency, it should be easier to separate the economic, technology, and drilling components of reserve growth.

Second, GSAM will lower the smallest field size class included in its undiscovered resource base. Many producing reservoirs have ultimate recoveries less than the 6 Bcf cutoff used by USGS in its 1989 national assessment. As technology improves, the "minimum" economic size class is likely to decrease. The estimated volume of the undiscovered nonassociated gas resource base used in GSAM will be reconciled with recent USGS estimates and extended to account for economically producible reservoirs as small as 1 Bcf recoverable.

Reservoir Performance Modeling

The need to evaluate technology and operating conditions dictates the level of reservoir modeling detail required. GSAM has developed a suite of dimensionless pressure decline type curves to estimate gas rate and ultimate recovery. The type curve method is grounded in accepted engineering theory and balances the need for explicit technology modeling with the limitations of available reservoir data.

These models were designed to evaluate the unique production mechanisms found in all significant nonassociated gas resources. Separate type curves were developed for various flow regimes (radial and linear), porosity types (single and dual), drive mechanisms (expansion, diffusion/desorption and water) and phases (one or two) (Figure 3).

GSAM uses an enhanced type curve approach that models a flow unit instead of a single closed boundary well. This method estimates well-to-well interference. providing the ability to evaluate the potential of up to two infill episodes. It accommodates changing skin, drainage area and flowing pressure over the well life to estimate the effects of performance degradation (e.g., perforation plugging, proppant embedment) or production practices (e.g., compression, liquids Production is allocated to each well removal). according to production allocation or proration rules specific to each field. At the user's option, the type curves may be run at several levels of detail that allow for faster processing time with a minimum loss of accuracy.

Technology Characterization

The core analytical feature of GSAM is the ability to represent technologies explicitly. Rather than ambiguously representing technology advances as "increased recovery" or "lower cost," GSAM characterizes technologies in terms of the parameters that affect the underlying gas flow equations in the reservoir model or costing algorithms in the economics model.

| Module | Reservoir Type | Drive Mechanism | Flow Geometry | Porosity Type | Number of Fluids | | |
|-----------|---|--------------------------|------------------|------------------|--|--|--|
| Ι | Conventional Tight | Fluid Expansion | Radial Flow | Single ø | Single Fluid* (Gas) | | |
| 11 | Horizontal well Induced fracture | Fluid Expansion | Linear Flow | Single ø | Single Fluid (Gas) | | |
| III | Conventional Tight | Fluid Expansion | Radial Flow | Dual ¢ | Single Fluid (Gas) | | |
| IV | Horizontal well Induced fracture | Fluid Expansion | Linear Flow | Dual ø | Single Fluid (Gas) | | |
| v | Conventional | Water-Drive | Radial Flow | Single ø | Two Fluids (Gas & Water) | | |
| VI | Coal/Shale | Diffusion/ Desorption | Radial Flow | Dual ø | 1 or 2 Fluids Gas or Water/Gas) | | |
| VII | Hydrates | Dissociation | Linear Flow | Single ø | Two Fluids (Gas & Water) Plus Hydrate | | |
| *Geopress | *Geopressured aquifers are analyzed using Module I, except the mobile phase is water. | | | | | | |

Figure 3 - GSAM Type Curve Models

It is inappropriate for a systems model to evaluate individual technologies (e.g., packer types, specific proppants, tubing, drill bits). GSAM is intended to provide insights and general guidance for R&D planning, leaving decisions about specific projects and priorities to METC R&D managers. Therefore, GSAM represents technologies as groups of hardware or processes with a common impact on both reservoir or cost performance, areas subject to a common focus of R&D. GSAM defines five major categories of technology:

- Exploration
- Reservoir Characterization
- Drilling
- Completion
- Production.

Within these categories are 16 subcategories (e.g., Drilling is divided into structures, equipment, fluids and orientation). The GSAM user specifies technology performance parameters for each subcategory for each resource type to be evaluated. Parameters are derived from field studies of existing technology effectiveness or detailed technology process simulations. Figure 4 shows a radial gas flow equation and provides examples of the parameters that might be used to represent changes in technologies or operator practices.

Reservoir Development

Operators decide how to develop a reservoir based on geologic characteristics, available technology and current gas markets. GSAM models each of these factors.

Reservoirs are typically delineated to some traditional average spacing to minimize interference. A plateau production rate from the initial wells is established that optimizes reservoir economics and accommodates field or state rules.

$$q = \frac{0.703 \ kh \ (P_c^2 - P_{wf}^2)}{T \ \mu \ z \left[\ln \frac{(r_e)}{(r_w)} - 0.75 \ + \ s \ + \ D_{q_s} \right]}$$

| Technology Performance Parameters | Example Technologies Represented by Parameter |
|--|---|
| h (net pay) | Formation evaluation, multiple completions, horizontal well |
| P _{wf} (flowing pressure) | Production practices, compression |
| r _e (drainage radius) | Well spacing, infill drilling |
| r _w (wellbore radius) | Slimhole drilling, cavity completions |
| s (skin) | Formation damage, completion/stimulation, effects, condensate blockage, well placement |
| D _q (rate dependent ^s skin) | Wellbore configuration, completion design,production practices |

Figure 4 - Representation of Technology Performance

When deliverability can no longer be maintained, the producer evaluates additional development options, including:

- Deplete initial wells
- Recomplete/stimulate initial wells
- Infill (one or more times)
- Combinations of the above.

Valuable information obtained from initial development about the distribution of reservoir properties creates the potential to high-grade additional development. To model this, GSAM separately evaluates additional development for "pay grades" of different reservoir quality. This feature represents the benefits of R&D to improve the accuracy of reservoir diagnostics and geological modeling.

In addition to available technology, costs and markets, additional development decisions are also influenced by the stage of reservoir depletion. GSAM evaluates the technical performance and costs of more than 50 additional development scenarios for each reservoir. Figure 5 shows the potential options available to an operator. Figure 6 shows the potential impact on production of some of these options.

Economic Evaluation

Detailed technology evaluation requires corresponding detail in costing. GSAM costs each characterized technology at the AFE level to determine whether its marginal contribution to reservoir performance justifies its marginal cost. Costs are derived from published sources and supplemented by vendor quotes. A discounted cash flow model is used to fully evaluate projects on an industry standard basis (i.e., pro forma project analysis, including state-specific and federal taxes and any incentives).

Exploration

GSAM models exploration based on expected value of discoveries for drilling in a play or group of plays. Because it is based on extension of past trends, the traditional discovery process method (originally developed by Arps and enhanced by Kaufman and others) is inappropriate to quantify the effects of specific exploration technology advances for a given geological setting.

GSAM is developing an alternative exploration evaluation method that estimates discoveries as a function of the interaction of geological character of the remaining resource base in a play and the resolution and accuracy of the geophysical data acquisition technology being evaluated. Some systems models increase the "artifact" of improved technology (e.g., lower dry hole rates) without accounting for the efficiency limits of the technology. This new method, largely made possible by the availability of detailed play- and size class-specific reservoir characterizations, will make it possible to estimate how long a technology improvement is likely to increase finding or success rates in a given play. Further development and calibration of this method have been deferred until Phase II, when detailed reservoir and exploration data are available.

Treatment of Uncertainty

There are inherent uncertainties in both resource description and extraction technology performance. In some cases, uncertainty reduction may influence operator decisionmaking and increase gas recovery more than technology efficiency improvements.

GSAM has been structured to address all types of uncertainty through one of several statistical techniques. Uncertainties that GSAM can evaluate include those outside of the scope of METC's Natural Gas R&D program (e.g., weather, oil prices). These are important to evaluate because, although not under METC control, they have major implications for the effectiveness of its Natural Gas R&D program success. Other types of uncertainty (e.g., technology process performance, resource characterization, information transfer) can be reduced by directed METC R&D efforts. Evaluation of uncertainty will a major focus of Phase II.

Other Gas Supplies

Other natural gas supplies are estimated at one of several levels of detail:

- Associated-dissolved gas production currently is derived exogenously from DOE's Tertiary Oil Information System (TORIS) and Crude Oil Policy Model (COPM), using technology, macroeconomic and cost assumptions comparable to those used in GSAM. Phase II efforts will provide more integrated estimation of nonassociated and A/D gas.
- LNG is estimated in Phase I as the gradual increase in throughput at existing terminals until current capacity is reached.
- Canadian and frontier resources will be evaluated by the same reservoir method as for the Lower-48, contingent on the availability of detailed reservoir and resource data.
- Synthetic gas sources will be included in Phase II.

| Tec | Technology Path* | | Current | Current- | Advanced | Advanced | I-Advanced |
|-----------|---------------------------|------|---------|----------|----------|----------|------------|
| Develo | pment Window** | Open | Close | Open | Close | Open | Close |
| Pay Grade | Development Option | | | | | | |
| 1 | Recomplete | | [| | | | |
| 1 | Infill | | | | | | |
| 1 | Recomplete plus infill | | | | | | |
| 2 | Recomplete | | 1 | | | | |
| 2 | Infill | | | | | | |
| 2 | Recomplete plus infill | | | | | | |
| 3 | Recomplete | | | | | | |
| 3 | Infill | | 1 | | | | |
| 3 | Recomplete plus infill | | | | | | |

*Technology Path incorporates the variation in additional development potential as a function of the relative efficiency of previously applied technologies.

**Development window indicates earliest time (at plateau break) and latest time (economic limit of initial wells) an operator would recomplete or infill.

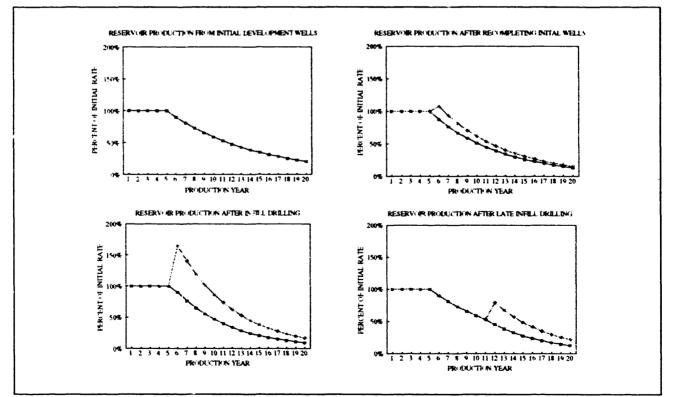


Figure 5 - Additional Reservoir Development Options

Figure 6 - Impact on Producing Rates of Development Options

Technology Transfer

Advanced technologies must make it into the marketplace to affect gas production or costs. Regardless of its technical merits, a technology R&D project should receive a low priority if market conditions, competing technologies or costs prevent its commercialization.

GSAM characterizes technology commercialization in terms of initial availability, rate of market penetration and market saturation. METC R&D can affect each of these factors, and GSAM can estimate the ability of specific technology transfer strategies to increase technology commercialization (Figure 7).

GSAM tracks the use of each technology by region, resource and over time. This provides the key data to determine whether a technology is likely to be a commercial success, separate from its technical efficiency. It may also identify technologies whose near-term high potential is largely eliminated by changing markets.

Downstream Module

The Downstream Module estimates gas and alternative fuel demand. storage and distribution capacities and costs, and adds transportation capacity as needed. These estimates are made at a more aggregate level (the demand region) than for the Upstream Module.

Downstream natural gas issues are currently a secondary focus of GSAM, but their impact on gas supplies and supply R&D could be significant. For example, the imposition of a carbon tax or emissions trading strategy would dramatically alter the volume and location of needed gas supplies. Widespread commercialization of gas cooling would alter seasonal gas demand, affecting storage needs.

An integrated gas systems model also benefits downstream R&D planning, including that pursued by METC. Fundamental understanding of the volumes and uncertainties of future domestic gas supplies provides the necessary context to evaluate effectiveness of downstream policies and technologies.

We briefly review the major downstream sectors: demand, transmission and storage, and distribution and seasonality.

Demand

Gas demand is modeled by end-use sector (e.g., residential, commercial, electric utility and industrial) for each of 14 demand regions. Transportation (e.g., natural gas vehicles) will be added as a fifth sector in Phase II.

Existing models and databases of gas demand and its drivers are incorporated into the Downstream Module. Models developed by the Electric Power Research Institute, EIA and ICF Resources are used to parameterize demand (e.g., boiler fuel demand). These models have been widely critiqued and were adapted with minimal enhancements for Phase I. Because of the importance of future gas demand for electric power generation, GSAM more explicitly models gas-powered utility generation. This structure allows GSAM to evaluate specific gas demand technologies, such as fuel cells or conversion to liquids.

GSAM also addresses interfuel competition and the impact of changes in "exogenous" factors such as weather, GNP, population growth and electricity demand.

Transmission and Storage

A detailed representation of the nation's gas transportation system is essential to estimate volumes and costs of future gas flows, especially as implementation of Order 636 is completed. GSAM models gas transmission from 26 supply regions and 14 demand regions, resulting in 71 transport links, each of which is characterized by directional capacity, costs and a sophisticated tariff structure (Figure 8).

GSAM endogenously evaluates and bilds new pipeline capacity if it is the least-cost alternative to storage, interruption, supplemental peaking or customer-initiated fuel substitution.

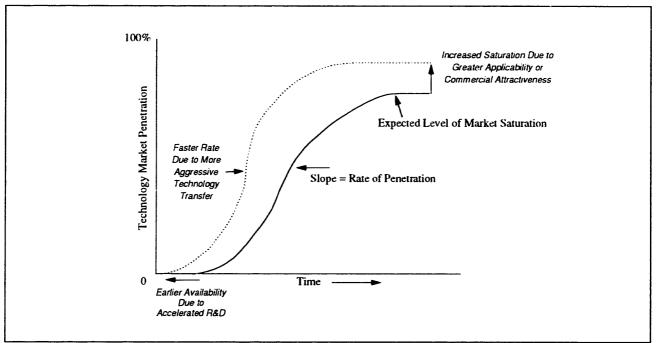


Figure 7 - Market Penetration

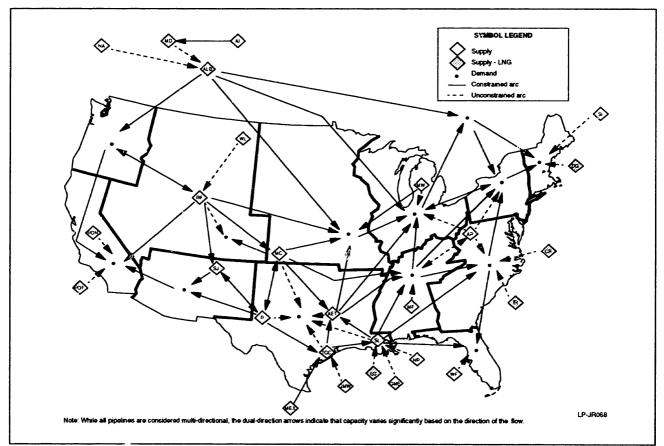


Figure 8 - GSAM Natural Gas Transmission Network

١.

Distribution and Seasonality

Distribution costs represent a significant portion of overall delivered gas costs, thereby affecting purchaser decisionmaking. Since gas demand is highly seasonal, GSAM provides a disaggregated representation of seasonality, storage and distribution.

Load duration curves have been developed from current market studies and proprietary in-house utility planning models. GSAM evaluates the least cost method to supply demand from pipeline, customer storage, propane, LNG or interruption.

Integrating Module

The Integrating Module balances regional demand, transport capacity, and interfuel competition to maximize consumer and producer surplus. For the Upstream Module, it sets the capital and drilling infrastructure constraints that drive exploration and reservoir development decisions.

Integration is implemented through a linear programming optimization that equilibrates regional supply and demand on net gas prices. The model estimates the marginal value of supply to allocate capital and rigs.

Based on the characteristics of the rig fleet and current returns to capital, GSAM retires and adds to drilling infrastructure. Therefore, full and variable drilling costs are explicitly evaluated.

RESULTS

GSAM's disaggregated resource and technology characterization allows it to assess alternative federal natural gas R&D, tax, regulatory and environmental policy initiatives at a previously unavailable level of detail. It will also be available to industry to support capacity planning and market analysis for various end users and provide comprehensive gas industry environmental impact assessments.

ICF Resources has developed a working prototype of GSAM and is now calibrating the model and data.

We reviewed relevant natural gas upstream, downstream and market models to identify appropriate analytic capabilities to incorporate into GSAM. We also reviewed commercial gas extraction technologies to better characterize performance and costs in terms of GSAM parameters.

We have developed databases for the gas resource base, engineering costs, exploration, pipeline capacity and volumes, alternative gas sources and gas utilization. Although an accurate reservoir-level database is not yet available, we have generated a synthetic reservoir-level database that broadly reflects the geological characteristics and volumes by region, depth and resource type. This database is being used to provide limited model testing and validation.

Reports on our evaluations of Natural Gas Models, Natural Gas Technologies, and GSAM Model Design, will be available at the conclusion of Phase I.

Future Research Activities

Phase II of GSAM will focus on securing reservoir level data and enhancing high priority features. Once the model is validated, GSAM will be used to support DOE and others in technology R&D planning, resource assessment or policy analysis. Potential GSAM enhancements include:

- Enhanced representation of reservoir heterogeneity
- Incorporation of the costs of environmental damage and regulatory compliance
- Enhancement of exploration method to address applicability of specific seismic and survey technologies
- Evaluation of alternative exploration or production tax or royalty incentives
- Refinement of downstream components to address current environmental initiatives or market structure changes.
- Inclusion of downstream gas technologies or issues of concern to METC R&D managers.

NG-7.2 Preliminary Analysis of GASIS User Needs

CONTRACT INFORMATION

| Contract Number | DE-AC21-93MC28139 |
|--------------------------|---|
| Contractor | Energy and Environmental Analysis, Inc. 1655 North Fort Myer Drive, Suite 600 Arlington, VA 22209 (703) 528-1900 |
| Contract Project Manager | E. Harry Vidas |
| Principal Investigators | E. Harry Vidas Robert H. Hugman |
| METC Project Manager | Harold D. Shoemaker |
| Period of Performance | May 17, 1993 to May 16, 1996 |

OBJECTIVES

A "User Needs" assessment for the planned GASIS data system has been underway since September of this year. It is designed to cover all major segments of the gas industry, including major and independent producers, state and federal agencies, pipelines, research organizations, banks, and service companies. The objectives of the evaluation are:

- to design GASIS to meet the needs of industry and the research community,
- to determine potential applications for GASIS in order to better design the database,

- to prioritize data categories and specific data collection activities,
- to evaluate industry software and data exchange requirements.

BACKGROUND INFORMATION

Scope of GASIS

The GASIS (Gas Information System) project is a three year effort to develop a personal computer-based (CD-ROM) natural gas database and information system for the United States. GASIS will have two components: a "Source Directory" documenting natural gas supply-related databases and information centers and a "Reservoir Data System" of information for individual gas reservoirs. The Source Directory will document the location, characteristics, and accessibility of natural gas supply information sources, such as bibliographic databases, engineering and/or geological data compilations, and natural gas information centers. The Data System will be the largest portion of GASIS and will contain geological and engineering data at the reservoir level.

The GASIS project will involve the compilation of existing public domain data, excerpts from Dwight's databases, and the collection of new reservoir data. Data assembly and collection will be prioritized by the User Needs study.

The GASIS database will not be designed to duplicate or compete with existing commercial databases, but is expected to be a major source of new data, primarily difficult-to-obtain reservoir properties. All GASIS data will be available for both users and commercial data vendors to incorporate into their databases. GASIS will contain standardized codes that will allow a user to link to other commercial or public data.

Value of GASIS

The Data System will be designed to meet the need for an easily accessible national database of reservoir level geological and engineering data, summary production information, and reserve estimates. The need for this type of information was the basis for the multi-year GRI/DOE Gas Atlas project, which has been well received by the oil and gas industry. Prior to the Gas Atlas project, public domain geological and engineering data at the reservoir level were widely scattered in regional oil and gas field compilations and other publications.

Information sources not in the public domain include commercial and proprietary data. With commercial data, there may be both cost and data coverage issues. The cost of some types of commercial data can be prohibitive for a large number of potential users. Also, while commercial data coverage for production and completion information is generally excellent, coverage of reservoir parameters is often incomplete. Major oil companies all have access to proprietary field and reservoir databases.

GASIS will be made available in a form that will allow either "stand-alone" manipulation or combination with other data. Individuals or small organizations without access to commercial data can use GASIS for a variety of summary or trend studies. Larger organizations are expected to supplement field and reservoir level data with selected components of GASIS.

Data Sources

GASIS will contain reservoir information collected for the Gas Research Institute/ Department of Energy Gas Atlas projects, as well as a large amount of supplemental reservoir information and linkage capabilities targeted to industry needs through the User Needs study. This supplemental data will come from multiple sources, and will be used to both fill in data gaps in the atlas coverage and to cover a wider range of information. Figure 1 illustrates the major data sources for GASIS. Data sources include new GASIS reservoir studies, Dwight's reservoir and completion databases, GRI databases, state records, and others.

Gas Atlas Project

ź

DOE and GRI are currently developing a series of regional gas atlases covering most of the major gas producing areas of the Lower-48. The gas atlas series was initiated in 1989 with the publication of the "Atlas of Major Texas Gas Reservoirs" by the Texas Bureau of Economic Geology for GRI. GRI also supported the Central and Eastern Gulf Coast and Mid-Continent atlases (recently published by the Texas Bureau of Economic Geology), and the Rocky Mountain atlas. The Appalachian atlas, funded by DOE, and the Northern Gulf of Mexico atlas, funded by DOE, GRI, and the Minerals Management Service, are still in progress.

The Gas Atlas projects include all reservoirs with cumulative gas production greater than either 5 billion cubic feet (Rockies) or 10 billion cubic feet (other areas) onshore or 20 billion cubic feet offshore. These reservoirs are expected to represent 85 to 90 percent of Lower-48 ultimate recovery (cumulative production plus reserves.) Additional smaller reservoirs could be added in the future.

GASIS will incorporate the best elements of the gas atlas project, and will combine the regional data into a national database. A major contribution of the atlas project is the grouping of gas reservoirs into geologically defined plays. These play definitions allow the analyst to study groups of reservoirs with similar characteristics.

GASIS Reservoir Studies

A major portion of the GASIS project will be the collection of data through individual reservoir studies. This work will be done by Dwight's geological personnel using standard subsurface methods and data sources. Each study will result in a full suite of parameters for

GASIS such as net and gross pay, porosity, water saturation, and productive area. Both average values and data ranges will be determined. This data collection effort will be carefully prioritized for each region of the country, based upon the results of the User Needs study and an evaluation of the data coverage for each Gas Atlas region.

Dwight's Databases

Dwight's EnergyData has agreed to release a large amount of information for inclusion in GASIS. Dwight's DPDS (Dwight's Petroleum Data System) "TOTL" field and reservoir level database contains over 300 data elements for each reservoir including annual and cumulative production (of oil, gas, water, and condensate), location, and geological and engineering information. TOTL will be the primary data source for reservoir level identification and production data, and will be a major source for reservoir parameters. Much of the engineering data in the TOTL file was originally included in the original PDS database developed by the University of Oklahoma in the 1960's. In order to improve and expand the database, Dwight's has been involved in a long-term effort to obtain additional geological and engineering reservoir data, concentrating initially in the Mid-Continent region.

Dwight's DOGR (Dwight's Oil and Gas Reports) gas completion database will be the primary source for completion and well level production and pressure data. This database contains records for more than 230,000 individual gas completions in non-Appalachian areas. We will also have access to the Dwight's Well Data System, which is a well completion history database.

Other Data

Other electronic databases that are available include the GRI gas composition database and the GRI tight gas database, both developed by Energy and Environmental Analysis (Hugman, et al, 1990; Hugman, et al, 1993). The GRI gas composition database is an enhanced version of the U.S. Bureau of Mines gas sample database, which contains gas composition analyses for over 15,000 wells (Moore, 1985). The GRI tight gas database identifies all of the reservoirs in non-Appalachian areas that fall within the Federal Energy Regulatory Commission tight gas areas.

PROJECT DESCRIPTION

Nature and Scope of User Needs Study

GASIS will be designed and developed to meet the needs of a wide range of potential users. The User Needs study has been planned to cover all major segments of the gas industry and is scheduled to take six months and include 80 interviews. Interviews are conducted at the potential user's location. Each interview consists of a presentation of the GASIS project, followed by a discussion of the issues and data priorities.

Topics Covered by the User Needs Study

Each User Needs meeting covers the following areas:

- (1) Potential applications for the reservoir database
- (2) Current sources of data for gas supply analysis
- (3) Regional priorities for data usage/data collection

- (4) Data category and element priorities
- (5) Database format issues

User Needs meetings typically begin with a discussion of the types of gas supply-related studies or projects for which the group is responsible. For discussion purposes, potential GASIS applications have been categorized into areas such as "play analysis," "technology assessment," or "planning and marketing." The industry representative is encouraged to discuss how the GASIS data system could be used in each area.

The next stage is a discussion of sources of production, completion, and engineering information that are available to the group or company. This includes commercially purchased or licensed data, in-house datasets, or public domain data. This information will be used to help define the appropriate scope and content of GASIS. It is also intended to help avoid duplication of effort in cases where nonproprietary data are available.

Next, regional data priorities are evaluated. Although GASIS will include data from all regions covered by the Gas Atlas project, regions in which the gas industry is most active or interested should be given extra weight in the data collection effort.

Evaluation of data element priorities is the most important aspect of the survey. A total of 154 individual data elements have been suggested for each reservoir. The suggested coverage is much greater than that of the Gas Atlas projects, which have typically reported only about 25 data elements for each reservoir. The goal is to determine the relative importance of data categories and specific data elements. A secondary objective is to determine which data elements (such as porosity or net pay thickness) should include a data range, rather than just an average.

Interview Status

Through October, 1993, a total of 22 User Needs interviews had been completed with 50 individuals. The breakdown by user group is as follows:

| | | No. |
|---------------------------------|------------|-----------|
| | Interviews | of people |
| Majors | 2 | 5 |
| Independents | 3 | 5 |
| Pipeline companies | 1 | 1 |
| Local distribution companies | 0 | 0 |
| Gas marketing affiliates | 1 | 1 |
| Banks | 2 | 3 |
| Service companies | 1 | 2 |
| GRI | 1 | 6 |
| DOE/EIA | 2 | 5 |
| USGS | 1 | 9 |
| MMS | 2 | 4 |
| Geological/Engineering consulta | ints 4 | 5 |
| Associations | 0 | 0 |
| State surveys | 1 | 2 |
| State regulatory agencies | 1 | 2 |
| Totals | 22 | 50 |

Our intent is to cover all of these groups to the extent necessary to evaluate the nature of potential GASIS applications and data needs.

Documentation

Interview documentation includes a verbal summary of applications, data sources, suggestions, and concerns, and a "checkoff" form for data priorities. Where possible, results will be tabulated for quantitative evaluation by user group. After the results are tabulated, the GASIS interview team will meet to interpret the results and decide on recommendations. The interview results and recommendations will be documented in a report.

RESULTS

Preliminary results of the User Needs study are as follows:

GASIS Applications

Figure 2 summarizes our preliminary list of applications by user group. Producers are expected to use GASIS for play analysis, modeling and forecasting, planning, and resource assessment and characterization. Majors and large independents are expected to combine elements of GASIS with in-house and commercial data.

DOE/METC is currently developing the Gas System Analysis Model (GSAM). This model will use the GASIS data as the primary gas supply component. METC will be using the GSAM model for technology assessment and program evaluation. Other likely user groups within DOE are the Fossil Energy and Policy groups in Washington, and the Energy Information Administration in Washington and Dallas.

The Gas Research Institute will use GASIS data primarily for technology assessment and as input into national supply modeling efforts. GRI supports a wide range of gas supplyrelated technology research. GASIS would provide a tool to assess the potential impact of improved recovery methods such as hydraulic fracturing or infill drilling. GRI also supports the annual GRI Baseline forecast of energy supply and demand in the U.S. using the Hydrocarbon Model, developed by Energy and Environmental Analysis. GASIS reservoir data are expected to be used in future gas supply studies in support of this model.

The U.S. Geological Survey and Minerals Management Service may use GASIS for play evaluation and resource assessment. Both of these organizations have access to other field and reservoir databases, but may use components of GASIS to augment their data.

Energy lending groups at major banks have indicated a strong interest in GASIS. These groups evaluate engineering and economic studies of oil and gas properties. While they have access to commercial production and well completion data, lenders have indicated that there is a need for a PC-based tool that will allow "reasonableness checks" on reserve and deliverability estimates and reservoir and fluid parameters.

Gas pipeline companies are now almost exclusively transporters of gas, and are less involved in reserve evaluation studies than in the past. However, planning groups for these companies are very interested in gas supply developments, both nationally and in their supply areas. They are expected to use GASIS for reserve and resource studies and planning activities. Under FERC order 636, most of the responsibility for purchasing gas reserves and maintaining deliverability has been shifted to Local Distribution Companies and large endusers. These groups will be increasingly involved in gas supply issues.

Service firms and equipment manufacturers could use GASIS to evaluate the potential market for new equipment or technologies.

Data Element Priorities

Figure 3 summarizes data priorities by category of data. The highest priorities are field and reservoir identification and linkages, reservoir parameters (such as net pay and porosity), and production and reserves. Slightly lower in priority are field and reservoir status and reference well information. Of moderate priority are gas composition, fluid properties, drilling and completion practices, and coalbed methane data. Rock properties (mechanical properties) and certain stimulation data (those specified as "typical" pressures and injection quantities for a reservoir) are the lowest priority.

Correct reservoir identification and uniform coding is critical. This includes standardized field and reservoir names and codes, state, county, district, basin, location, and play name. Uniform coding is critical because it will allow linkage between GASIS and both commercial and proprietary data. The EIA master field code file will be used for field identification. Uniform reservoir codes have been developed by most state regulatory agencies and will also be included. To assign these codes, each Gas Atlas reservoir will be matched with the corresponding reservoir record in the Dwight's DPDS reservoir database.

Most of the proposed reservoir engineering parameters are high priority. Highest priority elements will be those used in volumetric calculations -- net pay, porosity, water saturation, productive area, and pressures.

Summary production data, reserve estimates, and gas-in-place are key components. The published Gas Atlas data include cumulative gas production for almost all reservoirs. However, the data are not reported on a consistent year among regions (although they are consistent within individual regions), and will have to be updated using Dwight's data. The published atlas projects have not included gas reserve estimates. Two unpublished atlases, the Rocky Mountain and Northern Gulf of Mexico atlases, will contain reserve values. GASIS will include a reserve estimate for each reservoir, using production decline methods or reserve-to-production ratios where other data are not available. The GASIS system will

include an indication of the source of the reserve estimate.

Field and reservoir status information is a high priority and can largely be extracted from existing Dwight's data. This category includes field status, reservoir status, field and reservoir discovery year, number of producing and shut-in wells, and other information.

A reference well data section has been proposed. Reference well data may include estimated ultimate recovery, completion interval, and flow potential. Such information would provide a uniform basis for reservoir identification and could be used in search and retrieval applications.

Approximately 20 drilling, completion, and stimulation data elements were proposed. Potential users have indicated that summary information about drilling and completion practices would be of some value. Usefulness in a reservoir level database would be limited because such practices vary from well to well or through time, and classification would involve definitional problems and subjectivity. However, identification of which reservoirs have been stimulated (or are typically stimulated) and the usual stimulation method is considered important, especially for modeling and technology assessment groups, and an effort will be made to identify data sources or approaches.

Data Format Issues

GASIS must be available in a format that is easy to access and manipulate. Plans are for GASIS to be a DOS-based, stand-alone system on CD-ROM. Most potential users have access to CD-ROM hardware and are comfortable with that medium. GASIS will include basic retrieval, report, and export capabilities. For example, it will be possible to retrieve reservoir records on the basis of attributes such as basin, depth interval, formation, or ultimate recovery. A simple, menu-driven system is planned. Most users plan to export GASIS data and manipulate it with database software such as dBASE. GASIS data will be exportable via an ASCII text file, which can be readily converted to a database or spreadsheet file or uploaded and manipulated on a mainframe. Dwight's has extensive experience in preparing CD-ROM data.

No graphics data (maps or cross sections) are planned for GASIS, although maps, cross sections, or type logs such as those in the gas atlases could be added in the future.

FUTURE WORK

Upon completion of the User Needs study and approval by METC of our plan for the data system, database design and development will begin. Initial steps will include the development of data standards and definitions, and the development of the data matrix. A full comparison will be made of the Dwight's and Gas Atlas data to evaluate coverage and define problem areas. We plan to meet with each of the Gas Atlas groups where possible to evaluate methodology and data sources.

A detailed work plan will be developed for data collection in each region. Primary data sources and approaches for each element or group of elements will be established. Data collection and processing tasks will be assigned to the appropriate group.

A significant effort will be devoted to controlling data quality. This will include range and reasonableness checks, consistency and logic checks, and database comparisons. Current plans call for the development of a prototype version of GASIS near the end of 1994 or early 1995. The project is scheduled for completion in mid-1996.

REFERENCES

Hugman, R.H., P.S. Springer, and E.H. Vidas, 1993, "Tight Gas Field, Reservoir, and Completion Analysis of the United States --1993 Update," GRI Report nos. 93-0364.1 and 93-0364.2 (two volumes), prepared by Energy and Environmental Analysis for Gas Research Institute. Hugman, R.H., E.H. Vidas, and P.S. Springer, 1990, "Chemical Composition of Discovered and Undiscovered Natural Gas in the United States," GRI Report no. 90-0248, prepared by Energy and Environmental Analysis for Gas Research Institute. (An update to this report will soon be available).

Moore, B.J. and S. Sigler, 1985, "Analyses of Natural Gases, 1917-85," Bureau of Mines Information Circular No. 9129 (plus subsequent updates).

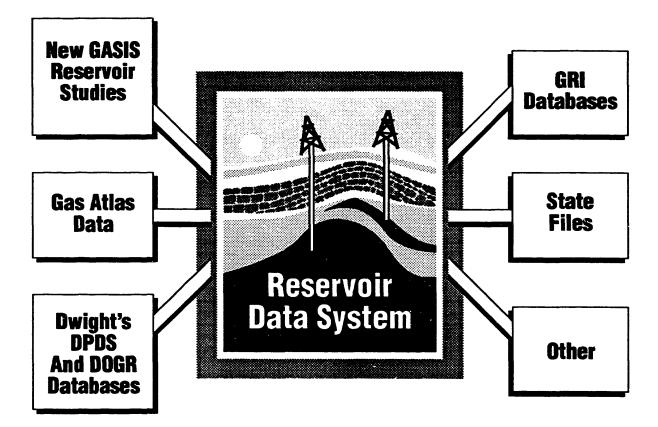


Figure 1. Data Sources for GASIS Data System

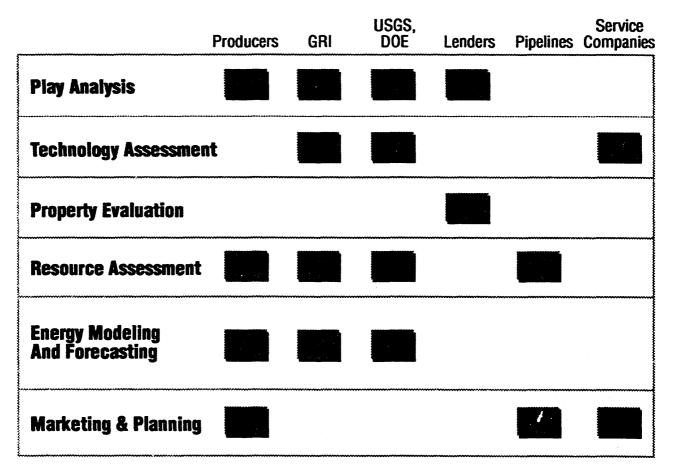


Figure 2. Potential GASIS Applications

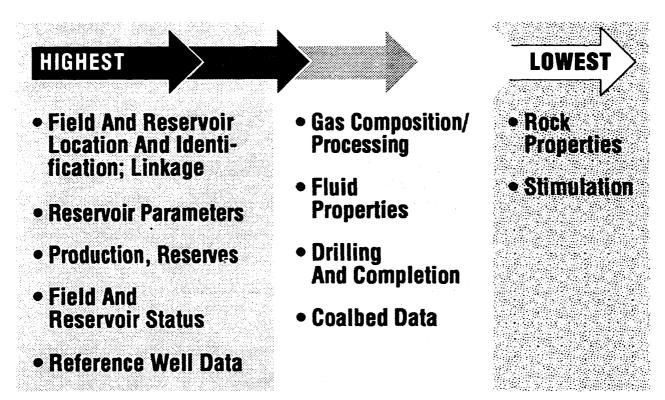


Figure 3. Preliminary Priorities for Data System

Session NG -- Natural Gas Technology

Session NG-8

Low-Quality Natural Gas Upgrading

NG-8.1 Low Temperature H₂S Separation Using Membrane Reactor With Redox Catalyst

CONTRACT INFORMATION

Contract Number

Contractor

DE-AI21-86MC23120

John J. Pellegrino

John J. Pellegrino Myong Ko Laurel Watts

Venkat Venkataraman Harold D. Shoemaker

National Institute of Standards and Technology Thermophysics Division, 838.01 325 Broadway Boulder, CO 80303 (303) 497-3416

Contractor Project Manager

Principal Investigators

METC Project Manager

Period of Performance

Schedule and Milestones

TASK

1. Develop Model

• phase equilibrium

• kinetic

reactor

2. Batch Reactor

- build system
- obtain 3 phase slurry data
- obtain spinning disk data

3. CCMR Reactor

- initial tests
- membrane w/high H_2S vs CO_2
- optimized tests

4. Design & Report

• preliminary design critique

• final report

| 199 | 92 | | 19 | 93 | | | | | | | | | | | 19 | 94 | | | | | | | |
|-----------|----|----------|----|----|---|---|---|---|----------|----------|----------|----------|---|---|----|----|---|---|---|---|---|---|----------|
| | | D | | F | M | A | M | 1 | J | A | S | 0 | N | D | | F | Μ | A | M | J | 1 | A | S |
| | | | | | | | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | <u> </u> | | | | | | | | | | | | | L |
| E | | E | E | E | | | | | | E | E | E | E | | F | | | | | | | | ┡ |
| | | | | _ | | | | | | | E | | | É | | | _ | | | | | | |
| \vdash | _ | ┝─ | | | | | | | | - | | | | | | | | | | | | | ┝ |
| | | | | _ | | | | | _ | | | _ | | | | | | | | | | | L |
| \vdash | | ┣— | | | | | | | ┞─ | ┣ | | | | | ┠ | ╞═ | | = | = | | | | L |
| E | | | | | | | | | | | | | | | | | | | | | | | L |
| \square | | | | | | _ | | | | | | | | | | | | | | | | | F |
| H | | | | | | | | | | F | F | | | | | _ | _ | | | | | | |
| | | | | | | | | | | | | | | | | | | | | | | - | |
| \vdash | - | | | - | | | | | ┢── | ┢ | \vdash | \vdash | | | | | | | | | - | | \vdash |
| | | | | | | | | | | \Box | | | | | | | | | | | E | | Ē |
| | | | L | L | | | | | L_ | | | | | | | L | | | | | | | |

October 1, 1992 to September 30, 1994

OBJECTIVES

We are combining a low temperature redox catalyst with an H₂S selective membrane to create a composite-catalytic-membrane-reactor (CCMR) to help reach pipeline-quality natural gas H₂S levels of below 4 ppm. The goal of this program is to identify the apparent kinetic and mass transfer parameters for the CCMR. Using these kinetic and mass transfer parameters a preliminary process design can be made to ascertain the potential of this technology for replacement of conventional amine scrubbing and Claus sulfur recovery processes. In pursuit of this goal the project contains the following activities:

• Construction of reactor and mass transfer equipment suitable for accurate measurements and safe handling of pure H₂S.

• Initial proof-of-concept experiments with a prototype CCMR.

• Obtain literature data and develop thermodynamic models for multicomponent natural gas components' solubility in electrolyte solutions.

• Make physical and chemical measurements on the catalyst.

• Obtain kinetic data using a 3-phase slurry reactor.

• Obtain kinetic data for a catalytic membrane under varying mass transfer conditions.

• Develop mathematical models to guide experimental work and for interpretation of results.

• Optimize the permselective membrane part of the CCMR using commercially available materials.

• Further proof-of-concept experiments with an optimized CCMR.

• Develop preliminary process design and economic analysis for the use of a CCMR in gas cleanup.

BACKGROUND INFORMATION

Pipeline-quality natural gas requires H₂S levels below 4 ppm. Alternatives to the conventional absorption-stripping and Claus processes are actively being considered. Among these alternatives membrane-based separations seem to have promise. Polymeric membrane processes have already found a niche in CO₂ removal and reinjection in the oil field and in the cleanup of natural gas (Spillman, 1989). But it is considered economically infeasible to try to reach 4 ppm H_2S in pipeline gas using only a membrane process (Funk and Li, 1990). A potential alternative is a hybrid process (McKee, et al, 1991) and Pellegrino and Giarratano, 1992). In this case a membrane removes the bulk of the H₂S and an amine scrubbing system chemically complexes the remaining H₂S to bring the gas stream to pipeline specifications. Ultimately the amine system is regenerated by raising the temperature with steam and stripping the H_2S off. All the segregated H_2S is sent to a Claus plant where it is eventually converted to elemental sulfur (Kohl & Riesenfeld, 1985). This project proposes another alternative.

We are combining a low temperature redox catalyst with an H₂S selective membrane to create a composite-catalytic-membrane-reactor (CCMR). In this membrane reactor the H₂S would form a polysulfide on the permeate side of the membrane. The result of this is to eliminate the buildup of H₂S in the permeate stream which otherwise decreases the driving force for mass transfer and increases the subsequent membrane area requirements and loss of CH₄ in a standard membrane process. The redox reaction occurs in a liquid stream of oxygensaturated NaOH. Elemental sulfur is recovered by neutralization of the liquid solution with HCl.

The process of creating a mesh with dispersed particles is a general one with several companies having patented products based on such a technology. The process for creating the particulate mesh membrane yields a microporous membrane, which would be unsuitable for doing gas separations. What it is suitable for is creating a very open network of unaggregated particles which would maximize their mass transfer accessibility. It also allows the particles to be easily handled and put into a variety of novel configurations. We will refer to this mesh membrane, with particles, as the "CAT" membrane.

A variety of liquid phase redox processes for H₂S oxidation are known and described in Kohl & Riesenfeld, Meyer et al. and Dalrymple et al.. None of them use a catalytic membrane reactor. In our approach we envision the CAT membrane coated with a thin film of an H₂S permeable gas separation membrane. Of particular interest to us is the use of the polyperfluorosulfonic acid (PFSA) polymer with which we have many years of experience and seems especially suitable for this application due to its inherent chemical inertness. We will refer to this PFSA-coated, CAT membrane as a composite catalytic membrane reactor (CCMR).

Prior work by our group has shown that liquid membrane/facilitated transport with ion exchange membranes can achieve very high selectivity for the removal of CO₂ and H₂S from mixtures containing H₂, CO, CH₄ and higher hydrocarbons at ambient temperatures. We refer to these membranes as enhanced transport, ion-exchange membranes or ET-IEX. The productivity of the ET-IEX membranes, on a per unit thickness basis, can be greater than or equivalent to the best of the passive membranes and more selective.

We also developed a heat-treatment solventswelling approach which dramatically increased the productivity of the membranes (Pellegrino et al, 1988 and Heaney and Pellegrino, 1989). Not only did the permeance of the membranes increase dramatically but so did the permeability. Further experiments with ternary mixtures of H₂, CO₂ and H₂S, using a variety of chemical carriers indicated that larger carriers could effectively be used to vary selectively between H₂S and CO₂ (Pellegrino et al, 1990). This experience will be drawn upon to maximize the selectivity of the permselective membrane for H₂S in the CCMR.

A CCMR offers several potential advantages versus the conventional liquid redox systems. These include: 1) contacting the catalyst with an enriched H₂S reactant, 2) segregation of the O₂ from the natural gas stream, 3) improved and consistent mass transfer area, 4) lower liquid circulation rates, and 5) compact operation amenable to small-scale operations. Of course the key to achieving any advantages lies in the kinetic properties of the catalyst and how well the reaction kinetics can be matched to the permeation of H₂S through the permselective layer. Additionally we need to consider the effect of other permeants on the catalyst's lifetime and activity.

<u>General Description of the Catalyst and H2S</u> <u>Oxidation Reaction</u>

The catalyst is formed with specific surface areas which vary from 5 to 1200 m²/g. The catalyst is perceived to operate due to specific chemisorption with the catalytic oxidation promoted by delocalized electrons.

The overall reaction and stoichiometry can be expressed as:

(2n+1) H₂S + n O₂ + 2 NaOH -----> NaS_{2n+1}Na + 2(n+1) H₂O

and the elemental sulfur is generated from solution by neutralization according to:

 $NaS_{2n+1}Na + 2 HC1 ----->$ 2n S + H₂S + 2 NaCl

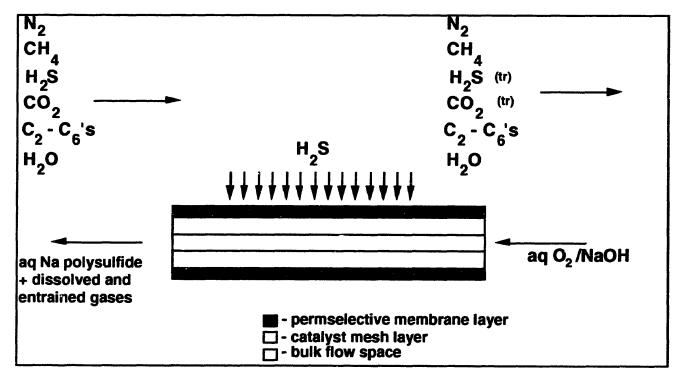
The following mechanism has been reported as being a likely route to the overall oxidation process (note, C designates the catalyst's active surface sites):

 $C + O_2 \rightarrow O_2 \cdot C$ $O_2 \cdot C + 4 \text{ HS}^- + 2 \text{ H}_2\text{O} \rightarrow$ $C + 4 \text{ HS}^- + 4 \text{ OH}^ 4 \text{ HS}^- \rightarrow 2 \text{ HSSH}$ $2 \text{ OH}^- + 2 \text{ HSSH} \rightarrow 2 \text{ -SSH} + 2 \text{ H}_2\text{O}$ $O_2 \cdot C + 2 \text{ -S}_x\text{H} \rightarrow$ $C + 4 \text{ S}_x^- + 2 \text{ H}_2\text{O}$

 $S_x^- + S_y^- \rightarrow S_x S_y^-$

Presumably the catalytic conversion involves sorption of dissolved oxygen at the active sites of the catalyst. Deprotonated H₂S in the aqueous NaOH solution forms free radicals with access to the oxidized sites. The free radicals can then combine and form oligomers which in turn become deprotonated and continue the process. The termination groups become the Na salts as the hydroxyl groups become used up leading to a solution of sodium polysulfide. The neutralization step with HCl frees one H₂S per polysulfide and generates a brine solution. Figure 1 presents a schematic of the composite membrane and the main components of the streams. The sour natural gas flows on the feed (high pressure) side of the module. The aqueous (aq) O₂/NaOH stream flows on the permeate side, ideally in a countercurrent fashion. (In plant-scale hardware countercurrent flow may not be plausible.) By controlling the permeation properties of the permselective layer the H₂S (and possibly CO₂) is the primary component permeating into the catalyst layer. Some of all the other components will also permeate but their fluxes should be small with respect to the acid gases.

The oxygenated NaOH (aq) penetrates into the CAT layer because the latter is a very open





mesh. The oxygen activates the sites on the catalyst and the NaOH promotes the formation of HS free radicals from the H_2S that is continuously permeating into the liquid phase. The reaction can proceed as described previously.

The formation of the polysulfide effectively creates a continuous "sink" for H_2S . Thus its

permeation rate, even when its partial pressure in the feed stream becomes very low, is never completely inhibited. If the rate of reaction and the mass transfer of HS free radicals in the liquid phase are both fast enough with respect to the diffusion rate of H₂S in the permselective layer, then there will always be a non-zero driving force for H₂S permeation through the membrane.

Ξ

Description of the CCMR Concept

PROJECT DESCRIPTION

The project is intended to identify the apparent kinetic and mass transfer parameters for a composite-catalytic-membrane-reactor (CCMR). Using these kinetic and mass transfer parameters a preliminary process design can be made to ascertain the potential of this technology for replacement of conventional amine scrubbing and Claus sulfur recovery processes.

Develop a model to describe the compositecatalytic-membrane-reactor.

The model will initially be a 2 dimensional steady state one. The previous Figure 1 can now be taken to represent a differential element. The mass transfer perpendicular to the bulk gas stream will include 4 layers:

• a gas phase mass transfer resistance,

• diffusion through the membrane using a solution-diffusion model,

• a reaction zone with volume averaged properties based on the catalyst loading and porosity, and

• a liquid film resistance.

Note that the gradients will be in opposite directions for many of the components and the species conservation equations will be coupled primarily through the reaction term. The exact form of the reaction term will be modified depending on the results of the batch kinetic experiments. This model is not particularly new and prior work in the literature will simplify its development. We will primarily rely on semi-analytical numerical solutions to exercise the model.

Develop initial kinetic and thermodynamic data.

In order to accomplish this objective we will:

• Construct an experimental apparatus suitable for obtaining apparent kinetic and mass transfer data for the semi-batch oxidation of H_2S using the catalyst.

• Obtain data for room temperature kinetics.

• Develop a thermodynamially-consistent model for predicting multicomponent gas solubilities in aqueous electrolyte solutions.

Prepare a CCMR and obtain preliminary data.

We will prepare a permselective layer of polyperfluorosulfonic acid (PFSA), or a suitable alternative, on the CAT layer and run experiments using synthetic natural gas feed compositions where gases are permeating through the permselective layer.

We will try to determine the apparent rate limiting steps between membrane permeation, liquid phase mass transfer (including H_2S , NaOH and O_2) and surface reaction. For this we will rely on data obtained in the slurry reactor studies.

We will also determine effects of pressure, temperature, pH and liquid phase composition over a limited range of values.

Prepare a Preliminary Process Design

We will use the model to evaluate a membrane process for H_2S removal from a natural gas stream. The membrane process will be compared to a conventional design obtained from the literature and/or developed with a flowsheet simulator.

RESULTS

Construction of Equipment

We have completed assembly of a flow system suitable for safe experimentation with pure H_2S streams, as well as CH₄ and other components of natural gas. The system will be used for:

1) measurment of apparent H_2S oxidation kinetics for a 3-phase slurry reactor in both batch and continuous flow modes;

2) measurment of apparent H_2S oxidation kinetics for a spinning disk reactor in both batch and continuous flow modes;

3) measurement of gas solubility in aqueous electrolyte solutions, and

4) measurements of permeation and reaction of synthetic natural gas streams in a membrane reactor test module.

The 3-phase slurry reactor will be used to develop a global rate model including effects of P_{H2S} , P_{O2} , T, pH, and ionic composition. The spinning disk reactor, depicted in Figure 2, will enable us to develop mass transfer correlations useful for modifying the rate model. The stirrer speed can be varied and the effects of external film mass transfer into the catalyst mesh layer can be quantified.

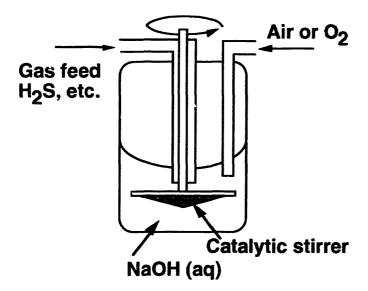


Figure 2. Schematic of Spinning Disk Reactor

Initial Proof-of-Concept Experiments

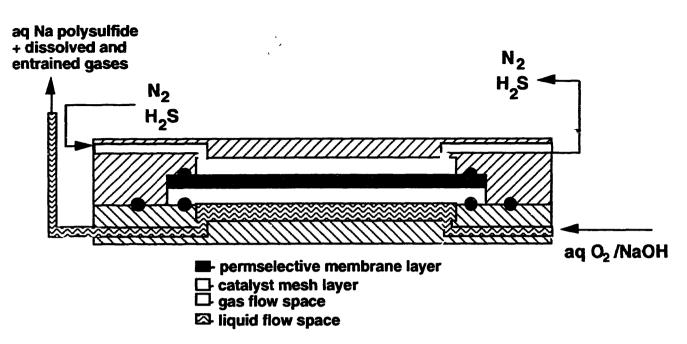
We performed four initial experiments using a catalyst mesh layer containing ~80% solids. This mesh was pressed into a polyperfluorosulfonate membrane (Na⁺ form) and mounted into a test cell as indicated in Figure 3. The experiments were performed at 296 K and 221 kPa (20 psig) and the results are listed in Table 1. The precipitate from the first experiment was analyzed using direct insertion mass spectrometry and found to be at least 99.999% sulfur. The sulfur productivity was based on the amount of elemental sulfur precipitated out of the recirculating NaOH stream. This sulfur productivity was similar to what we would expect for H₂S permeation through the membrane alone. This leads us to conclude that in these initial experiments the transport through the comparatively thick membrane film was the rate limiting step.

Physical-Chemical Measurements on the Catalyst

Several measurements using temperatureprogrammed desorption were performed which indicated that there was only physical sorption of CO, CO₂ and H₂O on the catalyst. An indication of the available reaction sites was estimated by the adsorptive capacity for several polar organic compounds: methanol - 1750 μ mol/g, ethanol -835 μ mol/g, and formic acid - 1656 μ mol/g. The surface area is estimated at > 1000 m²/g.

| | | position (v | | _ | _ | |
|------|-----------------|-----------------|------------------|------|-------|--|
| N 2 | CH ₄ | CO ₂ | H ₂ S | NaOH | Time | Sulfur Productivity |
| | | | | (N) | (min) | x 10 ¹⁰ mol/cm ² • s |
| 69.5 | - | - | 30.5 | 0.2 | 315 | 13.53 |
| - | 55.0 | - | 45.0 | 0.2 | 291 | 12.13 |
| - | 43.6 | 34.2 | 22.2 | 0.2 | 318 | 10.41 |
| 51.2 | - | 31.5 | 17.4 | 1.0 | 277 | 12.96 |

Table 1. Initial Results for Flow Experiments using CCMR Catalyst



•



| Known from literature or measurement | To be calculated |
|---|---|
| P, T gas phase mole fractions Үн ₂ s; Yo ₂ ; Үсн ₄ Henry's law constants for H ₂ O solubility Кн,н ₂ s; Кн,о ₂ ; Кн,сн ₄ | aqueous phase compositions [H ₂ S], [CH ₄], [O ₂], [NaOH] equeous phase ion concentrations [HS ⁻], [H ⁺], [Na ⁺], [OH ⁻], [S ⁼] |
| Total [NaOH] Vapor pressure of H ₂ O | |
| Liquid phase activities HKF method Gas phase fugacities, Redlich Kwong EOS | |
| Dissociation constants H_2S , NaOH, H_2O | |
| HKF - (Helgeson, Kirkham and Flowers, 1981) EOS - equation of state | |

Table 2. Approach for Determining Phase Equilibrium

Multicomponent Solubility Data and Models

Table 2 summarizes the approach for determining the liquid phase activities of the gaseous feed components and other key reactants during the kinetics experiments. We have determined sufficient data in the literature so that only those measurements which are directly performed during an experiment (i.e., pressure, temperature, pH, etc.) are needed. A computer program is currently being written to implement the thermodynamic model.

Simple Model of Integrated Reactor Performance

A numerical model is being written to implement the schematic problem depicted in Figure 4. It is an ideal case which assumes that a first order reaction occurs through the liquid phase. In using this model we are lumping many real, physical parameters into some pseudo-parameters, which include the partition coefficients of the gas phase constituents, H_i, the presummed velocity profile, V_z , and the overall reaction rate parameter, k. We are taking this approach initially because it may allow us to develop a semi-analytical solution that will be easier to use to explore the effects of changes in parameter values. The model will integrate the material balance of the gas and liquid phases in the z-direction and will be useful for design problems.

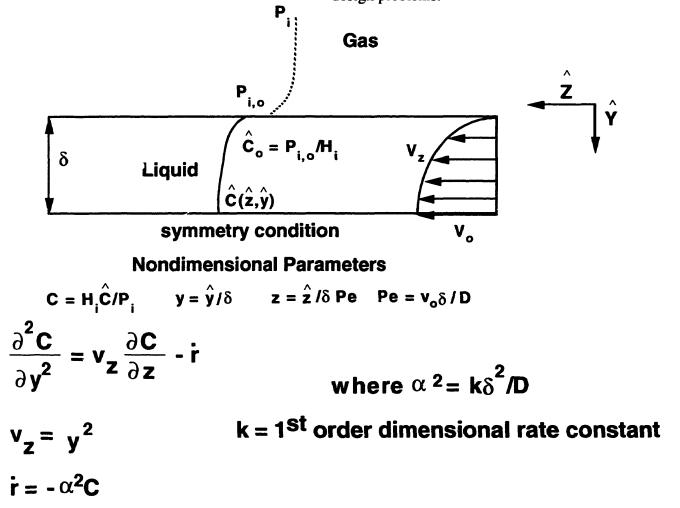


Figure 4. Schematic of Simple Model for the Integrated CCMR Performance

FUTURE WORK

Most of our experimental work is still ahead of us. We will perform the 3-phase slurry and spinning disk reactor measurements and complete the modeling efforts. Additionally we will try to optimize a permselective membrane layer to minimize CO₂ permeation. CO₂ reacts with NaOH to form carbonates which will unnecessarily use up reagent. Upon completion of the reactor work and modeling we will perform optimized proof-ofconcept experiments and develop a preliminary process design critique.

REFERENCES

Dalrymple, D.A, T.J. Trofe, and J.M. Evans. 1989. An Overview of Liquid Redox Sulfur Recovery, Chem Eng Prog, March, 43.

Funk, E.W. and N. N. Li. 1990. Purification of Natural Gas by Membranes, Gas Separation Technology, E.F. Vansant and R. Dewoińs (eds.), Process Technology Proceedings, 8, Elsevier, Amsterdam.

Heaney, M.D. and JJ Pellegrino. 1990. Increased Facilitated Transport Related to Microstructural Changes in Heat Treated Ion-Exchange Membranes, J. Membr. Sci., 47, 143.

Helgeson, H.C., D.H. Kirkham, and G.C. Flowers. 1981. Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: IV. Calculations of activity coefficients, osmotic coefficients and apparent molal and standard and relative partial molal properties to 600°C and 5 kbar. Am. J. Science. 281, 1249.

Kohl, A. and F. Riesenfeld. 1985. Gas Purification, 4th Ed., Gulf Publishing Co., Houston, TX.

McKee, R.L., M.K. Changela and G.J. Reading. 1991. CO₂ Removal: Membrane plus amine. Hydrocarbon Processing: 63.

Meyer, H.S., D. Leppin, and J.L. Savidge. 1990. GRI's Gas Processing Research and Development Program, Proceedings of 69th Annual Convention of Gas Processors Association, 149. Pellegrino, JJ, R. Nassimbene and R.D. Noble. 1988. Facilitated Transport of CO₂ through Highly Swollen Ion-Exchange Membranes: The Effect of Hot Glycerine Pretreatment, Gas Sep & Pur, 2, 3, 126.

Pellegrino, JJ, M. Ko, R. Nassimbene and M. Einert. 1990. Selective Transport of CO₂ and H₂S Using Facilitated Transport in Gel Ion-Exchange Membranes, Gas Separation Technology, E.F. Vansant and R. Dewolfs (eds.), Process Technology Proceedings, 8, Elsevier, Amsterdam.

Pellegrino, JJ and P.J. Giarratano. 1992. Ion-Exchange Membranes for Bulk Separation of H₂S and CO₂ from Natural Gas Streams. Proceedings of 1992 METC Fuels Technology Contractors Review Meeting, Contract No. DE-AI21-86MC23120.

Redlich, O. and J.N.S. Kwong. 1949. On the thermodynamics of solutions V. An equation of state. Fugacities of gaseous solutions. Chem. Rev. 44, 233.Schell, W.J. 1985. Commercial Applications for Gas Permeation Membrane Systems, J. Mem. Sci., 22, 217.

Spillman, R.W. 1989. Economics of Gas Separation Membranes, Chem Eng Prog, Jan, 41.

NG-8.2 Upgrading Natural Gas by Means of Highly Performing Polyimide Membranes

CONTRACT INFORMATION

| Contract Number | Contract Number | | | | | | DE-FG21-91MC28072 | | | | | | |
|---|-------------------------|---|-------|--|------------------------|-------|-------------------|-------|---|---|---|---|--|
| Contractor | | | | Syracuse University Office of Sponsored Programs 113 Bowne Hall Syracuse, NY 13244-1200 (315) 443-2807 | | | | | | | | | |
| Contractor Project Manag | ger | | | Dr. | S. <i>A</i> | Alexa | nder | Sterr | 1 | | | | |
| Principal Investigator | | | | | Dr. S. Alexander Stern | | | | | | | | |
| METC Project Manager | | | | Dr. V. Venkataraman | | | | | | | | | |
| Period of Performance | | | | 10/ 1/ 1991 to 9/ 30/ 1994 | | | | | | | | | |
| Schedule and Milestones | Schedule and Milestones | | | | | | | | | | | | |
| | | F | '94 P | rogra | am S | iched | lule | | | | | | |
| Test Plan Fabrication Testing Analysis | S | 0 | N | D | J | F | М | A | М | J | J | A | |
| | | | | | | | | | | | | | |

II. OBJECTIVE

The objective of the present research project is to assess the potential usefulness of membrane separation processes for the removal of acid gases (CO_2 and H_2S) and H_2O vapor

from low-quality natural gas.

III. BACKGROUND INFORMATION

The declining supply of domestic oil has

increased the importance of natural gas as a clean-burning fuel and chemical feedstock in recent years. It is estimated that the United States has natural gas reserves of over 1,000 trillion cubic feet [1]. However, many of these reserves are designated as being of "low quality" because of their high content of non-hydrocarbon gases, particularly CO_2 and in some cases H_2S . Low-quality natural gas cannot be upgraded economically to pipeline quality by means of conventional techniques for the removal of CO_2 and H_2S .

Membrane-based separation processes offer important advantages for the upgrading of low-quality natural gas [2,3]. One of the main advantages of membrane processes is that they are potentially energy-efficient. The process equipment used is simple, compact, and relatively easy to operate. Moreover, this equipment is modular and can be easily scaled up or operated at partial capacity. Membrane separation processes also adapt easily to variations in the flow rate, pressure, and composition of feed streams.

IV. PROJECT DESCRIPTION

The project comprises gas permeability and separation measurements, process design studies, and economic evaluations of membrane separation processes. The measurements are being made with new, highly gas-selective polyimide membranes developed in this laboratory.

The following tasks were performed during the first two years of the project:

1) A laboratory-scale apparatus for measuring the permeability and selectivity of polymer membranes to gas mixtures was built and tested. 2) The permeability and selectivity of seven new polyimide membranes to binary CH_4/CO_2 and ternary $CH_4/CO_2/H_2S$ mixtures were measured at 95°F (35°C) and at "upstream" pressures in the range from 58.8 psia to 200 psia (4 atm to 13.6 atm).

3) Gas separation measurements were made using binary CH_4/CO_2 and ternary $CH_4/CO_2/H_2S$ feed gas mixtures.

4) Process design studies and economic evaluations of membrane processes for upgrading low-quality natural gas were made using the experimentally obtained permeability and selectivity values for the three most promising polyimide membranes. For the sake of comparison, similar studies were made also for cellulose acetate membranes, which are at present being widely used on an industrial scale for the separation of CO_2 from natural gas.

V. RESULTS

A. Evaluation of New Polyimide Membranes for Upgrading Natural Gas

Experimental Techniques

All measurements were made with a laboratory-scale apparatus for measuring the permeability and selectivity of polymer membranes to gas mixtures. A diagram of the apparatus is shown in Figure 1. The measurements were made at 95°F (35°C) and at upstream pressures ranging from 58.8 psia to 200 psia (4 atm to 13.6 atm). In all cases, the downstream pressure was maintained below 0.39 psia (20 mmHg). The "stage cut" (the fraction of the feed gas stream allowed to permeate through the membrane) was varied from ≤ 0.001 to about 0.2.

Measurements at stage cuts ≤ 0.001 yielded gas permeability and selectivity data for the components of the gas mixtures used, whereas measurements at higher stage cuts showed the extent of separation possible with a particular polymer membrane and a particular gas mixture.

Four binary CH_4/CO_2 mixtures containing 10, 20, 30, and 40 mole-% CO_2 and four ternary $CH_4/CO_2/H_2S$ of compositions (in mole-%) 87.9 $CH_4/9.5$ $CO_2/2.6$ H_2S ; 84.1 $CH_4/9.2$ $CO_2/6.7$ H_2S ; 65.3 $CH_4/27.4$ $CO_2/7.3$ H_2S ; and 55.3 $CH_4/36.7$ $CO_2/8.0$ H_2S were used in the measurements. All gas mixtures were either primary standards or certified mixtures.

Seven new polyimide membranes developed in this laboratory, designated as A-3, C-1, D-2, E-1, F-1, G-1, and H-1 were evaluated for possible use as membrane materials for upgrading low-quality natural gas. All polyimides used, except the E-1 and the F-1 polyimides contained fluorine in their repeat units. The E-1 and F-1 polyimides contained sulfone groups in their repeat units. The polyimides were cast in the form of "dense" (homogeneous) membranes of 2-4 mil (50-100 μ) thickness.

Gas Permeability and Selectivity Measurements

The effects of the total upstream pressure and of the CO_2 content in the binary CH_4/CO_2 feed mixtures on the permeability and selectivity of the seven polyimides are exemplified by the results obtained with the C-1 polyimide. These results are presented graphically in Figures 2-4 and can be summarized as follows:

1) As commonly found for glassy polymers, the permeability of the polyimide to

CH₄ and CO₂ decreases with increasing upstream pressure. Thus, the permeability to CH₄ (Figure 2) measured with a binary CH₄/CO₂ mixture containing 10 mole-% CO₂ decreases from 0.16 x 10⁻¹⁰ to 0.15 x 10⁻¹⁰ cm³(STP) cm/s cm² cmHg as the total upstream pressure is raised from 58.8 psia to 147 psia. The corresponding decrease in the permeability to CO₂ is from 10.4 x 10⁻¹⁰ to 9.3 x 10⁻¹⁰ cm³(STP) cm/s cm² cmHg. This type of permeation behavior is usually described by the "dual-mode sorption" model.

2) At any given total pressure, an increase in the CO_2 concentration in the feed gas mixture enhances the permeability of the polyimide to CH₄. As shown in Figure 2, the CH₄ permeability of the C-1 polyimide at an upstream pressure of 147 psia increases by about 30% as the CO₂ content in the feed gas mixture is increased from 10 mole-% to 40 mole-%. Concomitant to this increase in the CH₄ permeability, the CO₂ permeability either decreases or remains unchanged. In the case of the C-1 polyimide, the CO₂ permeability remains essentially unchanged as the CO₂ concentration in the feed gas is increased from 10 mole-% to 40 mole-%.

3) As a consequence of the changes in the CH_4 and CO_2 permeabilities, the CO_2/CH_4 selectivities of the seven polyimide studied thus far decrease with increasing CO_2 concentration in the feed. For example, the CO_2/CH_4 selectivity of the C-1 polyimide, measured at 147 psia (10 atm), decreases from 61 to 46 as the CO_2 concentration in the feed is increased from 10 mole-% to 40 mole-% (Figure 4).

The permeability and selectivity of several of the new polyimides were also measured with ternary $CH_4/CO_2/H_2S$ mixtures at 95°F (35°C) and at 147 psia (10 atm). For example, the results obtained with the D-2

polyimide are presented in Table I. The results of the measurements with the ternary $CH_4/CO_2/H_2S$ gas mixtures, when compared with the results obtained with binary CH_4/CO_2 mixtures having approximately the same CH_4 and CO_2 concentrations, show that the permeabilities to CH_4 and CO_2 of the D-2 polyimide decrease in the presence of H_2S . Since the decrease in the CH_4 permeability is greater than the decrease in the CO_2 permeability, the CO_2/CH_4 selectivity of the polyimide actually increases in the presence of H_2S .

Thus, the CH₄ and CO₂ permeabilities of the D-2 polyimide, measured with a *ternary* CH₄/CO₂/H₂S mixture containing 27.4 mole-% CO₂ and 7.3 mole-% H₂S are, respectively, 49% and 33% lower than the corresponding values obtained with a *binary* CH₄/CO₂ mixture containing 30 mole-% of CO₂. The net result is an increase in the CO₂/CH₄ selectivity of the D-2 membrane from 63.5 to 84.1. It should be noted that the CO₂ and CH₄ concentrations of the two mixtures are very similar, and they differ only in that the ternary mixture contains H₂S in addition to CH₄ and CO₂.

Other polymers such as the A-3 polyimide and the F-1 polyimide exhibit a decrease in both the CH_4 and CO_2 permeabilities in the presence of H_2S with little or no change in their CO_2/CH_4 selectivities.

Gas Separation Measurements

The extent of separation of CH_4/CO_2 and $CH_4/CO_2/H_2S$ mixtures achievable with the D-2 polyimide was measured at 95°F (35°C) and at an upstream pressure of 147 psia (10 atm). The downstream pressure was maintained at about 0.39 psia (20 mmHg). The results obtained with a binary CH_4/CO_2 mixture containing 10 mole-% CO₂ are discussed below.

All polymers are more permeable to CO_2 than to CH_4 , and hence the retentate is enriched in CH4 whereas the permeate is enriched in CO_2 . This is shown in Figures 5 and 6 where the retentate and permeate compositions obtained from the measurements with the binary CH_4/CO_2 , mixture are plotted as a function of stage cut. Figure 5 shows that the CO₂ concentration can be reduced from a feed concentration of 10 mole-% to less than 2 mole-% (corresponding to a CH₄ concentration higher than 98 mole-%) in the retentate at stage cuts as low as 0.12. From Figure 6, the corresponding permeate concentrations of CH4 and CO₂ are 28 mole-% and 72 mole-%, respectively.

The extent of separation of the above CH_4/CO_2 mixture achieved with the D-2 polyimide membrane has been predicted for a much wider range of stage cuts by means of a mathematical model simulating "perfect mixing" conditions [4]. This model yields the most conservative estimate of the extent of separation. Figures 5 and 6 show that the experimentally obtained separation was better than expected for "perfect mixing" conditions (shown as solid curves in Figures 5 and 6). Similar results were obtained with the D-2 polyimide membrane and a ternary feed gas mixture of composition (in mole-%) 87.9 $CH_4/9.5 CO_2/2.6 H_2S$.

Comparison of Separation Performance of New Polyimides

The CH₄ and CO₂ permeabilities and the CO_2/CH_4 selectivities of the seven new polyimides are compared in Table II. The data for cellulose acetate are also listed for comparison. All data were obtained from measurements with a CH₄/CO₂ gas mixture containing 10 mole-% CO₂ at 95°F (35°C) and at an upstream pressure of 147 psia (10 atm).

Table II shows that all seven polyimides studied thus far have higher CO_2/CH_4 selectivities than cellulose acetate. The D-2 and H-1 polyimides exhibit CO_2/CH_4 selectivity values which were more than *twice as high* as that of cellulose acetate membranes under similar experimental conditions. The intrinsic permeabilities of the new polyimides to CO_2 are comparable to or higher than the CO_2 permeability of cellulose acetate. The permeability of the G-1 polyimide to CO_2 is more than *nine times* higher than that of cellulose acetate under comparable conditions.

B. Membrane Process Design and Economic Evaluations

Operating Conditions and Assumptions

Process design studies and economic evaluations of membrane processes for upgrading low-quality natural gas were made using the permeability and selectivity data for the most promising polyimide membranes examined thus far. Single-stage processes as well as multistage processes with product recycle were considered. The objective was to compare the performance of these new polymers with that of cellulose acetate (CA) in an industrial-scale membrane process for upgrading of natural gas.

The calculations assume a set of "basecase" conditions that are representative of an average acid gas removal plant (Table III). In the present study, the crude natural gas feed to be processed is approximated by binary CH_4/CO_2 mixtures containing 10-40 mole-% CO_2 . The feed is assumed to be available at a pressure and flow rate of 800 psia and 35 million standard ft³/day (MMSCFD), respectively. All calculations are based on reducing the concentration of CO_2 in the product gas (the retentate) to ≤ 2 mole-%, as required for pipeline-quality gas. The upgrading of low-quality natural gas containing H_2S as well as CO_2 is also being studied and preliminary results have been reported elsewhere [5,6].

Asymmetric or composite membranes made from the most promising polymers, as determined by the experimental studies, were considered for process design and economic evaluations. When asymmetric or composite membranes are used, the separation occurs by a "cross-flow" pattern, regardless of whether the high- and low-pressure gas streams on opposite sides of the membrane flow cocurrently or countercurrently to one another [7.8]. Therefore, in the present study, the process design calculations assume such a pattern. An effective thickness of 3.93 x 10^{-3} mil (1000 Å) was assumed for the asymmetric membranes.

The permeability values used in the membrane process design are listed in Table IV. The data for cellulose acetate were obtained from Donohue, Minhas, and Lee [9] and from Sada et al. [10].

Process Configurations

Previous studies [11,12] have shown that, from the many membrane process configurations that can be devised for the removal of acid gases from natural gas, three configurations are of special interest. Figures 7-9 show these three process configurations.

Config. 1 (Figure 7) is a single-stage permeator without product recycle. This configuration is simple, requires the least membrane area for a given separation, and has no power requirements since crude natural gas is available at elevated pressures. However, the CH_4 losses in the permeate are high for this configuration. Such a configuration may prove useful in special applications because of the low capital investment and the simplicity in operation.

Config. 2 (Figure 8) consists of two stages in a "cascade" arrangement, namely, the permeate from the first stage is used as feed to the second stage and a fraction of the retentate product from the second stage is recycled to the feed of the first stage. The CH_4 losses are thus greatly reduced, albeit at the cost of increased power and membrane area requirements.

Config. 3 (Figure 9) can be considered as a hybrid of Configs. 1 and 2. The advantageous features of Config. 1 (low membrane area requirement and no power requirement) and of Config. 2 (low CH₄ losses) can be effectively combined so as to reduce the cost of CO₂ removal from natural gas. Config. 3 consists of a "premembrane" stage, i.e., the single stage of Config. 1, connected to a twostage permeation "cascade" as in Config. 2. The retentate product stream from the premembrane stage is used as feed to the first stage of the cascade.

The process variables for each configuration and at each feed composition were selected so as to yield the lowest separation costs. The details of this optimization procedure have been reported previously [13].

Economic Evaluation: Procedures and Parameters

The procedure and economic parameters used in estimating the gas processing cost are given in Table V. It can be seen that the only capital investment involved in single-stage membrane separation processes is for the membrane modules. Multistage membrane processes also require an interstage compressor. The gas processing costs consists of the capitalrelated costs (calculated as 20% of the total plant investment), the variable operating and maintenance costs, and the CH₄ losses in the permeate stream. The components of each of these costs are listed in Table V. It should be noted that the capital-related costs consists of a 12% return on investment and an 8% depreciation of capital equipment. The gas processing costs are usually expressed in terms of per 1000 standard ft³ of feed (MSCF) or per million BTU of feed (MMBTU).

Economic Evaluation: Upgrading of Low-Quality Natural Gas

The results of the process design and economic evaluations for Config. 3 are presented in Figures 10-13. The gas separation costs for membrane processes utilizing D-2, G-1, and A-3 polyimides and cellulose acetate are presented in Table \vee I. The results can be summarized as follows:

1) Membrane processes utilizing the G-1 polymer have the lowest membrane area requirement, followed in order by polyimide A-3, cellulose acetate, and polyimide D-2.

2) Membrane processes utilizing the D-2 polyimide have the lowest power requirement of the four polymers examined.

3) In all membrane processes some CH_4 is lost in the permeate to an extent that depends, for a given set of operating conditions, on the membrane selectivity. For all the process configurations studied, the CH_4 losses for membrane processes incorporating the three new polyimide membranes are lower than those that result from processes utilizing cellulose acetate membranes.

4) Membrane processes utilizing the

A-3 and G-1 polyimides yield the lowest separation cost of the four polymers for all three process configurations examined.

5) For membrane processes utilizing A-3 and G-1 polyimides or cellulose acetate as membrane materials, the lowest separation cost is obtained for a three-stage process configuration consisting of a "premembrane" stage whose retentate product serves as feed to a two-stage "cascade" with product recycle (see Figure 9). This configuration minimizes the CH_4 losses in the permeate.

However, for membrane processes utilizing D-2 polyimide membranes, the lowest separation costs are obtained with a single-stage process configuration without recycle (see Figure 7). This is due to the fact that CH_4 losses are much smaller in this case because of the high CO_2/CH_4 selectivity of the D-2 polyimide.

6) Membrane processes that utilize any of the three polyimides (D-2, A-3, and G-1) are more economical than processes that utilize cellulose acetate for the removal of CO_2 from CH_4/CO_2 mixtures containing 10 to 40 mole-% of CO_2 . The savings in the gas processing cost range from 40-50% for the G-1 and A-3 polymers and 6-12% for the D-2 polymer.

7) In cases where the natural gas also contains more than 1,000 ppm of H_2S in addition to CO₂, the cost of upgrading the gas to pipeline quality (≤ 2 mole-% CO₂; ≤ 4 ppm H_2S) was controlled by the cost of H_2S removal.

VI. FUTURE WORK

The following tasks are planned for the third year of the project:

- Asymmetric and composite membranes,

currently being developed in this laboratory from the most promising polyimides, will be evaluated for potential use as membrane materials in the upgrading of low-quality natural gas.

- The evaluation of new, highly gasselective polyimides in the form of "dense" (homogeneous) membranes will continue.
- The permeability and selectivity measurements will be expanded to include measurements at upstream pressures up to 800 psia and with mixtures containing H_2O vapor.
- Process design and economic evaluations of membrane processes for the removal of CO_2 and H_2S from natural gas will continue as new data become available.

VII. REFERENCES

- 1. U. S. Department of Energy, Gas Research Program Implementation Plan, April 1990, DOE/FE-0187P.
- 2. S. A. Stern, New Developments in Membrane Processes for Gas Separations, Synthetic Membranes, M. B. Chenoweth, Ed., MMI Press, Vol.5, Harwood Academic Publishers, New York (1986).
- 3. W. J. Koros and R. T. Chern, Separation of Gas Mixtures Using Polymer Membranes, in Handbook of Separation Process Technology, R. W. Rousseau, Ed., Wiley-Interscience, New York (1987).
- 4. S. A. Stern and W. P. Walawender, Jr., Analysis of Membrane Separation

Parameters, Separation Science, Vol.4, no.2, 129-159 (1969).

- S. A. Stern, B. Krishnakumar, and A. Y. Houde, Upgrading Natural Gas Via Membrane Separation Processes, DE-FG21-91MC28072, Seventh Quarterly Project Status Report to Morgantown Energy Technology Center, U. S. Dept. of Energy, July 1993.
- S. A. Stern, B. Krishnakumar, and A. Y. Houde, Upgrading Natural Gas Via Membrane Separation Processes, DE-FG21-91MC28072, Eighth Quarterly Project Status Report to Morgantown Energy Technology Center, U. S. Dept. of Energy, October 1993.
- 7. C.-Y. Pan, Gas Separation by Permeators with High Flux Asymmetric Membranes, AIChE J., Vol. 29, 545-552 (1983).
- 8. A. Sengupta and K. K. Sircar, Membrane Gas Separation, in Progress in Filtration and Separation, Vol. 4, R. J. Wakeman, Ed., Elsevier, Amsterdam (1986).
- M. D. Donohue, B. S. Minhas, S. Y. Lee, Permeation Behavior of Carbon Dioxide-Methane Mixtures in Cellulose Acetate Membranes, J. Membrane Sci., Vol. 42, 197-214 (1989).
- E. Sada, H. Kumazawa, P. Xu, and S.-T. Wang, Permeation of Pure Carbon Dioxide and Methane and Binary Mixtures through Cellulose Acetate Membranes, J. Polym. Sci.: Part B: Polym. Phys., Vol. 28, 113-125 (1990).

- B. D. Bhide and S. A. Stern, Membrane Processes for the Removal of Acid Gases from Natural Gas. I. Process Configurations and Optimization of Operating Conditions, J. Membrane Science, Vol. 81, 209-237 (1993).
- B. D. Bhide and S. A. Stern, Membrane Processes for the Removal of Acid Gases from Natural Gas. II. Effects of Operating Conditions, Economic Parameters, and Membrane Properties, J. Membrane Science, Vol. 81, 239-252 (1993).
- S. A. Stern, B. Krishnakumar, and A. Y. Houde, Upgrading Natural Gas Via Membrane Separation Processes, DE-FG21-91MC28072, Sixth Quarterly Project Status Report to Morgantown Energy Technology Center, U. S. Dept. of Energy, April 1993.

Table I

| Composition | Pern | neability, P x | Selectivity, α^d | | | |
|-----------------------------|-----------------|-----------------|-------------------------------------|-------------------------------------|------|--|
| (mole-%) | CO ₂ | CH ₄ | (CO ₂ /CH ₄) | (H ₂ S/CH ₄) | | |
| (87.5/9.7/2.8) ^b | 6.37 | 0.0676 | 1.100 | 94.2 | 16.3 | |
| (90/10) | 7.25 | 0.0857 | | 84.6 | | |
| (65.3/27.4/7.3) | 3.82 | 0.0454 | 0.692 | 84.1 | 15.2 | |
| (70/30) | 5.66 | 0.0892 | | 63.5 | | |
| (55.3/36.7/8) | 4.15 | 0.0520 | 0.776 | 79.8 | 14.9 | |
| (60/40) | ó.12 | 0.1030 | | 59.4 | | |

Permeability and Selectivity of D-2 Polyimide for CH₄/CO₂/H₂S and CO₂/CH₄ Mixtures^a

^a Measurements made at 95.0°F (35.0° C) and at a feed pressure of 147.0 psia (10 atm)

^b Measurements made at 95.0°F (35.0° C) and at a feed pressure of 152.0 psia (10.3 atm)

^c Permeability coefficient in units of [cm³(STP).cm/s.cm².cmHg]

^d The selectivity or ideal separation factor, $\alpha^{*}(A/B)$, of a polymer toward a gas A relative to another gas B is given by the relation $\alpha^{*}(A/B) = \overline{P}(A)/\overline{P}(B)$.

Table II

| Comparison | of | New | Polymers ^a |
|------------|----|-----|------------------------------|
|------------|----|-----|------------------------------|

| Polymer | Permeabili | Selectivity ^c , | |
|-------------------|-----------------|----------------------------|----------------------------------|
| roiyiller | CO ₂ | CH₄ | CO ₂ /CH ₄ |
| D-2 Polyimide | 7.25 | 0.086 | 84.6 |
| H-1 Polyimide | 2.50 | 0.032 | 78.3 |
| C-1 Polyimide | 9.29 | 0.152 | 61.1 |
| A-3 Polyimide | 22.4 | 0.385 | 58.4 |
| F-1 Polyimide | 1.96 | 0.037 | 52.8 |
| G-1 Polyimide | 29.2 | 0.643 | 45.4 |
| E-1 Polyimide | 1.65 | 0.042 | 39.0 |
| Cellulose Acetate | 3.01 | 0.086 | 35.0 |

^a Measurements made at 95.0°F (35.0° C) and at a feed pressure of 147.0 psia (10 atm)

^b Permeability coefficient in units of [cm³(STP).cm/s.cm².cmHg]

^c The selectivity or ideal separation factor, $\alpha'(A/B)$, of a polymer toward a gas A relative to another gas B is given by the relation $\alpha'(A/B) = P(A)/P(B)$.

Table III

Base-case Operating Conditions

| Feed gas flow rate: 35 MMSCFD (million standard ft ³ /day) |
|---|
| Feed composition: 69 mole-% CH_4 , 1,000 to 10,000 ppm of H_2S , balance: CO_2 |
| Retentate composition: ≤ 2 mole-% CO ₂ , ≤ 4 ppm by vol. of H ₂ S |
| Effective membrane thickness: 3.93 x 10 ⁻³ mil (1000 Å) |
| Feed pressure: 800 psia |
| Permeate pressure: 20 psia |
| |

Table IV

| Membrane | D-2 Polyimide | | G-1 Poly | pyrrolone | A-3 Pc | olyimide | Cellulose Acetate | | |
|-----------------------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|--|
| Mole-% CO ₂ in Feed | ₽(CH ₄) | P(CO ₂) | Р(CH ₄) | ₱(CO ₂) | ₽(CH ₄) | P(CO ₂) | ₽(CH ₄) | P(CO ₂) | |
| 10 | 0.1008 | 7.45 | 0.8056 | 29.08 | 0.5617 | 24.54 | 0.355 | 7.46 | |
| 20 | 0.1124 | 6.47 | 0.8069 | 28.01 | 0.5715 | 22.32 | 0.365 | 7.68 | |
| 30 | 0.1210 | 6.28 | 0.8612 | 27.94 | 0.5895 | 22.26 | 0.375 | 7.89 | |
| 40 | 0.1380 | 6.38 | 0.9364 | 27.02 | 0.6682 | 24.77 | 0.386 | 8.11 | |

Permeability Values Used in Economic Evaluation^a

^a Permeability coefficient, $\overline{P} \ge 10^{10}$, in units of [cm³(STP).cm/s.cm².cmHg]

Table V

Economic Parameters and Assumptions

Total Plant Investment (TPI):

Membrane module cost (MC): $30/ft^2$ (includes cost of membrane element) Installed compressor cost (CC): $32,500 (HP/10)^{1/2}$ Fixed cost (FC) = MC + CC Base plant cost (BPC) = 1.12 x FC (Includes Home Office Cost = 0.12 x FC) Project contingency (PC) = 0.20 x BPC Total facilities investment (TFI) = BPC + PC Start-up cost (SC) = 0.10 x VOM (see below for explanation of VOM) Total Plant Investment (TPI) = TFI + SC

Annual Variable Operating & Maintenance Cost (VOM):

Contract & material maintenance cost (CMT) = 0.05 x TFI Local taxes & insurance (LTI) = 0.015 x TFI Direct labor cost (DL): 8 hr./day per 25 MMSCFD of feed (hourly wage: \$ 14) Labor overhead cost (LOC) = 1.15 x DL Membrane replacement cost (MRC): \$13.3/ft² Utility cost (UC): \$0.05 /kWHr Variable Operating & Maintenance Cost (VOM) = CMT + LTI + DL + LOC + MRC + UC

Gas Processing Cost (GPC):

Annual capital related cost (CRC) = 0.2 x TPI (5-year payout period)
Annual methane losses (CH4LS): \$1.5/MMBTU
Annual variable operating & maintenance cost (VOM) (see above)
Gas processing cost = CRC + CH4LS + VOM (/MSCF of feed or /MMBTU of feed)

Other Assumptions:

Membrane life: 3 years On-stream factor: 96% Compressor efficiency: 75%

| Table | VI |
|-------|----|
|-------|----|

| Comparison | of | Processing | Costs |
|------------|----|------------|-------|
|------------|----|------------|-------|

| CO ₂ in Feed | Processing Costs, (\$/ MSCF) | | | | | | |
|-------------------------|------------------------------|-------|-------|-------|--|--|--|
| (Mole-%) D-2 | G- 1 | A-3 | CA | | | | |
| 10 | 0.195 | 0.106 | 0.105 | 0.221 | | | |
| 20 | 0.267 | 0.147 | 0.157 | 0.299 | | | |
| 30 | 0.287 | 0.158 | 0.168 | 0.313 | | | |
| 40 | 0.284 | 0.168 | 0.158 | 0.304 | | | |

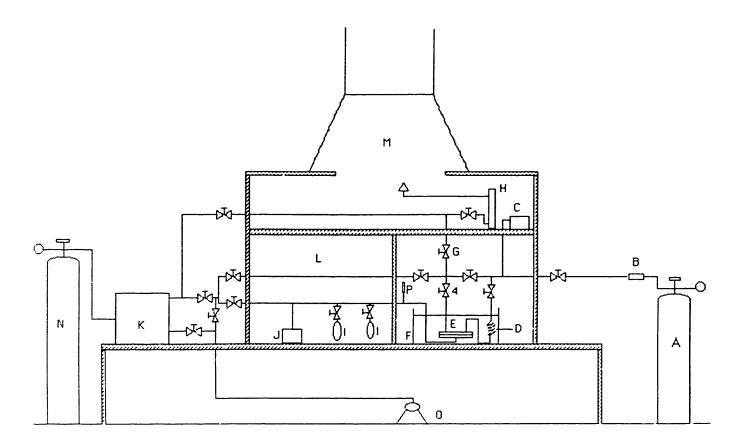


Figure 1. Laboratory-scale apparatus for studying permeation of gas mixtures through polymer membranes.

Key: A: feed gas cylinder, B: filter, C: digital high pressure gauge, D: heat exchanger, E: permeability cell, F: constant temperature bath, G: metering valve, H: digital bubble flow meter, I: receiving reservoirs, J: low pressure transducer, K: gas chromatograph, L: constant temperature air cabinet, M: fume hood, N: GC carrier gas cylinder, O: vacuum pump, P: relief valve.

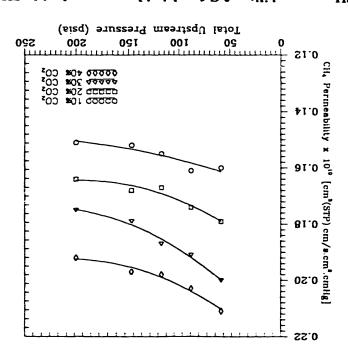


Figure 2. CH4 permeability of C-1 polyimide measured with CH4/CO2 mixtures of various compositions, plotted as a function of total upstream pressure. Measurements made at 95% (35° C).

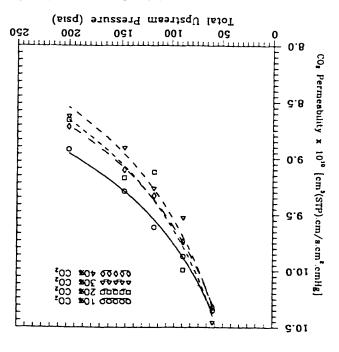


Figure 3. CO_2 permeability of C-1 polyimide measured with CH₄/CO₂ mixtures of various compositions, plotted as a function of total upstream pressure. Measurements made at 95% (35°C).

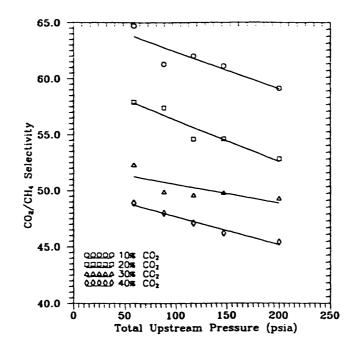


Figure 4. CO_2/CH_4 selectivity of C-1 polyimide measured with CH_4/CO_2 mixtures of various compositions, plotted as a function of total upstream pressure. Measurements made at 95°F (35°C).

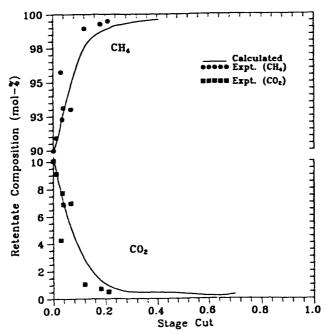


Figure 5. Retentate composition obtained in measurements with a D-2 polyimide membrane and a CH_4/CO_2 mixture containing 10 mole-% of CO_2 plotted as a function of stage cut. Measurements made at 95°F (35°C), at an upstream pressure of 147 psia (10 atm), and at a downstrem pressure of ≈ 0.39 psia (20 mmHg). Solid lines show results of simulations assuming "perfect-mixing" in permeation cell.

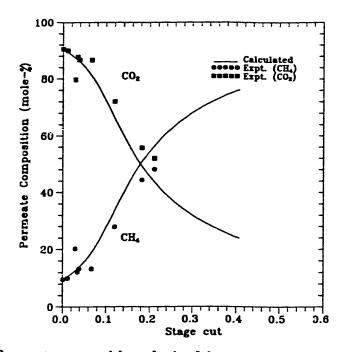


Figure 6. Permeate composition obtained in measurements with a D-2 polyimide membrane and a CH_4/CO_2 mixture containing 10 mole-% of CO_2 plotted as a function of stage cut. Measurements made at 95°F (35°C), at an upstream pressure of 147 psia (10 atm), and at a downstrem pressure of ≈ 0.39 psia (20 mmHg). Solid lines show results of simulations assuming "perfect-mixing" in permeation cell.

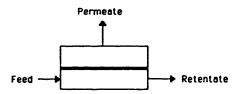


Figure 7. Config. 1: Single-stage permeator without product recycle.

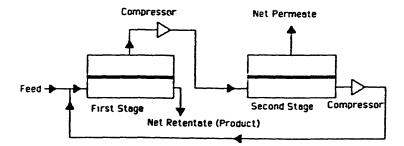


Figure 8. Config. 2: Two permeators in a cascade scheme with retentate recycle from second stage.

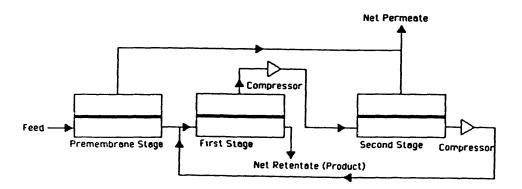


Figure 9. Config. 3: Three-stage process configuration with "premembrane" stage in series with a two-stage cascade arrangemet.

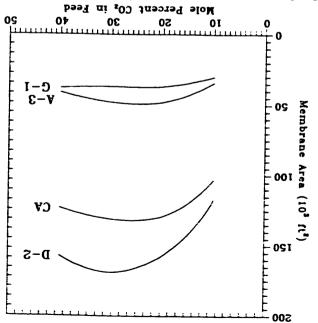


Figure 10. Membrane area requirement for processes using the $D-\Delta$, A-3, and G-1 polyimides, and celulose acetate membranes, plotted as a function of CO₂ content in the feed. Calculations assume a three-stage process (Config.3). Opertaing conditions and assumptions are listed in Tables III-V.

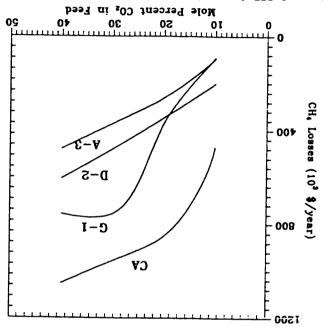


Figure 11. Annual CH₄ losses for processes using the D-2, A-3, and G-1 polyimides, and cellulose acetate membranes, plotted as a function of CO_2 content in the feed. Calculations assume a three-stage process (Config.3). Opertaing conditions and assumptions are listed in Tables III-V.

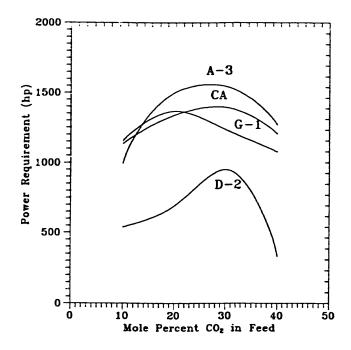


Figure 12. Inter-stage compressor power requirement for processes using the D-2, A-3, and G-1 polyimides, and celulose acetate membranes, plotted as a function of CO_2 content in the feed. Calculations assumed a three-stage process (Config.3). Opertaing conditions and assumptions are listed in Tables III-V.

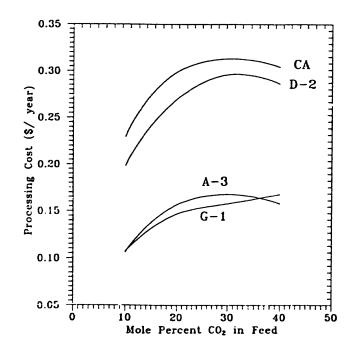


Figure 13. Overall separation cost for processes using the D-2, A-3, and G-1 polyimides, and celulose acetate membranes, plotted as a function of CO_2 content in the feed. Calculations assumed a three-stage process (Config.3). Opertaing conditions and assumptions are listed in Tables III-V.

NG-8.3 Low-Quality Natural Gas Sulfur Removal/Recovery With Membranes

by

K. A. Lokhandwala, K. A. Amo, R. W. Baker, I. Pinnau, L. Toy and J. G. Wijmans Membrane Technology and Research, Inc. 1360, Willow Road, Suite 103 Menlo Park, CA 94025

CONTRACT INFORMATION

.

| Contract Number | DE-AC21-92MC28133 |
|-----------------------------|--|
| Contractor | Membrane Technology and Research, Inc. 1360, Willow Road, Suite 103 Menlo Park, CA 94025 (415)-328-2228 |
| Contractor Project Managers | Hans Wijmans/Kaaeid A. Lokhandwala |
| Principal Investigator | Richard W. Baker |
| METC Project Manager | Harold Shoemaker |
| Period of Performance | September 29, 1992 - April 28, 1995 |
| Schedule and Milestones | FY93 Program Schedule |

| | S | 0 | N | D | J | F | М | Α | М | J | J | Α | S |
|--------------------------------|----------------|---|---|---|---|---|---|---|---|---|---|---|---|
| Prepare Membranes/Modules | | | | | | | | | | | | | |
| Construct Test Systems | | | | | | | | | | | | | |
| Stamp Gas Mixture Tests | | | | | | | | | | | | | |
| Modify Membranes | | | | | | • | | | | | | | |
| Module Gas Mixture Tests | | | | | | | | | 1 | | | | |
| Initial Survey of Applications | | | | | | | | | | _ | | | |
| Select Optimum Applications | | | | | | | | | | | | | |
| Program Management/Reports | (111) | | | | | | | | | | | | |

| Feed gas composition (vol%) | | | | | |
|-----------------------------|-------|-------|--|--|--|
| H ₂ S | CO2 | CH4 | | | |
| 0.000 | 4.00 | 96.00 | | | |
| 0.097 | 0.00 | 99.90 | | | |
| 0.081 | 3.92 | 95.99 | | | |
| 0.986 | 4.12 | 94.90 | | | |
| 1.830 | 10.80 | 87.34 | | | |
| 0.095 | 8.14 | 91.77 | | | |

| Table 1. Feed Gas Compositions Used in Parametric Testing | Table 1. | Feed Gas | Compositions | Used in | Parametric | Testing. |
|---|----------|----------|--------------|---------|------------|----------|
|---|----------|----------|--------------|---------|------------|----------|

RESULTS

The following gas mixtures were used to test the membranes to understand the effect of varying the feed composition on membrane selectivity.

Experiments were performed at 400, 600 and 970 psig feed pressure, using membrane stamps with exposed area of about 36 cm². All experiments were performed at very low (< 1%) stage cut. The following important observations could be made from the experimental data obtained.

1. In general, the pressure-normalized fluxes of hydrogen sulfide and carbon dioxide decrease with increasing feed pressure, whereas those of methane increase. The decrease in the hydrogen sulfide and carbon dioxide fluxes can be explained by competitive sorption of these components in the polymer. As the feed pressure increases, both hydrogen sulfide and carbon dioxide molecules compete for the fixed number of sorption sites in the polymer. This results in a lower solubility coefficient (the ratio of the concentration in the polymer to the partial pressure) for each component. At the same time, the polymer swells, resulting in a higher diffusivity for all components, including methane. The net result is an increase in the methane flux and a decrease in the fluxes of the acid gases (hydrogen sulfide and carbon dioxide).

2. Typically, for all ternary mixtures, the hydrogen sulfide/methane selectivity is between 70 and 50 for MTR 701 and between 60 and 40 for MTR 704 in the pressure range from 400 to 1000 psig. In the same pressure range, the carbon dioxide/methane selectivity is between 16 and 14. The hydrogen sulfide/methane selectivity of the MTR 701 polymer is about three times higher then that of cellulose acetate, which is presently being used for acid gas separation. However, the carbon dioxide/methane selectivity is somewhat lower then that of cellulose acetate.

Figures 1a and 1b shows the effect of the combined partial pressures of the acid gases in the feed mixture on the pressure-normalized

OBJECTIVES

The main objective of this program is to develop a membrane process for the separation of hydrogen sulfide and other impurities (carbon dioxide and water vapor) from low-quality natural gas. The overall program involves development and parametric testing of appropriate membrane materials in the form of thin-film composite membranes. These membranes will then be made on a larger scale and incorporated into modules which will be tested first in the laboratory, and then at different field sites. A technical and economic analysis of the membrane process will then be performed and compared with existing processes.

BACKGROUND INFORMATION

The natural gas production in the lower-48 states is expected to increase significantly in order to meet the rising demand. Natural gas supply is projected to increase by 25% between 1991 and 2010 with 70% of the increased production after 1995 coming from the Lower-48 gas fields⁽¹⁾. Recent studies of U.S. natural gas reserves have shown that an increasing fraction of the gas produced will be from smaller gas fields at remote locations, and will be sub-quality on hydrogen sulfide, carbon dioxide, and nitrogen specifications. More than 13% of current reserves are known to be contaminated with hydrogen sulfide⁽²⁾. When these subquality reserves are brought into production, new treatment facilities will have to be installed, and it is projected that between \$30-40 million will be invested every year⁽³⁾. Alternatives to currently available absorption based technologies are being sought for processing gas streams to pipeline specifications in an environmentally and economically acceptable manner.

Conventional amine processes are energy-intensive and, being complex, they require constant supervision and maintenance. They are especially prone to problems such as corrosion in the reboiler, foaming and solvent losses in the absorption column. Also, spent amines have increasingly to be disposed as hazardous wastes, which increases operating costs significantly. Membrane processes are simple and modular, offer greater operational reliability and lower maintenance costs. Membrane processes require almost no operator supervision, and, therefore, are ideally suited for operation in remote locations. Membrane processes would be very cost-competitive with conventional amine processes, especially for gas streams that contain high amounts of acid gases at low flow rates.

PROJECT DESCRIPTION

In Phase I of the program, an extensive experimental study has been performed to assess the performance of our membranes under various feed conditions. Composite membranes made from four different polymers were investigated to determine their hydrogen sulfide/methane and carbon dioxide/methane selectivity. Two polymers were then selected for a further parametric study. 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 at pressures in the range 400-Also as part of the Phase I 1,000 psig. evaluation, Hoechst Celanese Corporation will perform a complete economic analysis for the removal and recovery of a 1 Ton sulphur/day plant. In Phase II of the program, a bench-scale system will be constructed and long term tests will be performed. Also, this skid-mounted system will then be field-tested at one or more different field sites...

fluxes of all the three components in the feed. The figure shows that the pressure-normalized flux of hydrogen sulfide decreases slightly with increased acid gas partial pressure, whereas that of carbon dioxide is almost constant. The methane flux, on the other hand, increases slightly with an increase in the acid gas partial pressure.

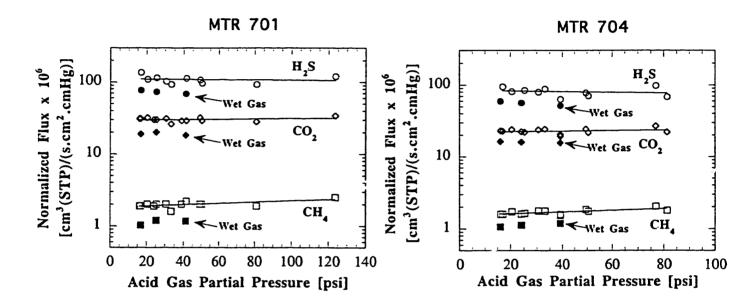


Figure 1. Pressure-normalized permeation flux of each component of the feed mixture as a function of the total acid gas partial pressure. Solid symbols represent data obtained when the feed gas was saturated with water vapor.

Figure 2 shows the effect of the acid gas partial pressure on the membrane selectivity for hydrogen sulfide and carbon dioxide over methane. This figure shows that both the hydrogen sulfide/methane and carbon dioxide/methane selectivities decrease with increasing acid gas partial pressure. At higher partial pressures, the selectivities appear to flatten out; for hydrogen sulfide/methane to about 50, and for carbon dioxide/methane to about 14.

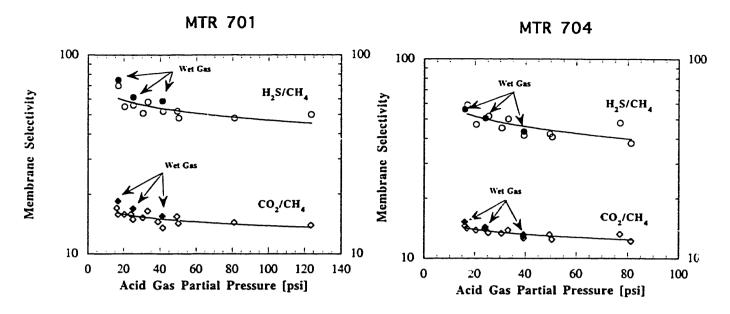


Figure 2. Selectivity for hydrogen sulfide and carbon dioxide over methane as a function of the total acid gas partial pressure in the two membrane investigated. The solid symbols represent data obtained when the feed gas was saturated with water vapor.

Figures 1 and 2 include data points that show the effect of saturating the feed gas with water vapor on the pressure-normalized fluxes and the membrane selectivities. In Figures 1a and 1b, the solid symbols represent the fluxes of each of the components through the membrane obtained with a water-vapor-saturated feed. These fluxes are lower then those obtained in the absence of water vapor. The pressurenormalized hydrogen sulfide and carbon dioxide fluxes were about 25% lower, and the methane fluxes were about 35% lower. Water, which is a strongly hydrogen-bonding molecule, is strongly sorbed by the polymer. The presence of water vapor in the polymer matrix can affect the permeation properties in two ways. Water molecules will displace both hydrogen sulfide and carbon dioxide from active sorption sites in the polymer. Also, by forming inter-chain hydrogen bonds, water vapor can restrict chain motion to some extent, and thereby decrease the diffusivity of other components. Both or any one of these effects would result in lower

permeation fluxes for hydrogen sulfide, carbon dioxide, and methane in the membrane. However, this flux decrease is completely reversible, and upon changing to a dry gas, the original fluxes were obtained again.

The solid symbols in Figure 2 show the effect of the presence of water vapor in the feed on the membrane selectivity. Neither the hydrogen sulfide/methane nor the carbon dioxide/methane selectivities change significantly. In comparison, a water saturated feed can irreversibly decrease the permeation flux of hydrogen sulfide and carbon dioxide in commercially available cellulose acetate membrane due to compaction resulting in a significantly loss of separation performance.

The effect of feed temperature on the pressure-normalized permeation flux of each of the three components in the feed gas, and on the membrane selectivity was also investigated. With increasing temperature, the permeation flux of each of the three components increases, indicating a endothermic permeation process. The highest increase in the permeation flux was for methane. This results in a lower membrane selectivity for hydrogen sulfide and carbon dioxide over methane at higher temperatures. The H_2S/CH_4 selectivity at a feed pressure of about 400 psig decreases from about 70 at 22°C to about 52 at 40°C.

In synopsis, the parametric study showed that the membranes exhibit a hydrogen sulfide/methane selectivity in the range 40-70 and 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 our membranes is comparable or higher than that of commercially available cellulose acetate membranes, whereas the hydrogen sulfide/methane selectivity of our membranes is two to three times higher.

We have been able to classify the opportunities for membrane processes in this area into two categories. The first opportunity exists in new gas fields or new acid treatment plants. The other opportunity is in debottlenecking existing amine treatment facilities, in order to either increase their gas treatment capacity, or in adjusting the feed composition in order to achieve pipeline specifications. In each of these two applications, it will be necessary to obtain a hydrogen sulfide enriched stream in an appropriate concentration range to be treated by either a Redox process, or by a Claus process for permanent fixation of sulfur. We are presently investigating the following membrane process configurations in order to achieve this objective.

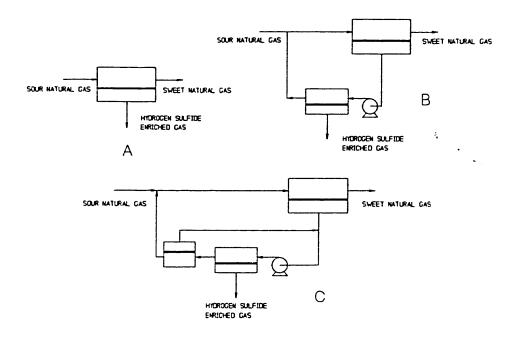


Figure 3. Membrane process configurations being studied for hydrogen sulfide separation from natural gas.

FUTURE WORK

We are presently scaling up the production of these membranes on our commercial coating machine. After optimizing the scale-up, we will incorporate membranes in spiral-wound modules. These modules will be tested by MTR using a high-pressure module test system, which has been designed for complete recycle operation. If the test results are acceptable, the modules will be tested for longer periods of time in a bench test. Hoechst Celanese Corporation will build and operate the skid-mounted field test system.

In further work, optimized designs for three of the most promising membrane applications will be developed. The technical and economic aspects of the processes will be compared to existing alternatives. After selecting the best application from the above, a complete conceptual design, including sulfur recovery and any other treatment to be combined with the membrane separation process will be prepared.

In Phase II of the program, MTR and Hoechst Celanese Corporation will build a bench-scale unit to further test the membrane modules for extended periods of time. The bench-scale unit will be skid-mounted such that it can be later transported to one or more fieldsites were additional tests will be conducted on real-life natural gas streams. Upon conclusion of the field tests, a revised technical and economic analysis will be performed for the membrane process.

REFERENCES

- "The Clean Fuels Report", J. E. Sinor Consultants, Inc., Nivot, Colorado 80544, 5(3), June 1993
- "Chemical Composition of Discovered and Undiscovered Natural Gas in the U.S. Lower-48 - Executive Summary", R. H. Hugman, E. H. Vidas, and P.S. Springer, Energy and Environmental Analysis, Inc., prepared for The Gas Research Institute, Chicago, II. March (1993).
- 3.
- "Gas Research Institute Program in Natural Gas Processing", D. Leppin and H. S. Meyer, Presented at SPE Gas Technology Symposium, Houston, Texas, January 23-25, 1991.