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TECHNOLOGY DEVELOPMENTS IN NATURAL GAS EXPLORATION, PRODUCTION AND PROCESSING

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Commentary

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Gas Storage Continues to Grow, Technology Still Needed

efficient and n dependable underground natural gas storage system is a critical part of our national energy infrastructure. The nearly 400 underground natural gas storage facilities throughout the United States provide a for the disparity way between cyclical demand and year-round production to be managed in an economically and operationally efficient manner. That efficiency will be tested in the years to come as natural gas demand is expected to grow from 22 Tcf/d today to 27 Tcf by 2030, according to

Energy Information Administration's Annual Energy Outlook 2006. This demand growth will be met largely by increased production of gas from unconventional sources and liquefied natural gas (LNG) imports and will place new burdens on the nation's pipeline and storage systems.

The total level of U.S underground natural gas storage working gas capacity and daily deliverability reached record levels of 4.01 Tcf/d and 83.7 Bcf/d, respectively, in 2005. Potential for increases in these benchmarks is represented by a substantial number of newsite storage projects with proposed in-service dates between 2006 and 2008. The inventory of pending 2006-2008 underground storage projects stood at 38 as of July (15 new facilities and 23 expansions), according to the



EIA's October report U.S. Underground Natural Gas Storage Developments: 1998-2005. If fully implemented, these additions would represent an 11% increase in daily deliverability and a 5% increase in working gas capacity by the end of 2008.

Eleven of the 15 proposed new natural gas storage facilities are salt-cavern sites. Saltcavern storage can be cycled multiple times within a season, and its high deliverability allows for quick reaction to daily (or even hourly) variations in customer needs. These features make salt cavern storage attractive to storage developers, whose profitability depends upon their ability to maximize turnover volumes. The process of developing a major new underground storage project may take 3 to 5 years from the time it is initially proposed until it is completed. Significant environmental considerations or public opposition can often extend this time period.

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These two factors, the need to develop storage capacity at the lowest possible cost and with the least possible environmental impact, support the call for continued research and development (R&D) to develop new technologies related to natural gas storage. Other factors are: increasing flexibility of storage services to meet market demands; maintaining and improving system reliability and safety, such as examining the effects of pro-

jected increases of higher-Btu LNG on storage operations; reducing operating costs; and responding to increased regulatory pressures, including making certain that new regulations are based on sound science.

This issue of *GasTIPS* includes two articles on the topic of gas storage. One outlines recent efforts to prepare a "roadmap" for gas storage technology R&D while the other provides an update on a project to employ natural wetlands as a tool for treating water produced during gas storage operations. We hope you find these articles and this issue of *GasTIPS* informative.

The Editors

C

The Rock Physics Connection

An understanding of rock properties is critical when integrating CSEM data and seismic data.

n increasing number of oil companies are recognizing the strength of controlled-source electromagnetic (CSEM) data for mapping fluid content. CSEM acquisition produces data that are sensitive to resistive regions in the earth. The overall conductivity of a porous rock is largely controlled by its fluid content. Since brines are conductive whereas hydrocarbons are not, the CSEM method offers a chance of distinguishing between brine-filled and hydrocarbon-bearing rocks.

However, this is not the full story. Massive limestones, salts and volcanics may also show low conductivities. Even in porous sandstones, the presence of clay minerals in the pore space may change the overall conductivity significantly. The conclusion is that rock conductivity is influenced by porosity, fluid type and to some extent mineralogy.

There are various rock physics models predicting conductivity from these properties. For example, Archie's equation relates conductivity to porosity, brine saturation and brine conductivity for clean sands. Modifications such as the Waxman-Smits formula account for the presence of clay minerals.

Similar remarks can be made for seismic data. They have been used successfully for many years to map structure. Amplitude variation with offset (AVO) and acoustic and elastic impedance inversion (AI and EI) are used to obtain seismic rock properties such as elastic moduli and possibly density. These in turn may be related to mineralogy, porosity and fluid properties through numerous rock physics relationships, for example those summarized in "The Rock Physics Handbook" by Gary Mavko and his colleagues. While AVO or AI/EI offers the possibility of fluid prediction, the potential ambiguity and risk of misleading results such as confusing fluid changes with lithology changes is generally higher than that from the CSEM data.

The seismic and CSEM data are controlled by different physics and are sensitive to slightly different aspects of the rock properties. We would like to combine them in a manner that exploits their respective strengths while ameliorating their weaknesses. The key to successful combination is using the rock physics consistently.

Rock physics modeling allows us to investigate the information carried by the different surface measurements. Figure 1 shows an example from the Nuggets prospect in the North Sea. We have used standard methods to calculate seismic rock properties, in this case acoustic impedance and elastic impedance (at 30° incidence angle) as they vary with gas saturation and porosity. For this reservoir, we see the AI responds mainly to porosity and only weakly to gas saturation. In the areas of good reservoir (higher gas saturation and moderate to good porosity), the EI is represented by a flat surface, indicating it contains little information about either reservoir property. On the other hand, the resistivity is controlled almost entirely by the gas saturation. In this particular case, then, we can combine the AI and CSEM data to obtain porosity and saturation estimates and omit the EI since it is not adding much useful information. This conclusion is reservoir-dependent, and in other cases we may find different combinations more useful.

As mentioned, Archie's equation is often used to predict resistivity from reservoir properties. It is important to bear in mind that it only holds for clean sands. The electrical properties of clay minerals are notoriously complicated, and their presence in pore



ROCK PHYSICS <

By Peter Harris, Rock Solid Images; and Lucy MacGregor, Offshore Hydrocarbon Mapping

Figure 1. Top: Acoustic impedance is plotted for a range of porosities (horizontal axis) and gas saturations (vertical axis). The contours of the Al are more or less vertical in the region of good reservoir (upper right of the plot), showing that Al in this well is mostly sensitive to porosity and not at all to gas saturation. Middle: Elastic impedance for the same range of porosity and saturation. The surface is rather flat, showing that El carries little information about either porosity or saturation.

Bottom: Resistivity for the same models. The contours here are almost horizontal, showing that resistivity is sensitive to saturation but not porosity. (All figures courtesy of Rock Solid Images)



space may change the effective rock conductivity significantly (Figure 2). We first compare the resistivity predicted from Archie's equation with the logged resistivity values. It is clear that the prediction is rather poor, and there is a wide scatter of points and no linear relationship between actual and predicted values, even for the clean sands. The same comparison using the Waxman-Smits model, which accounts for clay minerals in the pore space, shows a more linear trend, albeit with some scatter and some anomalous regions in the crossplot. Overall, though, accounting for the clay content improves the prediction significantly.

Ultimately the predicted electrical and elastic properties are used to generate synthetic data for comparison with the recorded CSEM and seismic data. For this purpose, it is essential to build a good-quality model from the target zone all the way back to the earth's surface. CSEM propagation is essentially a diffusive process, and thus the entire region above the target influences the recorded response. In the seismic case, the key point is to use the correct velocity trend in the overburden to model the relationship between offset and incidence angle accurately; otherwise AVO modeling may be misleading.

In the Nuggets study, the main interest is to estimate gas saturation in the reservoir. In the well, the gas sand stands out clearly as a high-resistivity, low-density layer about 80ft thick. This is seismically resolvable, and we have already seen from the modeling that the combination of resistivity and AI offers a good possibility of obtaining the desired information. A constrained inversion is applied to the CSEM data to produce an image of resistivity with depth, just as the seismic data are inverted to AI. For both types of



Figure 2. The left image shows the resistivity measured in the well against the value predicted using Archie's equation. The color coding shows the shale fraction. There is a large scatter of points, and most are located in the lower left of the point cloud, suggesting that the prediction is not very accurate. This is not surprising, since Archie's equation is intended for use in clean sands (the blue points). In the image on the right, the prediction uses the Waxman-Smits model. This accounts for the presence of clay minerals in the pore space, thus improving the quality of the prediction.

data, we must perform a well tie to ensure correct depth calibration. Well tie for CSEM data involves finding consistency between the resistivity logs and the inverted CSEM data. Just as with seismic data, the different vertical resolution of the two measurements must be reconciled by suitable scaling processes.

Despite these complications, a complete set of well logs coupled with careful rock physics analysis contains enough information to achieve our aim, at least in a semiquantitative sense. Calibration at the well allows us to combine the surface data and produce a gas saturation attribute (Figure 3). This is semi-quantitative: blue values represent high gas saturations and reds represent low values. The scatter of red points away from the reservoir formation is an indication of the uncertainty in the calibration process. It is clear that the CSEM data have good lateral resolution, marking the edges of the gas-bearing zones quite precisely. Vertical

resolution is controlled largely by the seismic resolution.

The Nuggets study demonstrates that careful rock physics analysis permits combination of surface seismic and CSEM data to provide useful reservoir information. The final result could not be obtained with either type of surface data alone. This is a promising start to the process of CSEM, seismic and well data integration, and OHM and RSI are working to further refine and broaden the applications of combined CSEM, surface seismic and well log data. ◆



Figure 3. Semi-quantitative estimate of gas saturation superimposed on the seismic wiggle traces. Blue colors represent high gas saturation and reds are low saturation. The uncolored regions are outside the bounds considered anomalous for resistivity or impedance.



Deep Gas Exploration using P- and S-Wave Seismic Attenuation

By Joel Walls, M. T. Taner, Richard Uden, Scott Singleton and Naum Derzhi, *Rock Solid Images*; and Gary Mavko and Dr. Jack Dvorkin, *Petrophysical Consulting Inc.*

Deeply buried gas reservoirs along the Gulf of Mexico shelf are an important future energy resource for the United States.

ne of the greatest problems operators encounter in the Gulf of Mexico is identifying commercially viable targets for drilling. This is largely because most common 3-D seismic methods for direct hydrocarbon indication, such as amplitude vs. offset (AVO) are not reliable at great depths. Many wells have been drilled on deep AVO anomalies, only to find noncommercial quantities of gas (the so called "fizz-water" problem). Other problems in detecting deep gas sweet spots result from inadequate offset in the seismic data acquisition and high fluid pressures, which tend to make gas look more like water in a seismic data volume.

In 2004, Rock Solid Images undertook a U.S. Department of Energy (DOE)-funded project to demonstrate novel and robust techniques for reducing hydrocarbon indicator risk in deep gas sands by exploiting an additional set of completely independent indicators – the rock inelastic properties.

Inelastic rock properties are often expressed as a "quality factor" or simply "Q." These inelastic properties of P-wave and S-wave energy (Qp and Qs) from multicomponent seismic provide a crucial added dimension that can be used to discriminate pore fluids and lithology.

The objective of this project was to develop and test a new methodology for computing P- wave and S-wave attenuation from standard well log data, using the well log-derived attenuation for generating P-wave synthetic seismic traces with and without attenuation effects, and then extracting seismic attenuation attributes from multicomponent P-wave and S-wave seismic data and relating these to the presence of oil or natural gas.

These goals were achieved, resulting in a new algorithm to compute Qp and Qs from conventional well log data, an algorithm to create full offset, full waveform synthetics incorporating the effects of attenuation, and two algorithms to compute attenuation from seismic data. The primary findings from this project were that P- and S-wave attenuation in seismic data:

- can be related to gas-bearing reservoirs;
- can be used as a reconnaissance tool in exploration;
- can have a substantial impact on seismic response, both post-stack and prestack, and cause significant changes in

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seismic amplitude with offset, especially at the bottom of a gas zone;

- should be used with other seismic attributes such as elastic attributes and geologic context to reduce risk in the search for direct hydrocarbon indicators; and
- can be a valuable tool in deep targets because AVO may fail in these environments.

The field experiment

Multicomponent ocean-bottom cable (OBC) seismic data were obtained from Seitel Data Inc. (Seitel) located in the Eugene Island area of the Gulf of Mexico. The OBC system deployed four receiver components – three orthogonal geophones plus one hydrophone. Seitel processed this data to PP (P-wave down, P-wave up) and PS (P-wave down, S-wave up) stack volume reflection amplitudes over the total area shown in Figure 1 (left).

Data for this project was acquired over the

southern area (about 12 miles by 6 miles – 20km by 10 km) shown in Figure 1 (right) covering partly or fully Eugene Island blocks **EI306** through **E1310**, **EI313** through **E1317** and **EI328** through **E1332**.

Amplitude and attenuation from the PP data

Interesting results from a qualitative standpoint are seen on



XLINE 2360 between 4,000 and 4,500 ms (Figure 2). Two different fault blocks are evident from the seismic amplitude display and both attributes show attenuation for the events at the top of the blocks. These events maintain their inelastic attribute response laterally away from this XLINE.

Figures 2b and 2c show that the Log Spectral Ratio Q estimation attribute has higher temporal resolution than the Frequency Shift Q estimation attribute but increased noise content. The Frequency Shift Q attribute indicates other event responses above and below the white-circled event that are not seen as well on the Log Spectral Ratio Q attribute response.

This is important since the attributes are responding differently some of the time. The deeper Frequency Shift Q estimation event below the circled event corresponds to strong amplitudes in Figure 2a not evidenced by the Log Spectral Ratio Q estimation response.

Amplitude and attenuation from the PS data

Both inelastic attributes were

generated from the PS stack data volume. The PS amplitude data in Figure 3a shows weaker amplitudes at depth. The PP time range of 4,000 ms to 4,500 ms is closely equivalent to 7,500 to 8,100 ms PS time.

The Frequency Shift Q estimation attribute shows a weak response at the top the white ellipse fault block but no response for the yellow ellipse event. A response is also seen for the syncline event just above the white ellipse event, similar to the response from the PP Frequency Shift Q estimation



Figure 2a. XLINE 2360 PP stack amplitude



Figure 2b. XLINE 2360 PP Frequency Shift Q attribute response



Figure 2c. XLINE 2360 PP Log Spectral Ratio Q attribute response

attribute. The Log Spectral Ratio Q estimation attribute shows no response anywhere in the section displayed, not even in the shallowest events up to 5-second PS time.

Discussion

Seismic Q Estimation on PP and PS Data— The PP amplitude data show indications of potential deep gas charged reservoirs. These data indicate a peak over trough response and if the phase of the response is close to zero-phase, then this would represent harder sand in slower shale background. This is possible given the overpressure evidenced by the velocity survey data analyzed previously and considering that deep sand could be cemented to some extent.

The deep (6,900 ms to 7,400 ms) PS data has a lower bandwidth than the corresponding (3,600 ms to 4,000 ms) PP data. This is mostly because of the slower propagation velocity of the PS compared with the PP data, and warping the PS to the PP time will effectively double frequency band making the PS band approach that of the PP data.

The deep (4,000 ms to 4,500 mg PP time) events are reasonably well imaged using PP data, but the corresponding PS events (7,300 ms to 7,800 ms PS time) are only partially imaged. This implies the PS data might be able to be used to support the PP structural interpretation in exploration of deep gas targets, but it would be difficult to use them alone.

From our theoretical work, the PP inelastic response for gas sand is expected to be strong, while the PS inelastic response for gas sand

is shown to be basically flat. The PS response is a combination of the P and S reflection travel paths, so we expect some intermediate response for PS as shown.

Analysis of these attributes on seismic data indicates they behave according to the theoretical models. The key in interpreting these attributes is finding strong responses with both algorithms, which occurs at specific reflectors. Such reflectors can be viewed as high-graded prospects for hydrocarbon exploration.



Summary and conclusions

In 2004, Rock Solid Images undertook a project to demonstrate novel and robust techniques for reducing hydrocarbon indicator risk in deep gas sands by exploiting an additional set of completely independent indicators – the rock inelastic properties. These inelastic properties of P-wave and S-wave energy from multicomponent seismic provide a crucial tool that can be used to disseminate pore fluids and lithology.

The primary conclusions from this work are:

- rock physics methods can be used to compute Qp and Qs from conventional well log data;
- Qp can be computed from PP and PS seismic data;
- attenuation can have a substantial impact on seismic response, both post-stack and pre-stack, and can cause significant changes in seismic amplitude with offset, especially at the bottom of a gas zone;
- attenuation in seismic data can be related to gas-bearing reservoirs and can be used as a reconnaissance tool in exploration; and
- attenuation should be used with other seismic attributes such as elastic attributes and geologic context. However, attenuation can be a valuable tool in deep targets where AVO is less reliable.

Rock Solid Images is using the

methods and tools developed in this project to help U.S.-based oil and gas exploration and pro-



Figure 3a: XLINE 2360 PS stack amplitude



Figure 3b: XLINE 2360 PS Frequency Shift Q estimation attribute response



Figure 3c: XLINE 2360 PS Log Spectral Ratio Q estimation attribute response

duction companies find and produce new gas resources in the U.S. Gulf of Mexico, onshore Texas and Rocky Mountain region. The company also has been granted a U.S. patent (No. 7088639) based on an earlier DOE funded project on Pwave attenuation. The patent describes a comprehensive method for using seismic attenuation in hydrocarbon reservoir characterization. ◆

Acknoldgement

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For more info contact:

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Updating the Roadmap for Natural Gas Storage Research

By Michael P. Whelan, *Pipeline Research Council International Inc.*; and Ramon Harris, *National Fuel Gas Supply Corp.*

Underground natural gas storage is an integral element of the nation's energy delivery system.

as from storage provides about half of the total gas consumed in the United States on a peak day. The ability to store and deliver these volumes increases the efficiency of the pipeline delivery system yearround, enables large end-users such as power plants to obtain more flexible, cost-effective gas supply and provides gas that cannot be physically supplied during periods of high demand by additional production or liquefied natural gas (LNG) imports. Natural gas storage research and development (R&D) is necessary to ensure the continuing productivity of these assets, meet new integrity requirements and cost-effectively develop new storage capacity. The Gas Storage Technology Consortium, managed by Penn State University and funded by the Department of Energy's National Energy Technology Laboratory, has furthered collaborative storage R&D with Pipeline Research Council International, a subscription membership organization comprised of 34 pipelines worldwide that plans and executes a collaborative R&D program addressing a range of pipeline issues, including gas storage. The consortium geographic membership is illustrated by the map.

As a part of its planning process, PRCI has developed an R&D roadmap that outlines the critical issues facing storage operators, and frames the selection and implementation of gas storage research projects. This roadmap identified five research objectives driven by the current business and regulatory climate:

- develop additional storage capacity at the lowest possible cost;
- · increase storage operating flexibility



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to meet market demands for shortterm services;

- maintain and improve system reliability and safety, including examining the effects of increased non-traditional supplies (including LNG) on storage operations;
- manage costs to protect customers and improve competitiveness; and
- respond to increased regulatory pressures for the integrity of existing facilities and new storage field development by ensuring new regulations are based on sound science.

Storage research program areas

The above objectives fall under three distinct program areas – Integrity, Improved Operations and Flexibility, and Inventory Management. These programs cover all forms of underground storage – porous media (depleted reservoirs and aquifers) and caverns.

Integrity

Facility and downhole integrity are key attributes of any storage operation. Industry steps to increase the safety profile of gas transmission operations, combined with an increased regulatory focus on storage facilities, have highlighted the need for improved technologies. Primary elements of an assertive storage field reliability program include the following:

Wellbore Tubulars—Corrosion or erosion of metal can result in degradation of the strength of casing or tubing. Current methods to assess metal loss can be improved, as can the interpretation of that information to determine the need for repair or replacement. Unusual casing corrosion may be related to particular vintages of casing materials, which can become an important parameter in an operator's integrity management program. When repairs are required, current repair methods can be improved. Nonmetallic casing materials hold the promise of reducing the occurrence of corrosion. The brine strings used in cavern wells present problems unique to that form of storage and need a general mechanical integrity model to assess their useful service life.

Ongoing wellbore tubular projects include: Kiefner & Associates (Worthington, Ohio) to include the effects of axial loads and external (reservoir) pressure to improve predictive tools that estimate the burst pressure of well casing that has lost metal because of corrosion. RESPEC (Rapid City, SD) is completing a comprehensive structural analysis of typical American Petroleum Institute threaded couplings to determine their useful life under a variety of salt cavern conditions, including subsidence, salt creep, pressure and temperature variations, and the initial loads experienced during well completion. Baker-Atlas (Houston) is developing a high-resolution MFL downhole tool to locate and assess critical defects that pose a safety threat and require remediation. PB Energy Storage Services (Rapid City) is compiling case histories of brine string failures, evaluating models for brine string failure and developing recommendations for maximizing brine string integrity. Edison Welding Institute (Columbus, Ohio) is conducting a state-of-theart assessment of alternative casing repair methods for downhole, in-situ repairs.

Cement Integrity-Cement used in wells is essential to contain the stored product. Flaws in the cement sheath around casing strings or cement degradation because of long-term cyclic loading may lead to loss of gas to other geologic horizons or to the atmosphere. The cyclic duty cycle of storage wells is different than a conventional producing well. Current logging technology used to assess the integrity of the cement sheaths is costly and does not give the degree of precision required to make economical decisions about repair needs. In addition, current repair methods (primarily squeeze cementing) are expensive and often ineffective. Therefore, cement assessment and cement repair improvements are required.

Ongoing projects include: University of Texas to characterize the effects of cyclic pressure and temperature-related stresses on cement hardening and cement adhesion, important parameters for cement/casing/formation seals. Baker-Atlas (Houston) is investigating new acoustic inspection techniques (EMATS) to evaluate highly modified, lightweight cements in gas-filled boreholes. Most inspections today require liquid-filled boreholes. URS (Austin, Texas) is evaluating tunable diode laser remote sensing to locate gas leaks from deteriorating exterior casing cement.

Inventory Integrity—Loss of stored gas is an economic, safety and environmental issue. There is a need to evaluate the dispersion modeling used to form and evaluate surface release contingency/response plans. Improving the ability to detect fugitive emissions will likely point to natural gas surface leaks in wellhead and gathering system valves packing where retrofitable modifications should be targeted. Schlumberger (Pittsburgh) is developing an inventory analysis software tool to improve operators' ability to effectively monitor inventory and resolve gas loss issues by automating more of the current inventory analysis process for more rapid results.

Technology Recomaissance—Scanning across the energy and mining industries for alternative approaches to integrity management has the promise of building on similar efforts to control costs as well as identifying related industrial imaging methods that may be adaptable to storage operations.

Operations/flexibility

The marketplace's increasing emphasis on flexible, short-term storage services is driven in many regions by the use of natural gas as the marginal fuel for electric power generation with some plants operating on hourly cycles and requiring highly flexible gas supply. New technologies and procedures to improve operations are crucial with respect to:

Cost Management—Competition between fuels is intense, and the overall competitiveness

of natural gas in the marketplace requires the lowest possible cost for storage services, particularly as wellhead gas prices have increased.

Market Response—Meeting demands for new storage capacity includes examining options to increase the flexibility of existing fields, be they conventional depleted gas reservoirs, aquifers or cavern facilities. Research and development that squeezes more capacity and/or deliverability out of existing assets is generally the most cost-effective means to expand storage, with minimal associated environmental impact or permitting delays.

Specific technology directions include:

Damage Remediation-The cyclic operation of storage fields and repeated injection/withdrawal cycles tends to damage the storage formation or the wellbore, reducing deliverability during time. This has been documented in many prior studies and investigations. However, improved diagnostic capabilities are needed to determine the specific mechanism responsible for deliverability loss at individual sites so the optimum preventive actions and remedial steps can be implemented. Research should target more cost-effective damage prevention/mitigation options to maintain/restore deliverability. A particularly prevalent form of damage is the precipitation of salts in the formation or wellbore. The use of coiled tubing technologies can potentially provide more cost-effective means of removing downhole salt or scale damage.

Ongoing projects include: *Correlations* (Socorro, NM) to evaluate the effectiveness of current methods to prevent or remediate salt precipitation, thus allowing operators to make more informed selection of precipitate inhibitor practice and treatments. *TechSavants* (Wheaton, Ill.) is evaluating the effectiveness of sonication (acoustic energy) on removing scale from well perforations and other critical flow passages.

Stimulation—Stimulation of new or existing storage wells can increase injection/withdrawal capacity and can also be part of a strategy to recover deliverability lost to damage. Stimulating new storage wells can lower the cost of new



storage developments by reducing the number of wells that need to be drilled and maintained. Although past R&D has focused on developing specific stimulation methods, determining the optimum stimulation method for a given field or well is not straightforward, and additional work is required to support operator decisions. The high cost of fluids used to rework storage wells calls for innovative means to recycle these materials and reduce this O&M cost component.

Ongoing projects include: *West Virginia University's* efforts to develop a statistical portfolio management approach to storage field workover and stimulation decisions that will lead to a set of algorithms allowing operators to maximize the effectiveness of their limited stimulation/workover budgets. Correlations (Socorro) is evaluating the extent to which surfactants increase the withdrawal rate (deliverability) from wells during high demand periods. The work will examine effects on different reservoirs (sandstone, carbonate and dolomite) in dry gas, depleted oil fields and water aquifers.

Water Handling-Storage operations routinely produce water from the formation or condensed water from the gas phase, which must be separated from the gas stream and disposed, presenting operational difficulties and a potential environmental hazard. The most common form of disposal is the use of disposal wells, which are subject to formation damage that can severely restrict their capacity. The presence of liquid water in wells and gathering systems can lead to the formation of gas hydrates, which literally plug wells and lines, and also pose a potential safety risk. Better control of hydrates is needed to assure reliability, increase safety and reduce costs. The most effective way to handle produced water is to separate it at the wellhead. To date, this option has been limited because of the cost of installing and maintaining wellhead separation equipment, thus highlighting the need for more cost-effective options.

Ongoing projects include: *Clemson University's* demonstration of the effectiveness of a series of hybrid constructed wetlands that serve as natural surface treatment sites to consistently treat waters produced from storage reservoirs (see related article in this issue). *CEESI* (Nunn, Colo.) is constructing a hydrates simulation loop to investigate hydrates formation and mitigation factors.

Reservoir Management-This is a key element in maintaining general system reliability and flexibility, and in maximizing the long-term value of storage assets. Alternatives to traditional reservoir simulation are needed as a management tool. Operational flexibility would be improved by automated well operations that are expensive since this reliable real-time data collection at wellheads. Unfortunately, current data systems are adapted from custody transfer applications and are more expensive than what is required for reservoir management. Improved wellhead measurement systems would not only facilitate reservoir management, but also would provide benefits to other areas of storage operations, such as hydrate control and scheduling maintenance and remediation activities.

LNG Storage—Imports of LNG will increase in the near future. There is a need to identify potential storage sites near import facilities to optimize the efficiency of this expanding source of supply. Liquefied natural gas imports will introduce gas with potentially significantly higher Btu content into storage systems where it will mix with more traditional gas supplies. The potential impact on reservoir dynamics and operations is not well characterized at present.

Inventory management

Effective management of storage inventory (base and working gas) is increasingly important as gas prices rise and demand for flexible services increases. Inventory management is important with respect to:

Cost Management—The value of storage inventory rises with the cost of gas. Minimizing base gas requirements can significantly reduce the cost of new capacity, as most existing fields contain base gas with a cost basis of \$0.50 to \$2.00/Mcf, while new capacity would utilize \$6 to \$8/Mcf base gas.

Flexibility—The design of new fields or the reengineering of existing fields for flexible services requires effective control of inventory. Increasing the working/base gas ratio is an effective means of providing additional service at minimum cost.

Reliability—Where nontraditional supplies of gas, such as LNG, are introduced into storage fields along with more traditional supplies, maintaining gas quality in withdrawal gas can be a challenge. This is not limited to the generally higher Btu LNG sources, but also includes lower-Btu gas from biomass, coalbed methane or future syngas blends.

The use of inert gas, nitrogen, for example, as base gas is promising. Although some work was done on this technique in the 1980s and 1990s, recent increases in gas prices have sparked renewed interest in this concept. Monitoring inventory can be costly in terms of direct costs to assess inventory and lost deliverability because of long shut-in times while field pressures stabilize. Lower cost and less timeconsuming means of inventory monitoring are desirable. The PRCI Underground Storage Technical Planning Committee will continue to work closely with the Gas Storage Technology Consortium to refine this technology so it captures the high-priority needs of gas storage operators. The close alignment of the consortium's mission: "To assist in the development, demonstration and commercialization of technologies to improve the integrity, flexibility, deliverability and cost-effectiveness of the nation's underground natural gas/hydrocarbon storage facilities" with PRCI's objective to "conduct research committed to enhancing the safety, reliability and productivity of the energy pipeline industry" drives the two organizations to a closely coordinated R&D program that carefully leverages the limited funding available. The roadmap illustrates that the need for research far outstrips available resources, and that program results can be put directly into application because of the hands-on involvement of storage field operators. \diamondsuit

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PRODUCED WATER

Management of Produced Waters from Underground Gas Storage

By James W. Castle, Evan H. Cross and Laura E. Kanagy, Department of Geological Sciences; and John H. Rodgers Jr. and Brenda M. Johnson, Department of Forestry and Natural Resources

Waters produced from natural gas storage pose a challenge for treatment because they vary widely in composition and volume. High costs associated with current methods of produced water management can limit expansion of existing gas storage fields and development of new fields.

wo methods are commonly used for handling produced water. The first involves transport of produced water to specialized treatment facilities followed by surface discharge of the treated water and the second is to reinject the water into the subsurface. While volumes of produced water increase, the cost of conventional treatment methods are escalating because of increasingly stringent surface discharge and re-injection regulations under the Clean Water Act through the National Pollutant Discharge Elimination System (NPDES) and Safe Drinking Water Act through the Underground Injection Control. Development of new approaches for treatment of produced water is essential for continued operation of many existing storage fields and construction of new facilities.

Water produced from gas storage facilities is often generated in relatively large volumes and can contain several constituents that limit disposal or reuse of the water. Constituents such as chlorides, hydrocarbons and metals are of concern in these waters. Although salinity of some produced waters may be low enough to meet NPDES discharge limits, concentrations of other constituents in these waters may preclude discharge, resulting in a need for treatment or disposal. Specifically designed constructed wetland treatment systems (CWTS) have been used to treat constituents in various types of waters. However, the use of CWTS has not been demonstrated previously for produced waters from gas storage fields. Wetlands facilitate unique reactions not occurring in other aquatic or terrestrial systems. Constructed wetlands can be poised or buffered to ensure that desired reactions (transfers and transformations) affecting the constituents targeted for treatment proceed at predictable rates over long periods of time (decades). The use of CWTS offers specific advantages:

- low construction cost;
- low operational and maintenance costs;
- reliability; and
- flexibility in design, so the approach is applicable to a range of water quality and quantity.

The purpose of this investigation by Clemson University in partnership with Dominion Transmission Inc. and the Gas Storage Technology Consortium is to demonstrate a low cost and readily implemented method for treating produced water as part of a system integrated with surface facilities of a gas storage field. The approach involves identifying and confirming targeted constituents in the gas storage produced waters, designing constructed wetlands for

treatment based on biogeochemistry and macrofeatures (hydroperiod, hydrosoil and vegetation), conducting carefully designed pilot and demonstration-scale studies to confirm performance and function, and efficiently and effectively monitoring performance and



Figure 1. Representative samples of gas storage produced waters provided by member companies of the Gas Storage Technology Consortium.



Figure 2. Pilot-scale constructed wetland treatment system for conducting experimental studies used to develop design parameters for building an onsite, demonstration-scale system.

function of the constructed systems.

The first phase of the investigation involved construction and performance monitoring of a pilot-scale CWTS built at Clemson University. Design criteria developed during the pilot project were used to build a demonstration

PRODUCED WATER

scale CWTS at a field location in West Virginia for onsite treatment of gas storage produced waters. Construction of the demonstration scale system is complete, and monitoring of treatment effectiveness is scheduled to begin this winter.

Pilot-Scale Constructed Wetland Treatment System Study

Characteristics of gas storage produced waters

Natural gas storage produced waters were characterized thoroughly to develop design parameters for the pilot scale CWTS. The composition of produced waters associated with natural gas storage differs widely depending upon the geologic formation from which the water originates, the extraction method utilized in the natural gas production process and the treatment chemicals selected for the process. Samples (Figure 1) and data provided by industry members of the Gas Storage Technology Consortium show ranges of values for many produced water constituents. The data, including more than 4,000 records, were statistically analyzed and compared using the Statistical Analysis System (SAS Institute, 2002). The waters were grouped into four categories based upon statistical analysis:

- fresh—low chloride concentrations (≤400 to 2,500 mg/L);
- brackish—medium chloride concentrations (2,500 to 15,000 mg/L);
- *saline*—high chloride concentrations (15,000 to 40,000 mg/L); and
- *hypersaline*—very high chloride concentrations (≥40,000 mg/L).

Based on our statistical analysis and previous studies (USEPA, 2000; Veil et al., 2004), several metals may be present in produced waters. Many of these metals are present in concentrations that are toxic to receiving system biota. This toxicity consequently leads to failure to meet NPDES permit limits. For our pilotscale project, cadmium, copper, lead and zinc were chosen for study based on their presence in produced waters, toxicity to receiving system biota and cost of analyses.

Performance criteria

To develop reasonable treatment performance goals for the pilot-scale CWTS, NPDES permits were obtained from a variety of sources including industry and government Web sites, the U.S. Environmental Protection Agency (EPA) and gas storage companies. Several EPA offices were contacted, including those in Ohio, Pennsylvania, New York and West Virginia, to obtain sample permits. These NPDES permits were used to create a list of possible constituents of concern and a range of surface discharge limits for the constituents found in produced waters. This information was used to define treatment performance goals for the pilot-scale CWTS.

Design and construction

Based on characteristics of gas storage produced waters and treatment performance goals, a pilot-



Figure 3. Example of treatment performance by the pilot-scale constructed wetland treatment system. The graph illustrates a decrease in aqueous concentration of zinc as simulated gas storage produced water moves through freshwater cells of the system. Two series of cells were used to evaluate performance.

scale constructed wetland system was designed and constructed (Figure 2). The major components of the design plan included a detention basin, an oil/water separator, two saltwater wetland cells, a reverse osmosis (RO) unit and two trains of four freshwater wetland cells each. The first two of the four freshwater wetland cells contained hydrosoil that created a bulk reducing environment, which promoted removal of metals and sulfates by the following processes: precipitation of metals, sorption, plant uptake and biodegradation. To create a reducing environment, the hydrosoil must possess a sediment oxygen demand greater than the rate at which oxygen is supplied to the system. This can be accomplished by using a hydrosoil with a large fraction of clay and sufficent labile organic matter. When hydrosoil of this type is combined with plants that do not strongly oxygenate the rhizosphere, a reducing environment capable of the aforementioned removal processes can be established. The final two freshwater wetland cells contained hydrosoil that created a bulkoxidizing environment, which promoted removal of water-soluble organics and metals through oxidative processes. A bulk-oxidizing environment is accomplished through hydrosoil with high sand content and little to

> no organic matter combined with plants that have high radial oxygen loss in the rhizosphere.

Measurement of treatment performance

Treatment performance was monitored for each of the four categories of simulated gas storage produced waters described above. Effective treatment performance by the pilot-scale CWTS was demonstrated by removal of metals and by toxicity tests for all four categories of produced waters. Effective removal of metals in the simulated fresh and brackish produced waters occurred in the freshwater wetland cells as indicated by decreasing concentrations measured in outflow from successive wetland cells (Figure 3). The saltwater wetland cells and RO unit were bypassed in the treatment of these waters because chloride concentrations were below NPDES discharge limits. For the simulated saline and hypersaline produced waters, which contained inflow metal concentrations greater than fresh or brackish produced waters, concentrations of the targeted metals decreased by 23% to 94% between inflow to the oil/water separator and outflow from the saltwater wetland cells. After these waters had passed through the RO unit, metal concentrations had decreased to levels that meet NPDES discharge limits.

Toxicity tests of the simulated produced waters show that decrease in toxicity to target organisms (*Ceriodaphnia dubia*) accompanies metal removal from inflow to outflow through the pilot-scale system. Toxicity was removed by the treatment system for simulated fresh, saline and hypersaline produced waters. For brackish waters, toxicity decreased from inflow to outflow although some reproductive impairment was observed in the outflow.

Demonstration-scale constructed wetland treatment system

A demonstration-scale CWTS was constructed at a field location in West Virginia for on-site management of waters as they are produced from gas storage (Figure 4). Results from the pilot-scale study served to decrease uncertainties and confirm design features for the demonstration-scale system. Dimensions of the planted area of the demonstration wetlands are 20ft by 33ft, and the system is enclosed in a greenhouse so treatment can be monitored readily throughout the year. The first half of the wetland is planted with Schoenoplectus californicus (California bulrush) to support a reducing aquatic environment. The second half is planted with Typha latifolia (cattail) to support an oxidizing aquatic environment.

Conditions within the greenhouse can be

regulated to facilitate assessment of the demonstration-scale system. Although enclosure within a greenhouse contributes to investigation of the demonstration-scale CWTS, the greenhouse may not be necessary for successful operation of the system at this site and others in a similar climatic zone.

Sampling the inflow and outflow water from the CWTS will monitor treatment of waters produced from nearby gas storage. These samples will be analyzed for concentrations of targeted constituents.

Performance of the CWTS will be evaluated by comparing the concentrations of constituents of concern in the inflow to concentrations in the outflow. Performance criteria will include analytical parameters (organics, metals and other elements of concern) as well as other explanatory parameters, such as temperature, pH, alkalinity, hardness and conductivity.

Conclusions

A hybrid pilot-scale CWTS was designed, constructed and found to effectively treat simulated gas storage produced waters. The pilot-scale study provided data regarding the feasibility of this approach for treating gas storage produced waters of varied composition. Results from the study demonstrated that fresh to brackish gas storage produced waters can be treated readily using CWTS. Higher salinity gas storage produced waters will require a hybrid system for chloride removal. Results also served to decrease uncertainties and confirm design features for constructing a demonstration-scale wetland treatment system at a field site in West Virginia.

The approach to our investigation incorporates the use of sound theory and fundamental principles, such as the Laws of Thermodynamics and basic biogeochemistry, to develop design parameters for constructed wetland systems to treat produced water from gas storage fields. An expected benefit of the



Figure 4. Construction of the demonstration-scale wetland system built to evaluate onsite performance for treatment of actual gas storage-produced waters. The wetland is enclosed in a greenhouse.

investigation is that the results will contribute to reduced cost of water management, which will potentially lead to expansion of existing storage fields. In addition, new geographic areas may be opened for development of gas storage fields due to anticipated economic advantages. \diamondsuit

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Water Detection Plays Critical Role

By Vincent Vieugue and Rune Sørhus, *Roxar AS*

An operator must measure water content to devise an effective flow maintenance plan.

crucial component of flow assurance today is the need to predict and measure the water production profile in the well.

There are a number of reasons for this, the biggest being the potentially devastating effects unchecked water can have on flow assurance. Water, especially saline, can cause scaling, hydrates and corrosion in wells and pipelines leading to the worst-case scenario of wells being shut down.

The damage is not just limited to flow assurance upstream. Excessive formation water, as a result of water breakthrough, may also exceed the water treatment and glycol regeneration capacities of the downstream plant.

By measuring the early onset of formationwater production in real time, operators can take preventative or remedial action, such as adjusting the pH in the MEG/water mixture, injecting the right amount of corrosion inhibitor or more drastically – choking the well or instigating zonal isolation.

Gas fields

There are a number of other recent drivers in the industry that have increased the need for accurate water production profiles.

Firstly, with natural gas becoming an increasingly important energy source, the numbers of major subsea gas fields are multiplying worldwide. The United States Energy Information Administration estimates world proven natural gas reserves to be about 5,210.8 Tcf. Much of this gas is wet gas – defined as being about 98% to 100% gas void fraction (GVF).

For such developments with typically high pressure and high flow rates and where it is difficult to detect the water production profile in the wet-gas well, the ability to detect water



A wet gas meter provides critical information, quickly, that allows operators to take remedial action and keep product moving. (Photo courtesy of Roxar)

is critical for optimizing production, preventing hydrate, scale and corrosion in the pipelines and ensuring a reliability of supply.

Secondly, the last few years have seen an increase in subsea tiebacks as a means of managing production costs and avoiding expensive platforms.

With tiebacks of more than 62 miles common and 310-mile tiebacks in the planning stages, there is the risk of not detecting water breakthrough early enough to avoid potentially disastrous consequences. The key is to know exactly when and how much water is being produced, requiring sensitive, accurate and reliable measurements of the water in the gas stream.

How accurate is accurate?

Against this background, it is clear that the accurate and quick detection of water is essential

to flow assurance, but to what degree of accuracy and sensitivity should we be aspiring, and how early does the water need to be detected?

The answer is highly accurate and very quickly.

Many fields have a desired water detection sensitivity of as little as 0.005% by volume, and it is important that any water is detected to this degree of accuracy.

The traditional multiphase meter, for all its effectiveness, is simply unable to measure to this degree of accuracy and sensitivity.

To fill this void, today's wet gas meter uses advanced microwave-based dielectric measurements and generates accurate gas and condensate flow rates based on standard delta pressure devices. The meter detects the resonant frequency in a microwave resonance cavity with the resonant frequency depending on the dielectric properties of the fluid mixture present in the cavity.

With the permittivity of water (about 60 to 200), much higher than that of gas (about 1) or oil condensate (about 2), the dielectric properties of the wet gas mixture are consequently very sensitive to the water content.

Performance tests on Roxar's Wet Gas Meter have shown the meter able to detect changes in the water production with sensitivity better than +0.005% volume while the absolute accuracy was +0.1% volume in high GVF (greater than 98.5%) cases.

In the **Carina Aries** field in Argentina, for example, water injection testing took place where 31 b/d was initially injected and then reduced by 6.29 b/d at each test point – what worked out at 41 L per hour. The measurements were precise and accurate with the company's wet gas meters detecting a 6.29-b/d change in a 188,700-b/d flow. This effectively amounts to 3 L of water in a room of 3,532 cu ft.

In addition to the microwave technology, a pressure, volume, temperature software package is an integral part of the meter and is used to calculate the individual liquid (condensate) and gas densities and the actual gas/oil volume ratio (GOR) at meter conditions. The calculated GOR is subsequently employed to discriminate between gas and oil and hence to deduce the oil fraction and gas fraction once the water fraction has been found through the meter. Condensed and saline formation water can also be distinguished.

To address the need of quick detection, the wet gas meter is able to perform online and direct measurements so water can be detected as soon as it starts to be produced.

Ormen Lange field

The **Ormen Lange** field is the largest natural gas field under development in the Norwegian Continental Shelf and lies 62 miles northwest of the Norwegian coast in water depths between 2,625ft and 3,281ft.

Proven gas reserves are 14 Tcf and production is expected to be 706 Bcf of gas per year, with the gas likely to cover 20% of the U.K.'s gas requirements for up to 40 years. The field will be going into production in 2007.

With a subsea tieback of more than 75 miles to Nyhamna on Norway's west coast, the need for the field to be operated remotely with no offshore platforms and the importance of a high degree of accuracy and sensitivity in water detection, Ormen Lange is an excellent example of how wet gas meters are helping improve flow assurance and are central to a field's development concept.

The instrument company is working with the operators – Hydro during the development stage and Shell after 2007 – to install eight subsea wet gas meters and implement remote management systems, which help optimize production.

The need for accuracy in water detection in the field is vital. Dependent on the flow assurance philosophy selected, studies show that even small amounts of saline water can result in large and rapid scaling problems with scale prevention requiring a sensitivity significantly better than what is required for hydrate prevention.

With the field not using conventional offshore platforms but instead connecting wellheads on the ocean floor directly by pipes to an onshore processing facility, scaling and corrosion in the pipelines is to be avoided at all costs.

Today, the desired water detection sensitivity for Ormen Lange field is 0.005% by volume – a detection accuracy of 9 gal of water an hour in a 100-MMcf/d gas well.

The wet gas meters are achieving these levels and helping ensure a future safe and reliable supply of gas production from this unique offshore field.

Snøhvit field

The importance of wet gas metering in fields where there are long tiebacks is also exemplified in the **Snøhvit** field wet gas field in the Barents Sea where the untreated well stream is piped 100 miles from the field to a gas liquefaction plant in northern Norway.

The consequence of not using wet gas meters for such a development would be unacceptably high with an over-injection of chemicals (hydrate inhibitors and others), as well as a loss of control of the long distance multiphase pipeline system.

By using the wet gas meters in the field, remedial action can be taken as soon as the water is detected whereas, without the wet gas meters, a lag of 3 days would ensue. The result would be a build up of large deposits of salt in the pipeline.

Optimize wells

At a time when exploration replacement rates, although important, remain insufficient for companies to reach their long-term targets of production replacement and growth, there is a growing focus on enhanced recovery and increased production.

By continually measuring formationwater production, operators are being able to operate each well aggressively "at the limit" of its water production and are well on their way to increased flow assurance, accelerated production and maximum reservoir performance. \diamondsuit

New Nitrogen-rejection Membrane Technology Commercialized

By Kaaeid Lokhandwala, Membrane Technology & Research Inc.; and Anthony Zammerilli, National Energy Technology Laboratory

An innovation in membrane design allows cost-effective separation of nitrogen from a natural gas stream. Upgrading low-volume gas streams with high nitrogen content—the largest component of low-quality natural gas resources—could add another 1 Tcf to America's natural gas reserves.

new membrane process to separate nitrogen from natural gas – a technology developed under a project funded by the U.S. Department of Energy (DOE) – has been successfully commercialized.

The success of the membrane separation process that Membrane Technology & Research Inc. (MTR), Menlo Park, Calif., developed under the project (DE-FC26-01NT41225) bodes well for efforts to upgrade low-quality natural gas (LQNG) in the United States.

Low-quality natural gas encom-

passes natural gas containing contaminants such as water, carbon dioxide (CO_2) , hydrogen sulfide, heavier hydrocarbons or nitrogen and other inert gases that must be removed from the raw gas stream to yield a pipeline-quality natural gas product. Low-quality natural gas accounts for almost one-third of America's known natural gas reserves – more than 60 Tcf of the nation's total proved natural gas reserves of more than 192 Tcf.

The DOE-backed technology targets cleanup of natural gas with a high nitrogen content. The standard U.S. natural gas pipeline specification for nitrogen content is less than 4%. On this basis, about 17% of known U.S. natural gas reserves, or more than 32 Tcf, falls short of pipeline-quality levels specifically linked to high nitrogen content. That makes nitrogen the largest target for



Figure 1. Skid-mounted nitrogen-rejection membrane separation unit destined for North Texas Exploration's field site.

cleanup in the LQNG resource base.

Some of this high nitrogen content gas can be upgraded to pipeline specifications through dilution with low nitrogen content gas – when it's available – or through treating and conditioning at large commercial cryogenic gas processing plants. Processing high nitrogen content gas at large cryogenic plants, however, warrants substantial production to operate economically: between 50 MMcf/d and 500 MMcf/d. In addition, cryogenic plants are designed specifically for fixed inlet gas composition and cannot be used when inlet conditions vary widely during a short period of time.

A large part of the nation's high nitrogen content gas lies in many modest-size deposits – mainly operated by small, independent operators – that cannot justify cryogenic gas-processing economies of scale. Consequently, about 1 Tcf of this discovered resource remains economically unproducible. That volume is equal to almost 5% of U.S. annual consumption of natural gas.

If America's significant resource of subquality natural gas is to be fully developed, advances in alternative nitrogen separation technologies are needed. The main gas separation methods in use today are liquefaction/distillation, absorption, adsorption and membrane-based processes. While membrane technology may be

costly in some applications, it is generally a passive and energy-efficient process and may be the only practical method for some natural gas cleanup needs. Membrane separation technology is gaining greater attention these days in natural gas production and processing, especially in small skid-mounted and packaged field processing units. Industry is pushing the envelope on cutting costs and improving efficiencies in membrane technology to make this the preferred option for a broader array of marginally economic subquality gas deposits.

The DOE funded a 5-year research project by MTR to develop and demonstrate a membrane separation process to separate nitrogen from natural gas with high nitrogen content. The project marked the first demonstration of a new membrane technology to treat a low volume (1 MMscf/d) of otherwise unusable high nitrogen content natural gas.

The technology already has drawn the attention of one the world's biggest multinational engineering and construction firms, ABB Lummus Global. MTR signed a marketing and sales partnership with the firm to help market the technology through ABB Lummus Global's Randall Gas Technology Group, a supplier of equipment and processing technology to the natural gas industry. Since then, the partnership has sold six commercial nitrogen-rejection natural gas membrane separation units based on the technology. Commercial sales to date total almost \$2.6 million.

The DOE's National Energy Technology Laboratory manages the MTR research project, which is expected to conclude in spring 2007. The DOE is funding about \$650,000 of the project's \$1.5 million cost.

How the process works

MTR's nitrogen-rejection membrane-based separation process is especially suited for small fields, with production rates up to 10 MMscf/d to 15 MMscf/d. The process essentially divides the natural gas into two streams: a pipeline-quality product gas and a high nitrogen content gas stream burned as fuel to power the membrane unit compressor or to provide other onsite power requirements.

Contained within a skid-mounted, mobile unit (Figure 1), the MTR process is ideal for wellhead processing of gas produced during well workovers when nitrogen is used in hydraulic fracturing to stimulate production. In such circumstances, significant volumes of nitrogen-rich vent gases that cannot be piped are produced at the wellhead and must be vented for several days. This represents an environmental issue as well as a significant product loss.

The transient nature of high nitrogen content gas released during well workovers is wellsuited to membrane processing; feed gas nitro-



gen content can be as high as 50 mole % at the start of the workover and decline to between 6 mole % and 10 mole % during time.

In the mid-1980s, membrane systems for removing CO_2 from natural gas were introduced into the gas processing industry. These membranes separate gases by difference in molecular size and can permeate CO_2 10 to 15 times faster than methane. However, the difference in molecular size between methane and nitrogen is small, so size-selective membranes were not able to achieve economically useful separations for rejecting nitrogen.

About 5 years ago, MTR developed membranes that separate according to differences in the solubility of the two gases in the membrane. Because it is more condensable than nitrogen, methane is about seven times more soluble in certain polymers. This difference in solubility has been used to develop membranes three to four times more permeable to methane than to nitrogen.

Membranes used industrially to separate gases are dense polymeric films that contain

no pores. The permeating gas molecules dissolve in the polymer film as in a liquid and then diffuse through the membrane down a gradient in a concentration created by the pressure difference across the membrane. Gas permeability is expressed as the product of a diffusion coefficient (the mobility of the individual molecules in the membrane material) and the gas sorption coefficient (the number of molecules dissolved in the material). The ability of a membrane to separate two gases, or the ratio of gas permeabilities, is called membrane selectivity. The ratio of the two gases' diffusion coefficients, reflecting the different sizes of the two molecules, can be seen as mobility selectivity. The ratio of sorption coefficients, reflecting the two gases' relative condensabilities, is termed solubility selectivity.

In all polymer materials, the diffusion coefficient of a gas decreases with increasing molecular size because large molecules interact with more segments of the polymer chain than do small molecules. Accordingly, mobility



Figure 3. Exploded view of a spiral-wound membrane module.



selectivity always favors the passage of small molecules over large ones.

At the same time, the sorption coefficient increases with greater condensability of the permeate. This means the sorption coefficient increases with molecular size, because large molecules typically are more condensable than smaller ones.

With high nitrogen content natural gas,

nitrogen molecules are smaller but less condensable than methane molecules, so membranes can be made that preferentially permeate nitrogen by relying on mobility selectivity or that preferentially permeate methane by relying on solubility selectivity.

For its nitrogen-rejection membranes, MTR uses hydrophobic rubbery polymers with small diffusion selectivity terms and with

solubility selectivity terms close to the theoretical maximum of a factor of 6 to 7 (Figure 2). Under these conditions, MTR obtained membranes with a selectivity factor of 3 to 4. The membranes also have to be mechanically strong, thin and capable of supporting pressure differentials of 500psi to 1,500psi.

To be used commercially, the composite membranes must be formed into modules that can provide compact access to the membrane areas required to carry out large-scale separations. One such approach is the spiral-wound design, which typically is produced as 8-in. and 12-in. diameter modules (Figure 3). The complexity and cost of the modules increase with the nitrogen content of the gas.

The pressurized feed gas passes across the surface of the membrane. As the methane preferentially permeates the membrane, the gas spirals inward to a central collection pipe. Nitrogen is rejected and exits as the residue stream. The permeate, depleted of nitrogen, is re-pressurized, while the residue is used as fuel. A flow scheme of the unit pictured in Figure 1 is shown in Figure 4.

The process achieves more than 90% methane recovery in the product gas and even greater Btu recovery because the membrane permeates essentially all of the ethane, propane and higher hydrocarbons from the residue gas. The product gas consists of <4% nitrogen, methane and little else. The permeate gas is recycled and mixed with the incoming feed gas. A residue stream of 25% to 50% nitrogen gas can be used as compressor fuel.

Pilot scale experience

The original project proposal called for building and operating a 1-MMscf/d pilot wellhead gas treatment system to be operated in a natural gas field near Waverly in Jackson County, Ohio, owned by Butcher Energy Corp., Granville, Ohio.

The pilot test results demonstrated a methane/nitrogen selectivity close to the laboratory data and confirmed the basic membrane performance using an actual gas field feed (Figure 5). It also showed the membrane performance improved as temperatures were reduced and that impurities in the gas didn't harm the membrane. The overall test ran about 9 months, and field data showed the membranes were able to maintain their selectivity during that time.

Based on the performance of the field test, MTR calculated the economics for two levels of nitrogen concentration in the gas (see chart). These values are favorable, considering the alternative would be to keep the well shut-in.

The gas produced in the Ohio field test contained 17% nitrogen. During project precommissioning, a series of well tests showed the volume of gas in the field was significantly smaller than expected and the nitrogen content of some of the wells was high at 25% to 30%. After evaluating the revised cost of the project, Butcher Energy decided the plant would not be economic and withdrew from the project.

MTR and Randall sought to demonstrate the technology further with a final test at facilities operated by a small independent company, North Texas Exploration (NTE), in a Texas/Oklahoma natural gas field. This effort involved upgrading a 1-MMscf/d gas stream



Figure 6. Twin Bottoms LLC unit installed at Louisa, Ky.

with a 24% nitrogen content to 4% nitrogen for pipeline delivery. Flow rates proved inadequate, and the NTE installation was halted and the system moved to Houston for storage.

MTR has signed a contract with Towne Exploration, Isleton, Calif., supplied a system to the company and successfully started up the system for processing 2

MMscf/d in a semi-commercial environment.

Two commercial installations have been operating since the Ohio field test:

- one commercial proof-of-concept system was installed to fractionate a small gas stream containing as much as 6% nitrogen into a 3% nitrogen gas stream, to be used in a fuel cell, and a high nitrogen residue gas, to be used as boiler fuel. This unit has been operating without attention in a virtually maintenance-free mode for 3 years; and
- a second commercial installation, in a wellhead configuration for Twin Bottoms LLC at Louisa, Ky., has been



Figure 5. Methane/nitrogen selectivity as a function of gas temperature in lab tests vs. field tests at Butcher Energy's Ohio gas field.

online virtually 100% of the time since November 2004 (Figure 6).

Four more units have been sold since late 2005, bringing to six the total number of commercial units that have been sold based on the MTR nitrogen/natural gas separation technology developed during the project.

The promising field test data thus far and the early success at commercialization show that small, independent producers have another option aside from shutting in wells when it comes to high nitrogen content natural gas. That opens the potential for adding a significant increment to America's natural gas reserves. \diamondsuit

Performance, Costs of Membrane Nitrogen Rejection Process					
	Configuration A	Configuration B			
Process Characteristics					
N_2 in feed, %	8	15			
Feed flow rate, MMscf/d	10	10			
N ₂ in product gas, %	4	4			
Methane recovery, %	86	86			
Methane in fuel gas, %	87	75			
Methane in waste gas, %	50	35			
Product gas flow rate, MMscf/d	8.2	7.6			
Power requirements					
Power required, Hp	750	2,000			
Capital, operating costs					
Equipment cost, \$1,000	1,800	3,500			
Processing cost, \$/Mscf	0.27	0.56			

PUBLICATIONS

► GAS HYDRATE R&D

The U.S. Department of Energy (DOE)/National Energy Technology Laboratory maintains a Web site describing its gas hydrates program at www.netl.doe.gov/ technologies/oil-gas/FutureSupply/ MethaneHydrates/maincontent.htm/ Recent publications related to the government's gas hydrate research and development (R&D) program include a quarterly newsletter highlighting methane hydrate R&D efforts around the world, Fire in the Ice. The December 2006 issue is available for downloading at http://www.netl.doe.gov/technologies/oilgas/FutureSupply/MethaneHydrates/newsletter/n ewsletter.htm where interested individuals can also subscribe.

Also available on the site are downloadable copies of topical and technical reports by private research partners. Recent reports added to these pages include:

- Chevron/DOE Joint Industry Project (JIP) Cruise Report: a 196-page report describing the scientific activities and findings of the shipboard science team from the March 2005 expedition of the Uncle John;
- *JIP Semi-annual Report*: a 143-page report outlining the findings of the JIP through March 2006; and
- *BP/DOE* Alaska North Slope Resource Characterization Project Semi-Annual Report: a 222-page report describing the

scientific activities and finding of the project through June 2006.

To access these and other project information, please visit www.netl.doe.gov/methanehydrates and click the link Methane Hydrate Projects under the section Key links.

SEVERAL NEW EIA REPORTS AVAILABLE ONLINE

The Energy Information Administration has recently published two informative reports related to natural gas.

Technology-Based Oil and Natural Gas Plays: Shale Shock! Could there be Billions in the Bakken? presents information about the Bakken Formation of the Williston Basin, including production, geology, resources, proved reserves and the technology being used for development. This is the first in a series intending to share information about technology-based oil and natural gas plays. Released 11/8/2006.

U.S. Underground Natural Gas Storage Developments: 1998-2005 examines the current status of the underground natural gas storage sector in the United States and how it has changed since 1998, particularly in regard to deliverability from storage, working gas capacity and ownership. Released 10/17/2006.

Both of these reports are available at http://tonto.eia.doe.gov/reports/reportsD.asp?type =Natural%20Gas/

Events

SPE ICoTA Coiled Tubing and Well Intervention Conference and Exhibition

March 20-21, The Woodlands, Texas. Held at the The Woodlands Waterway Marriott Hotel & Convention Center. *www.spe.org*

► AAPG ANNUAL CONVENTION AND EXHIBITION

April 1-4, Long Beach, Calif. Held at the Long Beach Convention & Entertainment Center. For more information, visit www.aapg.org

OFFSHORE TECHNOLOGY CONFERENCE

April 30 – May 3, Houston. Held at the Reliant Center at Reliant Park. For more information, visit www.spe.org

SEG INTERNATIONAL EXPOSITION AND 77TH ANNUAL MEETING

Sept. 23-28, San Antonio, Texas. For more information, visit www.seg.org

SPE ANNUAL TECHNICAL CONFERENCE AND EXHIBITION

Nov. 11-14, Anaheim, Calif. Held at the Anaheim Convention Center. For more information, visit www.spe.org

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