GasTIPS®

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Technology Developments in Natural Gas Exploration, Production and Processing

A Publication of Gas Technology Institute, the U.S. Department of Energy and Hart Energy Publishing, LP

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Commentary

Giving Good Ideas a Boost

Part of the U.S. Department of Energy's National Energy Technology Laboratory's (NETL) primary mission is to "*…resolve supply, reliability and environmental constraints of producing and using fossil energy resources.*" In similar fashion, the Gas Technology Institute (GTI) seeks to *"provide U.S. gas produces with technology solutions that reduce cost and increase natural gas resources…"* Results of research performed or funded to further these goals as it specifically relates to natural gas exploration and production, are what *GasTIPS* is designed to disseminate. NETL and GTI efforts to resolve the constraints of producing fossil resources include a mixture of longer-term, basic research targeting fundamental challenges and shorter-term efforts that help to advance ideas more quickly into solutions for domestic producers.

Workers prepare to shoot seismic in Wyoming.

This mix is particularly important in the case of natural gas for two reasons. First, the U.S. gas resource is a mixture itself. Natural gas reservoirs in the United States vary from tight sands and coals of the Rocky Mountains, to the fractured shales of the Appalachians, to the high productivity formations of the Gulf of Mexico. Productivity rates range from shallow stripper wells producing less than 60 Mcf/d to deep offshore wells making 20,000 Mcf/d. The problems faced by the operators of such widely different wells are just as different.

The second reason is that while some major producers and service companies continue to fund limited applied research in certain areas, the problems of the small independent producer are much less likely to get attention. While upstream exploration and production research funding has declined during the past 10 years, funding for efforts focused on low-volume gas producers (such as GTI research) has dropped even quicker. At the same time, small producers need solutions to keep properties producing day to day. Thus, finding ways to keep our less-prolific wells producing in the meantime is important. Often, relatively small amounts of funding can help boost promising ideas to a stage where the marketplace can evaluate them. In many cases, these ideas address the problems of smaller domestic producers.

For example, a small company had an idea for a hydraulically driven diaphragm pump that could be used to pump debris-laden fluids from wells. Pumping Solutions Inc. (PSI) believed this device could be employed in stripper gas and oil wells to sweep debris to the surface, reducing the need for costly cleanouts. With funding from the NETL-supported Stripper Well Consortium (SWC), PSI was able to demonstrate the pump and gather the data needed to prove its potential. The result: Smith Lift LLC is introducing a low volume, submersible diaphragm pump that incorporates the PSI diaphragm-pumping concept. Designed to produce 50 bbl to 400 bbl of fluid per day from depths up to 6,000ft, including up to 2% fines, the pump consumes about one-third the power required to drive a conventional rod or centrifugal pump.

Another example concerns a new tool that helps producers analyze seismic data more accurately and reliably to pinpoint promising hydrocarbon deposits. Called InSpect℠ – for Instantaneous Spectral Analysis – the tool is particularly valuable for evaluation of unconventional gas-bearing formations such as coalbeds, shales and tight sands. Fusion Geophysical and the Oklahoma University Geophysical Reservoir Characterization Consortium worked with GTI to develop the software tool. In simple terms, InSpect "breaks apart" stacked seismic data to yield output data of higher resolution than conventional methods. In beds as thin as 16ft, it can identify reservoir discontinuities not discernible on conventional seismic sections. Just as important, InSpect can more accurately differentiate between gas and brine. Fusion Geophysical offers a service employing InSpect, and GTI is seeking relationships with parties interested in using the tool to evaluate unconventional-gas formations.

In these examples, NETL or GTI provided the leverage needed to introduce a technology for industry review. Maintaining the flow of good ideas is an important prerequisite to maintaining the flow of gas and oil from domestic reservoirs. ✧

The Editors

Faster Drilling, Longer Life: Thermally Stable Diamond Drill Bit Cutters

by Robert Radtke,
Richard Riedel
and John Hanaway,
Technology International Inc.

The U.S. Department of Energy's National Energy Technology Laboratory and Gas Technology Institute are working together to develop advanced drilling systems that employ improved thermally stable diamond drill bit cutters.

Technology International Inc. (TII) manufactures the cutters, known as ENDURUS™ diamond cutters, which differ from previously available thermally stable diamond (TSP) materials in that they maintain sharpness at temperatures up to 2,191°F and are stronger to withstand drilling impact forces. Drill bits employing the new cutters are capable of reducing overall system costs by increasing rates of penetration and bit life. The thermal stability of the cutter is specially suited for economic drilling of hard and abrasive formations where high frictional heat increases the wear rate of conventional polycrystalline diamond cutters (PDC). Thermally stable diamond cutters have not generally been economic because of low rate of penetration with small available sizes that are surface-set in drag bits, and because of insufficient attachment and impact strength in the larger self-sharpening PDC configurations. TSP material, with significantly increased fracture resistance, can now be brazed with high attachment shear strength using microwave and combustion synthesis brazing. Newly developed TSP manufacturing processes result in a 36% increase in fracture resistance and an attachment shear strength greater than 50,000psi. ENDURUS diamond cutters and hard rock drill bit designs have been tested at the Sandia National Laboratory and Diamond Innovations Inc. Cutter Wear Facilities. Hard rock drill bit tests have been performed at the Terra Tek Drilling Laboratory simulating deep drilling conditions. A special hard rock drill bit also was tested at Gas Technology Institute's Catoosa test well. Field tests are planned at locations

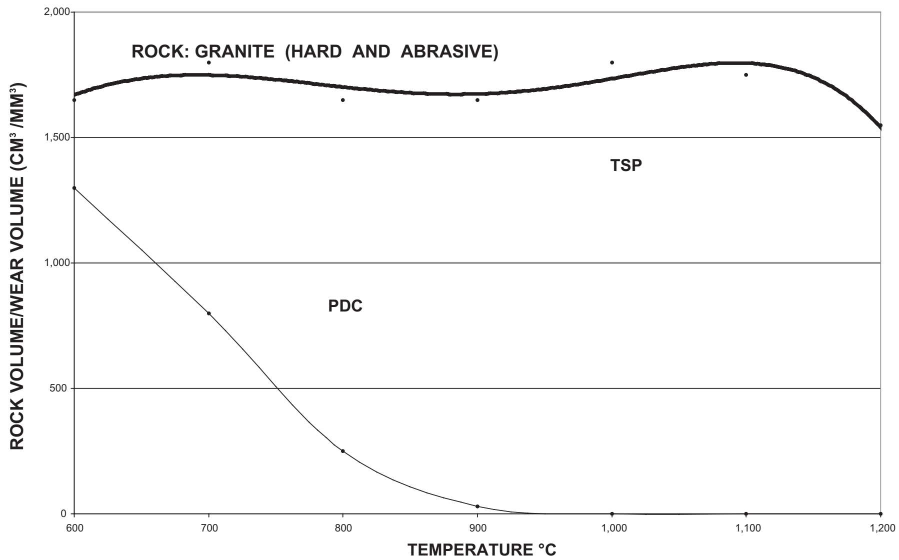


Figure 1. Effect of PDC and TSP cutter temperature on wear rate.

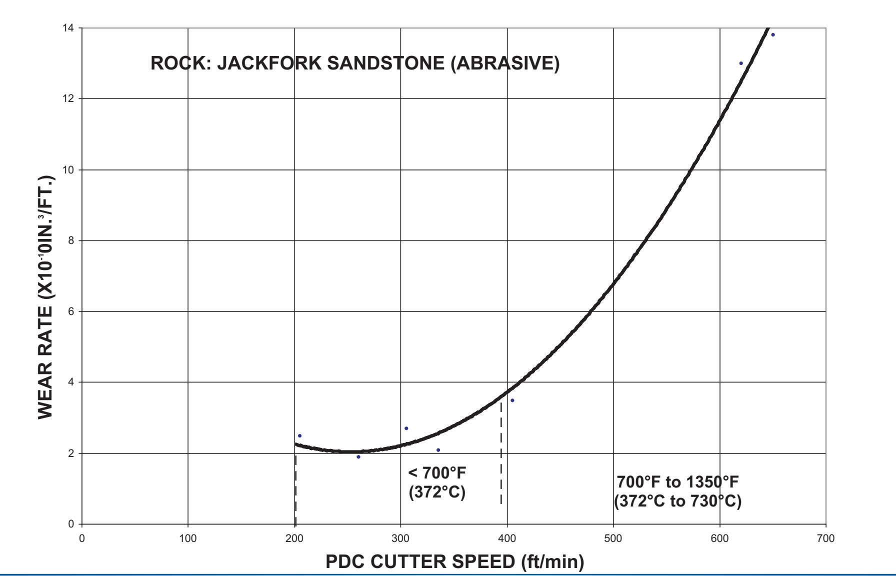


Figure 2. Effect of PDC cutter speed on wear.

including the Rocky Mountain Oilfield Testing Center. Drill bit rates of penetration can be doubled using ENDURUS diamond cutters in hard and abrasive rock. This reduces well drilling costs by about 15%, with overall drilling project cost savings of 7.5%.

The high frictional heating associated with hard and abrasive rock drilling applications creates cutter tip temperatures that exceed the thermal stability of PDC. Figure 1 shows that the PDC wear rate when cutting hard granite greatly exceeds that of the TSP at temperatures above 932˚F. Additional evidence is shown in Figure 2, whereby increases in the PDC cutter linear speed and cutter temperature in Jackfork Sandstone result in exponential increases in PDC wear rate at temperatures greater than 700˚F. The relative drilling rates for the tri-cone, PDC and impregnated diamond bits vs. revolutions per minute (rpm) is illustrated in Figure 3. As shown for the TSP bit, the potential for superior performance may be in well-stabilized moderate to high rpm applications. The TSP bit will be the fourth-generation drill bit for petroleum and geothermal drilling applications.

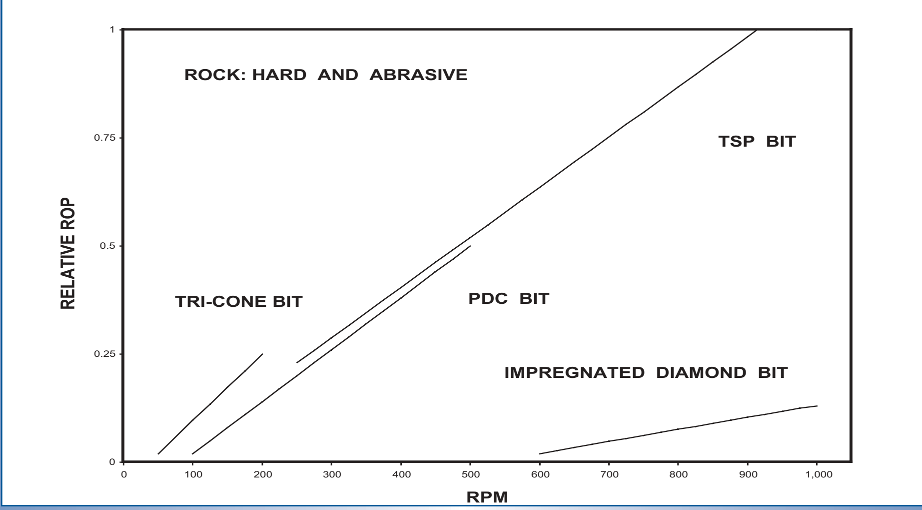


Figure 3. Effect of bit type and revolutions per minute on relative rate of penetration.

Background

GE Superabrasives made the PDC material available to the petroleum bit industry in 1972. During 5 years of brazing process, development was required before new metallurgy enabled required shear strengths greater than 50,000psi between PDC and cobalt-bonded tungsten carbide substrates. In 1979, a drag bit brazing process was developed for attaching the PDC cutter to a matrix-type drill bit. During the early 1980s, there were two commercially available TSP materials – one was a slightly porous polycrystalline diamond produced by acid leaching the thermally incompatible cobalt binder, and the other was a polycrystalline diamond with a thermally compatible silicon carbide binder. There also are cutters with a thermally stable diamond layer on a PDC substrate.

Since the early to mid-1980s, the petroleum drilling industry has been aware of the need for larger TSP cutters with a strong support/attachment bond. It also has been known that an increase in attachment shear strength alone would not provide the impact strength desired.

Conventional brazing techniques produce insufficient TSP to cobalt-bonded tungsten carbide substrate braze strength (20,000psi to 35,000psi). Diamond stress cracking occurs because of the difference in thermal expansion of the two materials.

Technical path

The methodology to develop TSP cutters with sufficient attachment and impact strength is as follows:

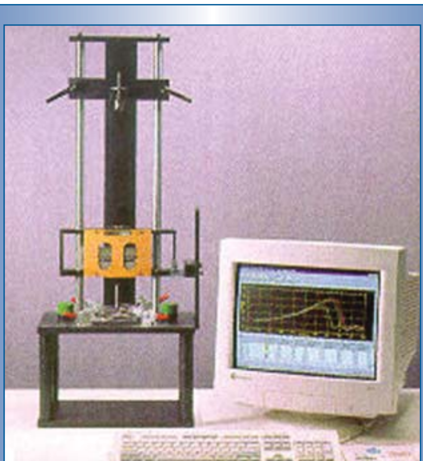
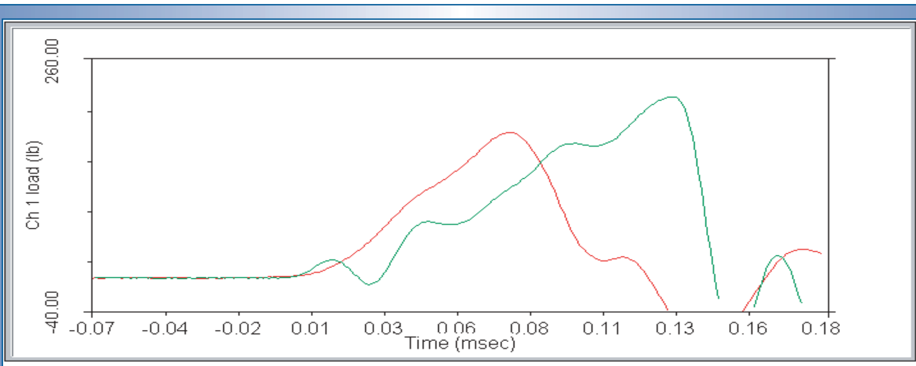


Figure 4. An instrumented drop weight impact tester is shown above.



	Impact energy (1) (ft-lb)	Impact velocity (1) (ft/sec)	Maximum load (1) (lb)	Energy to max load (1) (ft-lb)	Total energy (1) (ft-lb)	Batch ID
(red)	0.2572	2.43	173.08	0.0137	0.0220	PZ-060-01
(green)	0.2577	2.43	215.16	0.0290	0.0332	PZ-060-01T

Figure 5. The above graphic shows increased fracture resistance of an ENDURUS diamond (green) compared with an conventional thermally stable diamond (red).


Figure 6. Sandia National Laboratory hard rock test facility.

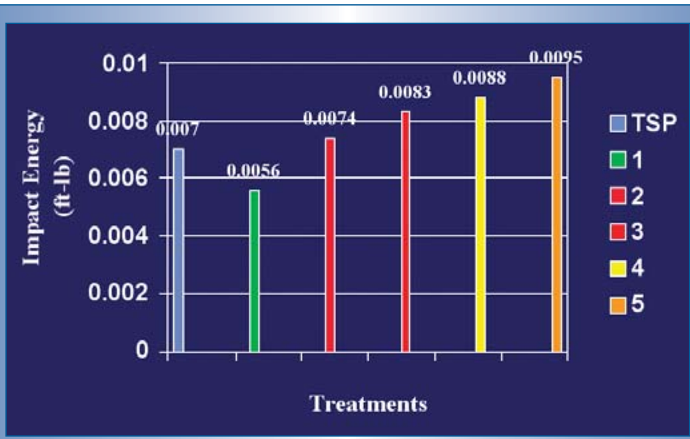


Figure 7. The effect of treatments on TSP diamond impact strength.

- characterize critical physical properties of commercially available TSP materials;
- perform finite element modeling to calculate the nature and magnitude of residual thermal stresses as a function of brazing parameters and cutter design;
- develop TSP to cobalt-bonded tungsten carbide brazing methods that control residual thermal stress, prevent TSP cracking during cool-down and achieve attachment shear strength greater than 50,000psi; and
- produce TSP materials with more than 30% fracture toughness and new cutter designs that exhibit sufficient impact resistance while cutting hard and abrasive granite rock.

This article will report on five aspects of the TSP cutter development process:

- finite element modeling;
- unique brazing techniques;
- increased fracture resistance;
- laboratory hard rock drilling; and
- hard rock drill bit testing.

Finite element modeling

The purpose of this investigation was to calculate the thermal residual stresses developed in TSP joints using a finite element model. TSP discs are brazed to tungsten carbide cylinders using a braze filler metal at high temperatures. Residual thermal stresses then develop during cool-down from the brazing temperature. Conventional brazing processes can result in delamination/debonding between the diamond and the tungsten carbide components or cracking and failure of the diamond during usage. These failures result from residual stresses generated during cooling from the brazing temperature to room temperature because of the considerable differences in three physical properties of diamond and tungsten carbide – coefficient of thermal expansion, Young's modulus and Poisson's ratio. Brazing of TSP discs to tungsten carbide could be a viable process if a means were developed to control thermal residual stresses, principally in the TSP layer.

Upon cooling from the braze temperature, the diamond and tungsten carbide components contract at different rates because of the difference in the thermal expansion coefficients. Assuming an unconstrained differential shrinkage, the tungsten carbide will shrink to a larger extent than the diamond. But, in practice, the two pieces are joined together with uniform radial tensile and compressive stresses imposed on the tungsten carbide and diamond, respectively. To achieve displacement compatibility, the total force remains zero. Bending also is allowed to occur to balance such a moment induced by the asymmetric stresses. If the extent of bending is large, then the diamond layer will crack.

Finite element modeling was performed to determine the magnitude of the critical thermal residual stresses that would occur during conventional vacuum furnace brazing. When critical, the stress was found to be sufficient to cause the diamond to crack. With the assumption the TSP and tungsten carbide are uniformly heated, conclusions of the study were as follows:

- critical stresses in the TSP increase with raising braze temperature. Braze temperatures in excess of 1,292°F can cause the TSP to crack; and
- critical residual thermal stress occurs in the TSP with braze filler metal thickness of less than 0.002-in.* The thicker the braze layer, the greater the stress relaxation, with a maximum occurring when the braze layer deformed plastically.

* It should be noted that the advantage of the microwave and combustion synthesis brazing methods is to attain maximum attachment shear strength using a braze filler metal thickness of 0.002-in. and less.

Brazing techniques

Novel methods for brazing TSP to tungsten carbide have been developed:

- microwave heating;
- combustion synthesis using the self-propagating high-temperature synthesis reaction of nickel and titanium; and

- combinations of the above.

Each process results in preferential heating of the lower thermal expansion TSP. Both methods provide the ability to have the dissimilar material pair shrink compatibly on cool-down.

Microwave brazing—When TSP discs are brazed to cobalt-bonded tungsten carbide substrates, high residual thermal stress develops during cool-down. The microwave brazing method has the capability to control the magnitude of thermal residual stresses when joining these dissimilar materials. The process results in preferentially heating the lower thermal expansion TSP, thus providing the ability to match the thermal expansion of the dissimilar material pair. This unique microwave brazing technology was granted U.S. Patent No. 6,054,693 and the inventors received the NASA 2002 Space Act Award for Innovation.

Combustion synthesis brazing—Combustion synthesis brazing is achieved by putting a multi-layer deposit of titanium and nickel between the TSP and the tungsten carbide. A conventional braze alloy foil can be placed over the multi-layer titanium-nickel (Ti-Ni) coating in some cases. On heating the assembly, a combustion (exothermic) reaction occurs between Ti and Ni, and this heat generated preferentially heats the TSP because of its higher thermal conductivity. The brazing temperature is controllable and designed to join the TSP to tungsten carbide with high attachment shear strength.

Fracture resistance

An Instron Instrumented Impact Tester (Figure 4), was used to measure the impact energy required to plunge a 0.037-in. diameter flat-end diamond striker through the center of 0.539-in. diameter TSP discs. The discs were supported circumferentially over a hole in a steel test block. With a selected mass above the striker, the impact device was released. As the striker passed through a light gate, its velocity was measured. A piezoelectric sensor positioned above the striker measured the vertical force, and a graph of force vs. time was then prepared. The impact energy required to fracture the sample also was calculated as the integral of the area under the curve. Figure 5 shows the increased fracture energy as a result of new metallurgical processes being applied to conventional TSP diamond materials. This test technique is being presented to the ASTM Committee 28C on Advanced Ceramics for adoption as a standard test for PDC and TSP materials.

Hard rock drilling tests

Drilling tests on ENDURUS diamond cutters were conducted at the Sandia National Laboratories' Hard-Rock Drilling Facility (HRDF) shown in Figure 6. A 3ft x 3ft x 3ft Sierra White Granite block was drilled at 30ft/hour with varying bit weight and 100 rpm applied to a 3.25-in. core bit. The bit had three approximately 0.5-in. diameter cutters. The TSP test cutter was in the center of the bit kerf, and outside and inside cutters were replaced periodically to maintain bit balance. The TSP cutter was inspected under magnification for microcracking after drilling each 3-ft hole.

Fracture resistance testing

New metallurgy this project discovered has significantly increased the impact resistance of the TSP cutter. The objective to increase the fracture resistance of TSP was achieved (Figure 7). Measurements with the Instron Instrumented Drop Weight Impact Tester showed that specially treated ENDURUS diamond fracture resistance could be significantly increased. The untreated TSP required impact energy of 0.007 ft/lb to fail. The first treatment was not beneficial, with a value of only 0.0056 ft/lb. The next four treatments yielded increases in impact energy from 0.0074 ft/lb to 0.0095 ft/lb, up to a 36% increase.

Laboratory hard rock drilling tests

Specially treated and brazed ENDURUS diamond cutters have superior impact resistance in laboratory hard rock cutting tests. Typical impact damage to the conventional TSP cutter in laboratory and field applications is illustrated in Figure 8. The fracture pattern has been observed in laboratory and field drilling tests, and has been called a "halo crack" or "edge chipping." While barely visible under magnification, it was necessary to draw a dash line on the photograph below to illustrate the location of the microcrack. The fracture extends across the higher stress area of the rock cutting edge.

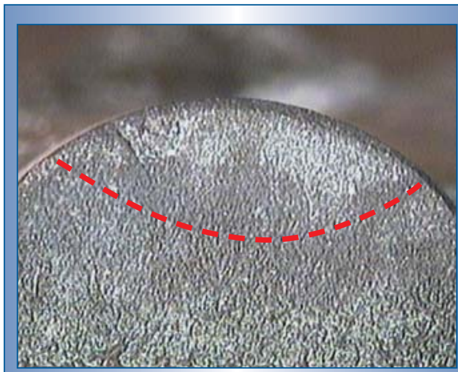


Figure 8. The above photo shows typical impact damage to a conventional thermally stable diamond cutter.

Figure 9. The above photo shows no impact damage to the improved thermally stable diamond cutter.

Initially, conventional and specially designed diamond cutters were tested using a typical standard industry impact test. In this test, cutters are mounted on the rotating head of a horizontal mill. With the cutter rotating at 300 rpm, an interrupted cut in a 3.58-in. cube of berre granite was made with each rotation. During each pass, a 0.03-in. layer of rock was

Figure 10. The ENDURUS diamond cutter.

removed from the surface of the rock. The untreated TSP cutter had the usual halo crack pattern after the removal of the first layer of rock. ENDURUS diamond cutters with improved fracture toughness removed 15 layers of granite with no visual cracking before the test was terminated.

Drill bit tests employing these cutters at HRTF also have shown that halo cracking did not occur with a combination of metallurgical treatments (Figure 9).

The diamond cutter shown in Figure 10 consists of a 0.526-in. diameter x 0.138-in. thick ENDURUS diamond brazed to a tungsten carbide substrate.

Hard rock drill bit tests

Initial testing of special hard rock drill bit at the GTI Catoosa Test demonstrated the performance needed for the design of a successful drill bit employing ENDURUS diamond cutters. The design and fabrication of an improved drill bit employing these diamond cutters was successfully tested in simulated deep drilling of a hard and abrasive rock at the Terra Tek Drilling Laboratory.

Conclusions

Based on finite element modeling calculations, when using uniformly-heating brazing methods, TSP to cobalt-bonded tungsten carbide joint residual thermal stress increases with increasing braze temperature when using a smaller thickness of braze filler metal. Therefore:

- the lowest permissible brazing temperatures should be used consistent with attaining maximum attachment shear strength; and
- the filler metal thickness to preclude delamination or TSP fracture must be 0.002-in. or greater.

Microwave brazing, combustion synthesis brazing or combinations thereof are capable of producing ENDURUS diamond cutters with controlled levels of residual thermal stress:

- the attachment shear strength was more than 50,000psi.

Specially treated ENDURUS diamond cutters had superior impact strength in laboratory hard and abrasive rock drilling tests:

- the instrumented drop weight impact data indicated a 36% increase in fracture resistance;
- ENDURUS diamond cutters with improved fracture resistance demonstrated superior impact resistance; and
- microcracking was not observed in the laboratory when drilling White Sierra Granite at 30ft/hour.

The increased durability of the ENDURUS diamond cutter sanctions geothermal and petroleum drilling field tests to prove applicability in conjunction with suitable operating parameters, and, perhaps, unique bit designs:

- testing of a special drill bit at the GTI Catoosa Field test well demonstrated its applicability to the use of the ENDURUS diamond cutter for rock drilling;
- testing of the above diamond cutter has been completed at the Terra Tek Drilling Simulator for deep hard and abrasive rock drilling; and
- field tests of the hard rock test bit will include the Rocky Mountain Oilfield Testing Center.

For more information, contact author Robert Radtke at *radtke@kingwoodcable.com* or (281) 359-8520; or Bill Gwilliam at *william.gwilliam@netl.doe.gov* or (304) 285-4401.

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Real Time Half Duplex Communications Wireless Gauge with Downhole Power Monitors Deep Well Gas Production

by Scott Kruegel
and Paul Tubel,
Tubel Technologies Inc.;
and Gary Covatch,
U.S. Department of Energy/National Energy Technology Laboratory

The high-temperature, high-pressure system utilizes acoustic waves for communications, and low-power electronics and sensors to acquire and process in real-time data related to production and geological formation parameters.

Monitoring and control of the processes required to produce hydrocarbons constitutes an ongoing industry concern, which is partly because of the expenses and risks associated with the execution of those processes, as well as environmental and safety factors. The ability to provide wireless monitoring of wellbore parameters also has increased completion reliability and decreased completion costs. In an effort to address these issues, Tubel Technologies was funded by the U.S. Department of Energy's National Energy Technology Laboratory to develop a new real-time downhole wireless pressure and temperature gauge for the optimization of natural gas production. This system utilizes the production tubing as the medium for the transmission of the information from downhole to the surface.

The complexity and cost of exploring for oil and gas has increased significantly during the past few years because of intelligent wells, multilaterals and deep gas field developments. New challenges for drilling, completing, producing, intervening in a well, environmental regulations and wide swings in oil prices have changed the role of technology in the oil fields. The industry is relying on technology to affect the costs of exploring for hydrocarbons in the following ways:

- *reduce operating expenses* by automating the processes used to explore and produce hydrocarbons, reducing the frequency of unplanned intervention, and improving information and knowledge management to decrease operating inefficiencies;
- *increase net present value* by providing systems that enhance the recovery of hydrocarbons from reservoirs. The new technologies improve production techniques to delay and/or reduce the production of water from downhole; and
- *reduce capital expenditures* by creating processes that will decrease the number of wells drilled and reduce the number of surface facilities required. The surface equipment requirements to handle increasingly larger quantities of hydrocarbons at these facilities should also decrease with the implementation of new technologies.

New processes for drilling, completion, production, artificial lift and reservoir management have been created by advancements in technology in fields such as high temperature sensory, downhole navigation systems, composite materials, computer processing speed and power, software management, knowledge gathering and processing, communications and power management. Horizontal drilling and new fracture techniques have allowed operators to produce hydrocarbons profitably from areas uneconomical just a few years ago.

Sensor technology in conjunction with data communications techniques provide on-demand access to the information necessary to optimize hydrocarbon production levels and achieve costs goals. Surface and downhole sensors are changing the way hydrocarbons are produced by optimizing production from downhole, supporting and extending the life of artificial lift systems and providing information used to update reservoir and production models.

A new technology that combines sensors with wireless telemetry provides the operators with new versatility and capability to place sensors in areas of the wellbore that were prohibitive because of technical difficulties and/or economic justification. The ability to communicate in and out of the wellbore using wireless systems can increase the reliability of the production system and decrease the amount of time required for the installation of the completion hardware in the wellbore. The elimination of cables, clamps, external pressure and temperature sensors, as well as splices on the cable that can fail inside the wellbore, provides a significant advantage to existing gauge technologies.

The wireless wellbore digital data communications and sensing system provides the capability to communicate through the production tubing using stress waves to transmit and receive digital data and commands

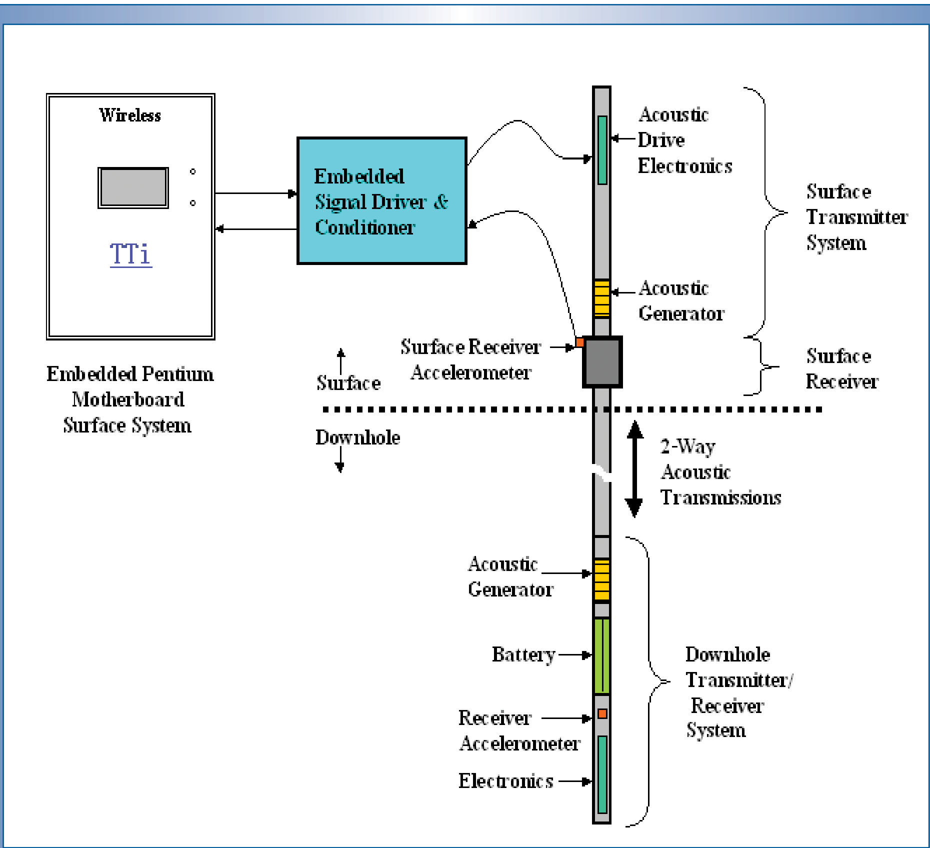


Figure 1. A two-way communication wireless gauge well configuration block diagram is shown above.

inside the wellbore. The system provides information from inside the wellbore that is transmitted at intervals determined by the customer and programmed before the tool is inserted in the well. The downhole system is composed of the wireless transmission hardware, microprocessor system for data acquisition and power management, pressure and temperature gauges and a power generation unit. The surface system is composed of a detection and transmission module and a surface supervisory control and acquisition box for data acquisition and processing. Figure 1 shows a block diagram of the two-way communication system.

The wireless gauge hardware creates the acoustic signals from electrical pulses generated by the electronics system after the sensor information is digitized. The acoustic waves are coupled to the production pipe minimizing the amount of energy losses having a tight fit between the acoustic generator and the production pipe. The waves traveling up the pipe to the surface are immune to losses related to fluid coupling and tubing threads.

The electronics system provides the process control, data acquisition, data processing, data encoding, command decoding and operator interface. The system provides a power saver mode while in the wellbore to maximize the downhole power efficiency. The electronics sample and digitize the information from the gauges at specific time intervals programmed before the tool is deployed inside the wellbore. The data is processed and encoded for transmission to minimize the number of bits of data required to be sent to the surface. The microprocessor then generates the electrical pulses used to drive the acoustic generator to produce the information related to the pressure and temperature data obtained inside the wellbore. Upon completion of the information transmission to the surface, the processor places the tool in a power saver mode until it is awoken to perform the data acquisition tasks again. The system also can receive commands from the surface, and an acoustic detector wakes the processor for the data acquisition and process.

The sensors are composed of silicon on sapphire pressure gauges and thermocouples for sensing temperature. The sapphire gauges provide high-resolution pressure measurements on the annulus and tubing while the thermocouples inside the pressure assembly measure temperature for pressure compensation and well monitoring. This new sapphire technology eliminates the well fluid coupling requirements to maintain the sensor assembly free of well contamination. The sapphire is in constant contact with the wellbore fluids to provide a more accurate measurement of the pressure. Higher stability also is a major advantage of the sapphire gauges to strain gauges, as the gauges are built into the tool eliminating any outside connections.

The surface system provides data acquisition, processing, storage and display capabilities for the data received from inside the wellbore. The surface system is composed of three modules:

- *surface data detection transmission on tubing*—A surface module attached to the wellhead or just below the surface is used to detect the transmitted downhole signal. It converts the signal from an acoustic wave into digital electrical pulses transferred via surface cable to the data processing module. It also converts electrical pulses into acoustic commands;
- *surface processing module*—This provides the data acquisition, processing, display and interfaces to a pump controller or a computer. The data received from the acquisition module is conditioned and pre-processed to eliminate noise. The data is next processed in the time

domain to obtain the actual parameter values gathered by the sensors inside the wellbore. The information is converted into 4-miliamp to 20-miliamp analog signals to be transmitted to a pump controller or recorder. The information also is converted into Modbus protocol data stream to be transferred to other computer systems; and

- *a personal computer* (PC) interfaces with the surface-processing module to obtain the downhole information. A software package for the PC processes the data for viewing the information in a graphical mode or in a tabulated format.

The wireless communications tool does not disrupt the flow of production fluids because it provides full tubing inside diameter. Since the signals are carried by stress waves in the production tubing, the data is virtually unaffected by the well fluid.

There are four issues that affect the system performance:

- *the strength of the data signal that can be produced*—The higher the energy generated inside the tool because of voltage levels and transmitter/tubing coupling, the longer the distance between the transmitter and receiver modules;
- *the attenuation of the transmission path*—The pipe being in contact with casing over extended lengths affects the wellbore signal path. The tubing has to be continuous from the tool to the surface for the signal to reach the surface detector;
- *the allowable signal- to-noise level for data acquisition*—The signal levels have to be in the micro g's (g is equal to the acceleration of gravity at 9.81m/second^2) for the surface system to detect the acoustic data on the tubing. The downhole tool power level has to be designed to assure the acoustic signal will have a level high enough to be detected by the surface hardware; and
- *the noise environment of the well*—The signal-to-noise ratio (SNR) in the passband of the surface system's filters is critical for communication. The SNR must be maintained above a certain level for the packets to be correctly decoded by the surface system.

The advantages of an acoustic wireless gauge can be compounded if the capability for two-way communications is added. Communication parameters such as data refresh rates and sensor selection must be set at the surface before deployment and cannot be modified until the gauge is recovered. The ability of a gauge to receive surface communication removes this limitation, since a command set allowing communication parameter modification can be implemented. The first command to have been implemented was an asynchronous request for a sensor reading. This significantly reduces power consumption, since sensor readings are taken only when required. Another potential command includes changing communication parameters such as transmission frequency. This is useful because each well has a unique acoustic profile and ambient noise environment. Modifying the transmission frequency in use allows communication even in a dynamic noise environment. Selecting a transmission frequency also allows multiple gauges to be deployed in a well with a single surface transceiver for the entire gauge set.

Half-duplex surface system

The major subsystems include an acoustic transmitter, an acoustic receiver, an amplifier, an analog to digital converter and a Pentium-based processor board.

The acoustic receiver was implemented as a 5-g accelerometer along with the required drive circuitry. The output from the accelerometer was fed into a variable gain amplifier stage, where it was amplified by about 2000. The exact gain provided by the amplifier was determined by the intensity of the signal received from the half duplex gauge. The gain was chosen to maximize the SNR without saturating the amplifier.

The output of the amplifier stage was fed into the analog digital converter (ADC), which was operated at a sampling frequency of 11,025 Hz with 16-bit resolution. Decoding software, which is user-configurable and not highly sensitive to absolute gain level, processed the data acquired from the ADC.

The decoding software was implemented as a set of interlocking finite state machines, each of which handles a different level of the communication protocol. For example, there is a separate state machine for bit detection, received packet formation and received packet validation. Bit detection is accomplished by a time-frequency transform, accompanied by energy level hysteresis for noise immunity and energy level debouncing to avoid detection of false bits. Packets are constructed by concatenating a fixed number of bits. Packet validation occurs by throwing away any packet that does not conform to the defined packet structure.

For communication in the opposite direction, there is another set of software modules responsible for encoding packets. Again, interlocking state machines were used to generate packets, with each protocol layer represented by a separate state machine. Some of the more important transmission machines include bit generation and transmitted packet formation.

The acoustic transmitter consists of an electronic driver module, a transformer and an acoustic generator. These components are identical to those in the half-duplex downhole gauge. Since power consumption is not an issue at the surface, transmitting at the maximum level of output can optimize transmission.

Half-duplex wireless gauge

Surface panel application development is relatively straightforward, since, for all practical

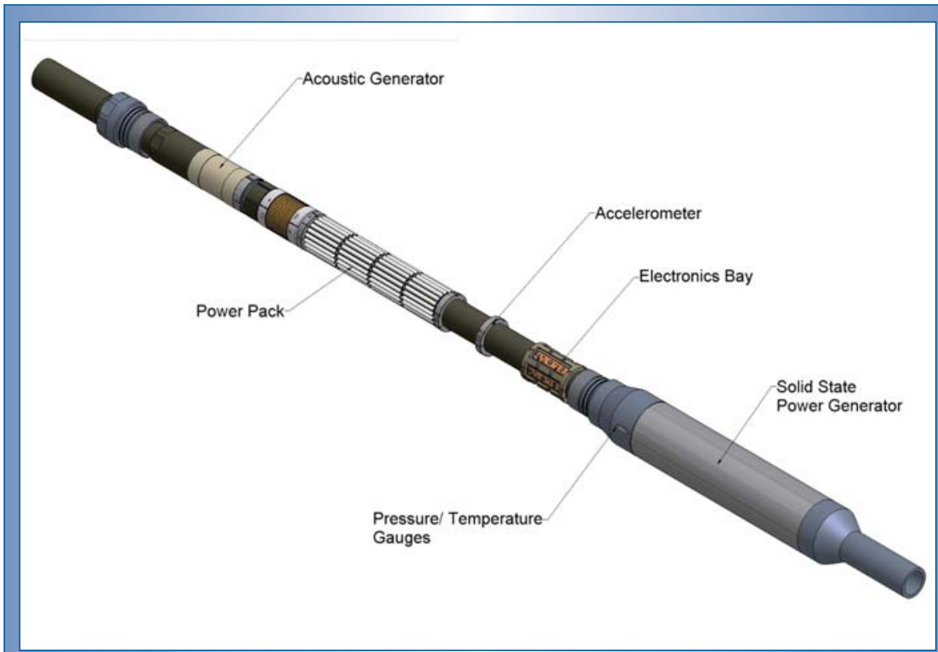


Figure 2. The above graphic shows a half-duplex communications self-powered downhole wireless gauge.

purposes, there are unlimited resources in terms of memory, processing power, storage, etc. Downhole application development has none of these advantages. Instead, the downhole tool is limited in memory, sampling resolution and especially processing power.

The processor has eight integrated A/D converters capable of 10-bit resolution, which is a limiting factor in tone detection, since it corresponds to a dynamic range of only 60 dB. The surface system used had a 16-bit A/D with a corresponding dynamic range of more than 96 dB.

The processor is being operated as a microcontroller, which means the internal random access memory (RAM) is being used. There are 1,536 bytes of internal RAM, which limits the size of the sampled data array that can be processed. Since sampling must continue during processing, two data buffers are required: one for signal processing, and one for current data acquisition. This can be compared with the RAM available to the surface system, 512 MB.

Figure 2 shows the schematic of the half-duplex wireless gauge.

Downhole power generator

The downhole power generator was designed to be part of the wireless gauge mandrel to reduce the length and cost and increase the system reliability. The power generator was designed to provide a direct action between the wellbore and power generator hardware. The new power generator design is solid state and obtains energy from hydrocarbon flow as well as wellbore vibration. The power generator was designed as with a modular approach, where multiple generators can be stacked as part of the downhole wireless gauge based on the amount of energy required in the well. The amount of energy that can be generated is related to flow and vibration levels in the wellbore.

Signal detection algorithms

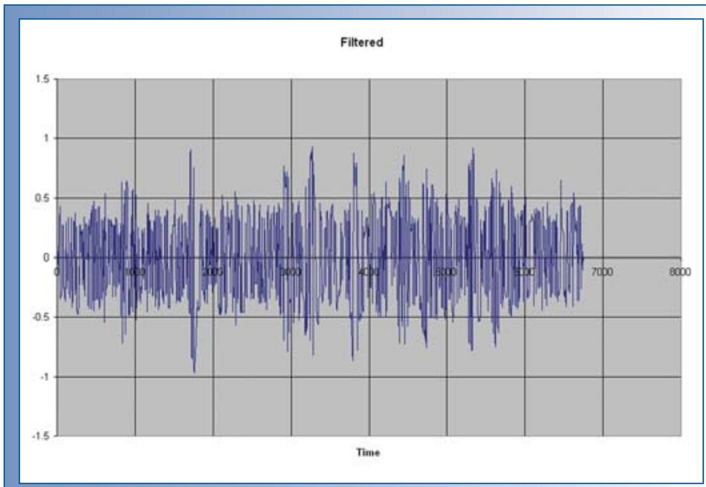
Since many off-the-shelf implementations exist for the fast Fourier transform (FFT), the first time-frequency transform tested was the FFT. Most of these implementations are floating point, since rarely do applications have the resource limitations listed above or are required to operate in real time. For development speed, one of these implementations was modified for our application.

The frequency of the signal for the purpose of this article determined the sampling rate, which combined with the duration of the signal led to the bin size. The result of the testing showed the algorithm was highly successful in signal detection. Unfortunately, processing a single bin took more than a second, which exceeds the available time.

To reduce the processing time, the floating point software was converted to a fixed point. Although it reduced processing time significantly, bin processing still exceeded the maximum acceptable. The next step in increasing efficiency was to truncate the 10-bit input from the A/D converter to eight bits so single-cycle multiplications could be used. The maximum acceptable processing time was still exceeded. No further efficiencies could be identified, so algorithm testing switched to Goertzel's algorithm. Although this does not provide information about the entire spectrum, it is highly efficient for energy detection at a limited number of discrete tones.

Documentation on Goertzel's Algorithm is almost universally based on a floating point implementation. Therefore, development started using a floating point implementation. The first attempt was made using the full 10-bit output of the A/D. Testing showed the speed of processing was still insufficient. To reduce processing time, phase information was ignored. By doing this and discarding the two least significant bits, processing time was reduced to 15 milliseconds, which were significantly below the requirement, so further optimization was not needed. Just as in the case of the FFT, the next step would have been to move to a fixed point implementation.

The integration interval, which also was the basic mechanism for advance in the bit detection finite state machine, was deter-



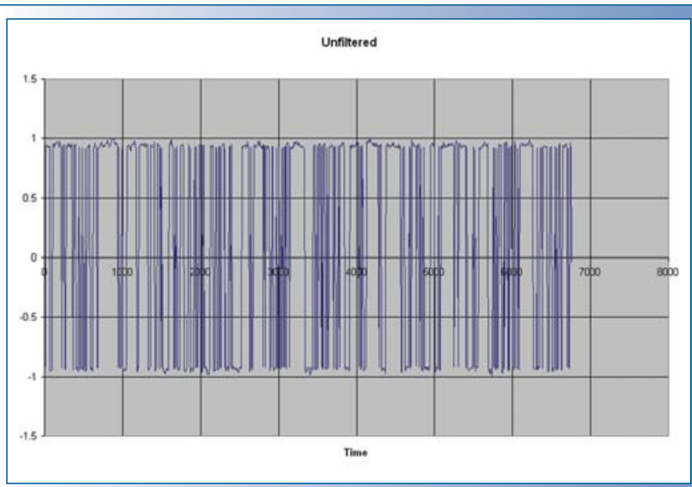


Figure 3 (left) shows the filtered data and Figure 4 (right) shows the digitized unfiltered data.

mined by the bit design and packet structure.

The other input to the finite state machine (FSM) was a threshold energy determined experimentally. Exceeding that energy would allow the FSM to advance, while energy detection below the threshold would lead to a reset of the state machine.

For noise immunity, threshold levels for bit detection and bit absence were used.

Experimental results

On April 26, the prototype gauge and surface system was tested for surface to downhole communications at the north test well at the Carrollton, Texas, facility of Halliburton. The wireless gauge was deployed in the test well using 3½-in. diameter tubing above the gauge. The downhole to surface communications for the wireless gauge had been prreviously tested in a horizontal well at 6,900ft where the completion hardware included packers, sliding sleeve, gas lift valve and safety valve located above the wireless gauge. The system was deployed at 200ft in the well, and the transmitter from the surface to downhole was attached to the top of the tubing string at the surface slips. The surface to downhole transmitter module was connected to the processing panel and the PC. A command was initiated from the computer to request data from the tool. The transmitter transferred the information into the wellbore using acoustic waves. The downhole tool received the acoustic information, processed it and responded to the request for data providing annulus pressure readings.

The downhole module was lowered to 500ft in the wellbore. The surface module was re-attached to the top of the tubing string and a command was transmitted in the wellbore. The downhole acoustic receiver was not capable of detecting the downhole information because of a high software threshold level implemented in the tool. A software modification was performed to lower the threshold to allow the downhole tool to receive smaller signals consequently being able to go deeper in wellbores. With this modification, the downhole wireless gauge should be able to detect acoustic signals transmitted from the surface at distances up to 12,000ft. The wireless gauge evaluation and tests will continue with another well test scheduled for July.

Conclusion

A new downhole gauge has been developed for monitoring deep well gas production. The system is self-sufficient where power, sensors and communications are built as one tool. The new system can provide pressure and temperature measurements and generate power inside the well. A power storage module is capable of capturing, conditioning and storing the energy generated for utilization during the data transmission to the surface. A surface to downhole communications module also was developed to transmit information to the downhole gauge to provide the ability to change data rates or ask for data in a master-slave configuration. A new digital signal-processing module for the downhole tool has been proven to work in the wellbore environment and capable of differentiating signal from noise. It also is capable of detecting and processing the commands issued at the surface.

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The Electrodialysis Alternative for Produced Water Management

by Tom Hayes,
Gas Technology Institute

Twenty billion to 30 billion bbl of produced water are generated each year with the production of oil and gas in the United States. The management of this water, however, produces a costly problem, as large volumes are produced in dispersed locations and must be managed in an environmentally and health-conscious manner.

Produced waters can contain significant levels of inorganic and organic constituents. The waters usually contain elevated levels of total dissolved solids (TDS) concentrations between 2,000 mg/L and 100,000 mg/L. Produced waters also may contain significant concentrations of hydrocarbon compounds including free oil; dissolved oils; volatile acids; and benzene, toluene, methylbenzene and xylene (BTEX). Typical compositions of produced waters are shown in Table 1. Regulations that apply include the Federal Clean Water Act, the Resource Conservation and Recovery Act, and a tapestry of State and Regional environmental, natural resource and water management laws.

More than 90% of produced water generated from oil and gas fields is disposed of using Class II salt water disposal (SWD) wells, which are deemed geologically isolated from potential sources of drinking water. But in a number of regions, such as parts of the Rocky Mountain states, produced water outputs (per field and per unit of energy produced) are significantly increasing, while re-injection capacities are remaining the same or declining because of permitting and wellsite field injection constraints. Discharge of produced waters to surface waters would, in most cases, require control of oil and grease, removal of soluble organics, reduction of suspended solids and demineralization prior to surface discharge under a National Pollutant Discharge Elimination System (NPDES) permit to meet water quality standards. This regional challenge has created concern among producers that if new disposal capacity is not found, the future energy production potentials of certain basins of the Rocky Mountains could be adversely impacted.

An example of how produced water output is beginning to constrain energy production is found in the development of coalbed natural gas in various basins around the United States, such as the Powder River Basin. An extensive review of issues related to coalbed methane (CBM) produced water is provided by ALL Consulting's 2003 handbook and has been the subject of a three-part series in *GasTIPS* (Arthur, *et al*, 2003). As these sources note, management costs for treatment and disposal of produced water severely impact the economics of CBM development in the western United States, where high volumes of produced water and limited SWD injection capacities exist. Desalinization to reduce brine volumes requiring SWD disposal is one of the broad options under consideration. Using this approach, a desalinization process would process each gallon of produced water to generate a small volume of concentrated brine (less than 0.25 gal) and a larger volume (greater than 0.75 gal) of demineralized water that could be discharged to surface waters or used for beneficial purposes, such as irrigation, groundwater recharge, livestock watering and industrial utilization.

Some energy companies have explored using reverse osmosis (Figure 1) to reduce brine volume for CBM waters and conventional gas-well produced water. For both types of produced water, pilot tests have shown that although a 3:1 reduction of brine volume could be achieved, and although a deionized product stream of good quality water could be initially produced, many operational problems involving membrane fouling surfaced in the initial attempts in the field to deploy the technology. These problems arise from the complex composition of the produced water and the effects of certain constituents on the membrane material. Some of these inorganic constituents consist of divalent cations such as calcium and magnesium that form precipitates abrasive to sensitive membranes used in reverse osmosis systems. Free and dissolved oils collect on reverse osmosis membranes, causing them to lose their permeability. Soluble hydrocarbons including volatile acids and BTEX can promote the growth of microbial films on reverse osmosis membrane surfaces, causing them to lose separation performance. These fouling

Table 1. Typical values for produced water quality compared with end-use criteria.

Parameter	End Use Criteria (ppm)			CBM Water	Non-CBM
	Drinking	Irrigation	Livestock		(Conventional Gas Well) Water
pH	6.5 - 8	-	6.5 – 8	7 - 8	6.5 - 8
TDS, mg/L	500	2,000	5,000	4,000 – 20,000*	20,000 – 100,000
Benzene, ppb	5	5	5	< 100	1,000 – 4,000
SAR**	1.5-5	6	5-8	Highly Varied	Highly Varied
Na+ , mg/L	200	See SAR	2,000	500 – 2,000	6,000 – 35,000
Barium, mg/L				0.01 – 0.1	0.1 – 40
Cl - , mg/L	250	-	1,500	1,000 – 2,000	13,000 – 65,000
HCO_3 mg/L	-	-	-	150 – 2,000	2,000 - 10,000

* Total Dissolved Solids (TDS) range estimated for the lower 50th percentile.
** SAR = ratio of Na to Ca and Mg levels.

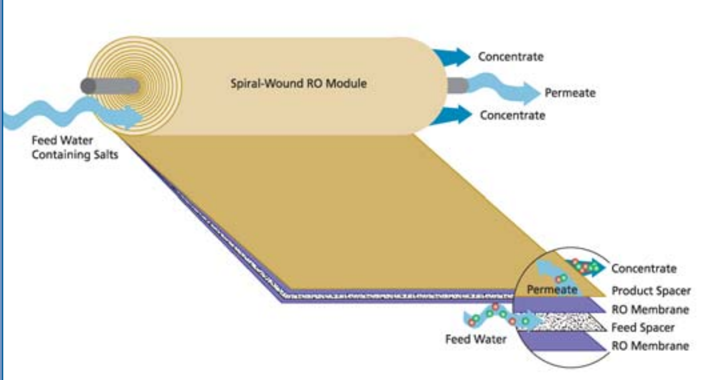

Figure 1. The reverse osmosis (RO) process.

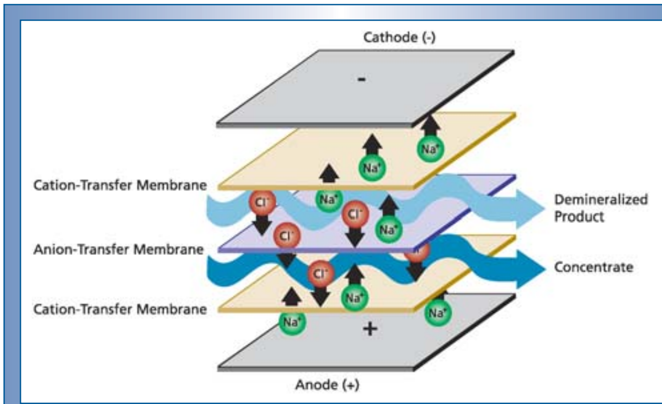

Figure 2. The electrodialysis process.

problems are largely responsible for the lack of deployment success of reverse osmosis in the oil and gas industry. Recent advances in applying rigorous preprocessing of produced water show potential for improving the reliability of reverse osmosis in achieving economical brine reduction; however, successful preprocessing is often complex and site-specific.

The choice of reverse osmosis for demineralization of produced waters is understandable, given that it is the predominant desalting technology in the United States. In 1997, there were about 2,000 U.S. reverse osmosis plants, with a total capacity of 800 million gal/d. Most of these plants process brackish waters and seawater to supplement water supplies for municipalities and industry. The second most-used process was electrodialysis, with 250 plants and a total capacity of about 40,000 gal/d. Though there have been numerous reverse osmosis tests on produced waters, little attention has been paid to the use of electrodialysis for the treatment of produced waters of modest concentrations of dissolved solids.

Many produced waters, including most of the same streams in CBM areas, contain modest TDS levels – less than 20,000 mg/L. These waters may require only partial demineralization to achieve good brine volume reductions and yield a demineralized steam suitable for surface discharge or beneficial use. In recent years, Gas Technology Institute (GTI) has evaluated an electrodialysis demineralization approach that may offer a cost-effective solution for the economical management of many produced water streams with low to moderate levels of contaminants.

The electrodialysis alternative

Electrodialysis is an electrically driven membrane separation process capable of separating, concentrating and purifying selected ions from aqueous solutions (as well as some organic solvents). In this process (Figure 2), ions are transferred through ion-selective membranes by means of a direct-current voltage.

Electrodialysis has been used in the United States for decades. It was commercially available in the 1960s, about 10 years before the introduction of reverse osmosis. During the past 40 years, electrodialysis has provided separations for the manufacturing of many products, including dairy foods, beverages, pharmaceuticals, metals and commodity biochemicals (such as organic acids). The development of the first generation of electrodialysis processing also represented a cost-effective way to desalt brackish water.

Figures 1 and 2 show the differences between reverse osmosis and the electrodialysis process. With reverse osmosis, separation is achieved by size exclusion of molecules larger than water. A saline solution is passed under pressure through the membrane and is separated from the solutes (the dissolved material). Pressure drops across the membrane usually range from 250psi to 400psi for the treatment of brackish water and from 800psi to 1,180psi in the treatment of concentrated salt water and seawater (above 30,000 mg/L of TDS). The major energy required for this process is applied to the pressurization of the water.

Electrodialysis, on the other hand, is an electrically driven separation process conducted at low pressure drops across the process (usually less than 25psi). Electrodialysis for the treatment of salt water depends on a number of principles. Soluble salts exist in water as ions. This includes positively charged ions (cations) such as sodium, calcium, magnesium and metals, as well as negatively charged ions (anions) such as chloride, sulfide, sulfate and bicarbonate. When electrodes are connected to an outside source of direct current, an electrical current is passed through the water and the ions migrate to the electrode of the opposite charge.

To achieve good separation, the movement of ions (TDS) is controlled by the addition of selectively permeable membranes that form watertight compartments (Figure 3). Each anion transfer membrane allows only the transfer of negatively charged anions, and the cation transfer membrane allows only the passage of positively charged cations. The membranes are electrically conductive and impermeable to water flow, even under pressure.

Using this arrangement, concentrated and diluted solutions are produced in the spaces between the alternating membranes. The spaces between the membranes are called cells, and two adjacent cells are called a cell pair.

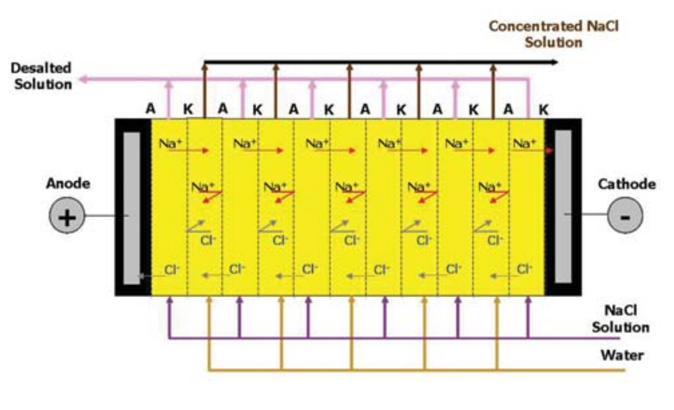

Figure 3. A schematic of industrial electrodialysis.

Figure 4. A commercial electrodialysis system for water treatment. (Photo courtesy of Ameridia, a division of Eurodia Industrie S.A.)

The conventional electrodialysis process consists of several hundred cell pairs and is called a membrane stack. In practice, the electrodialysis system is composed of a series of stacks. Periodically, chemicals can be passed through the stack to achieve a clean-in-place operation.

A commercial electrodialysis system used in the demineralization of water is shown in Figure 4. An electrodialysis processing train usually includes the following components and steps:

- pretreatment;
- membrane stack;
- low-pressure circulating pump;
- power supply for delivering direct current; and
- post-treatment for water conditioning.

During the past 30 years, a number of features have been developed to improve the electrodialysis process. In the 1970s, the electrodialysis reversal process was introduced into the commercial sector. This process operates on a similar principle as the conventional electrodialysis unit. First, the brine and product channels are constructed identically. Second, the polarity of the electrodes is reversed several times per hour, and the flows are simultaneously switched so the brine channel becomes the product water channel and vice versa. The reversal feature is useful in breaking up films, scales and other deposits, and flushing them out of the process before they can foul the membranes. The electrodialysis reversal process configuration, however, does add some complexity in design and control. For example, for many water treatment applications, effective clean-in-place operations can be accomplished with conventional automated chemical treatments.

In practical operation, conventional electrodialysis and electrodialysis reversal process can reduce salt concentrations to less than 200 mg/L of TDS before the internal resistance of the solution to current flow – and, therefore, power demand – rapidly increases. To maintain electrical conductivity (low resistance) at low salt concentrations, a further improvement was made in the process by placing ion exchange media between the membranes. This process, commercially known as electrodeionization (EDI), achieves low salt concentrations (below 10 mg/L of TDS) of salts at reduced power inputs and is widely used in the industry where high-quality water streams are required for manufacturing.

During the years, electrodialysis has been applied to achieve partial demineralization of brackish saline waters to meet criteria for surface discharge or water supply uses. Most of these applications did not require or utilize EDI. Although valuable for many industrial applications requiring the generation of ultra-high quality water, the performance of EDI usually exceeds the levels of treatment required for upgrading brackish water or for the desalinization of produced waters, where effluents containing less than 500 mg/L of TDS would be environmentally acceptable.

Electrodialysis has the following potential characteristics that would facilitate its application to the treatment of produced waters:

- the ability to simultaneously separate a wide range of ionic constituents – not only sodium and chloride ions, but also barium, heavy metal cations, and volatile acids (at neutral pH levels) – that may comprise the majority of soluble organics in most produced waters;
- applicability to treating produced waters of moderate strength (up to 10,000 mg/L of TDS);
- the capability for high recovery of demineralized water where the product stream is more than 90% of the flow of the influent stream (compared with 50% to 70% with reverse osmosis);
- the possibility to reduce brine volume by a factor of 10:1 or more (compared with 3:1 with reverse osmosis);
- good control over the degree to which salts are removed from the water stream through adjustments of flow and electrical energy inputs;
- higher tolerance for higher levels of suspended solids compared with reverse osmosis (requiring less rigorous pretreatment for particulate removal);
- low chemical use for pretreatment; and
- membrane life expectancy of 8 years to

10 years for electrodialysis (compared with 1 year to 2 years for reverse osmosis).

Preliminary field evaluation of electrodialysis

In recent years, GTI initiated an effort to examine the performance and costs associated with the application of electrodialysis to produced water management. The first electrodialysis test on such water was accomplished in a pilot unit at a conventional-well field site in the Wind River Basin near Lysite, Wyo., (Figure 5). Produced water at this site contained about 8,300 mg/L to 10,000 mg/L of TDS, comprised mainly of sodium, chloride, calcium and bicarbonate. These ions accounted for about 93% of the dissolved inorganic salts. The produced water also contained 65 mg/L of oils and greases, and more than 330 ppm of biological oxygen demand as measured with the standard 5-day test (BOD_5) – 70% of which was made up of acetate and other volatile acids. The BOD_5 parameter is a predictor of the amount of oxygen required in natural streams to oxidize the organic carbon in a sample and is proportional to the biodegradable total organic carbon (TOC). The goal was to treat the produced water to meet the NPDES criteria for surface discharge and meet specifications for use of the discharge water for irrigation and livestock watering.

The following unit processes were used in the pilot treatment train:

- de-oiling via induced gas flotation to remove oils and greases to achieve NPDES oil and gas limits and protect downstream unit processes;
- dissolved organics removal using two biological fluidized bed reactor (FBR) processes in series: 1) an anoxic, nitrate-consuming FBR to achieve large reductions in soluble TOC; and 2) an aerobic FBR to ensure efficient oxidation of soluble TOC and BTEX to low levels; and
- partial demineralization to achieve NPDES criteria for TDS, chloride and sulfate.

The pilot system was operated for 65 days to obtain water-quality data and assess treatment economics. A schematic of the pilot process train is shown in Figure 6. Produced water flow to the induced gas flotation process and the FBR processes was 15 gpm. A split stream of treated water from the aerobic FBR was fed to the on-site electrodialysis unit, which was designed and operated for batch recirculation flows of about 0.5 gpm to 4 gpm, depending on the final TDS target for the effluent. The electrodialysis unit was operated in continuous mode for most of the 65-day period. The operation was interrupted by 12 brief batch tests to determine the energy inputs necessary to achieve 5,000 mg/L, 2,500 mg/L and 1,000 mg/L of TDS. An acid wash was applied to the membranes daily, in accordance with the manufacturer's recommendation for maintenance. During the operational period, samples were collected throughout the pilot system to determine the effectiveness of each unit process in the treatment of Lysite produced water. At the conclusion of the 65-day test, the electrodialysis stack was dismantled and key electrode and membrane components were sent to the manufacturer for inspection.

Results from the electrodialysis field pilot system are summarized in Table 2. Overall, the integrated treatment system performed well throughout the test period. Consistent with the nature of conventional natural gas wells, the produced water contained elevated levels of oils and greases, approaching 100 mg/L. However, the combination of induced gas flotation – using a coagulant dose of 5 mg/L – and biological treatment was able to reduce the oil and grease to 4 mg/L or less, which offered sufficient protection to avoid fouling of the electrodialysis unit. The "front-end" preprocessing was also able to achieve nearly 90% removal of soluble organics before the produced water was introduced to the electrodialysis stage. The electrodialysis unit was able to decrease the salinity of the product water from 9,000 mg/L to the desired target levels of 5,000 mg/L, 2,500 mg/L and 1,000 mg/L TDS. Power costs required for each of these levels is shown in Figure 7 (based on an electricity price of $0.6/kwh), based on actual electrical energy needed to reach the target TDS level. These results showed the Lysite electrodialysis pilot system was capable of demineralizing a conventional gas produced water stream from 9,000 mg/L to as low as 1,000 mg/L for only $0.03/42-gal bbl, or about $0.01/bbl to reach 2,500 mg/L.

Figure 5. A granular activated carbon-fluidized bed reactor and induced gas flotation unit is shown at the Gas Technology Institute electrodialysis pilot site near Lysite, Wyo.

Table 2. Performance results for the integrated electrodialysis pilot unit.

Parameter	Influent, mg/L	Effluent, mg/L	Overall Removal, %
Oil and Grease	90	4	95.5
BOD_5 *	330	51	84.5
BTEX**	11	0.1	99.1
Total Dissolved Solids (TDS)	9,100	1,000***	88.9

* BOD_5 = Biological Oxygen Demand measured in a 5-day test.
** BTEX = Sum of benzene, toluene, ethylbenzene and xylenes.
*** Generated at peak performance of the electrodialysis unit.

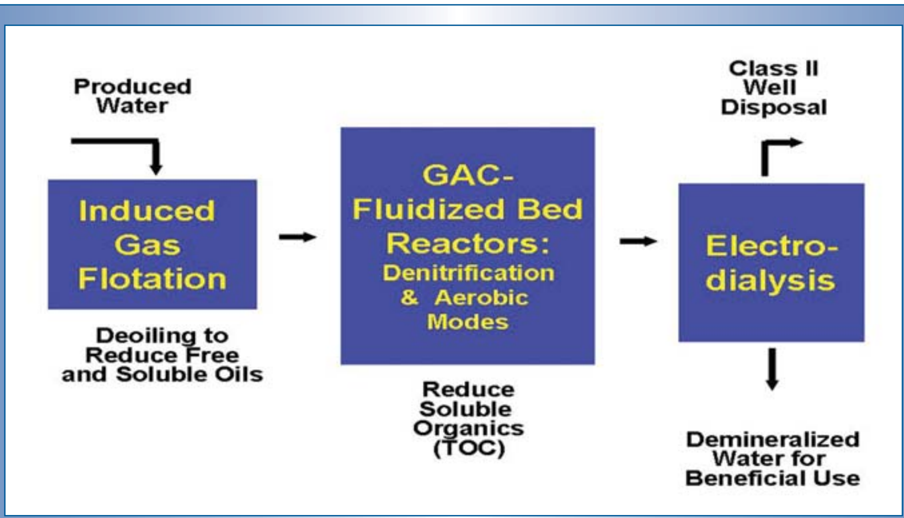

Figure 6. Schematic of the Gas Technology Institute electrodialysis pilot unit.

Projected economics

Compared with current costs for SWD well disposal, which can exceed \$0.50/bbl, the pilot results show that power costs (\$0.01/bbl to \$0.03/bbl) for electrodialysis treatment to achieve NPDES criteria or beneficial end-use goals can be reasonable for processing produced waters containing up to 10,000 mg/L of TDS. Above this concentration, however, the power costs increase exponentially. For example, the cost to treat a 15,000 mg/L TDS influent to below 2,000 mg/L are projected to be about \$0.40/bbl, which may be prohibitive for most field applications.

Based on these power cost relationships, it appears electrodialysis may be a good solution to the partial demineralization of CBM produced waters, which tend to be lower in TDS concentration and very low in organic content. For example, the processing of 35,000 bbl of produced water per day to decrease the TDS from 3,000 mg/L to 1,700 mg/L would require about 16,000 sq ft of electrodialysis cell surface area. The power cost for electrodialysis demineralization would be less than \$0.01/bbl. Total processing cost would be less than \$0.10/bbl, including preprocessing, electrodialysis, adsorption polishing and calcium addition for adjustment of the sodium absorption ratio – amortized capital, labor, power cost and labor included.

Preprocessing of CBM produced waters likely would not require the rigorous biological treatment needed for conventional gas-well produced water. Soluble organics probably would be less than 50 mg/L, and oil and grease levels would be less than 10 mg/L. Preprocessing, therefore, would only require optional de-oiling, suspended solids filtering and surfactant-enhanced ultrafiltration to provide adequate pretreatment (Figure 8). This would yield savings of more than \$0.06/bbl compared with a system that included biological treatment in the preprocessing. In addition, any soluble organics present in the CBM produced water, in the form of volatile acids (such as acetic), would be efficiently removed in the electrodialysis process because these acids predominate in the ionic form at the normal pH range of produced waters (above pH 6.5). The resulting concentrated produced water brine that would require SWD well disposal is projected at 0.08 gal for every gallon of produced water introduced into the electrodialysis unit. This represents a brine reduction greater than 92%, which is based on previous electrodialysis performance levels observed with brackish water treatment.

Potential for implementation

Electrodialysis is not commercially applied to produced water treatment due to the dominance of reverse osmosis and the lack of operational experience with electrodialysis in the oil and gas industry. In view of numerous successful electrodialysis applications in manufacturing processes and in the commercial treatment of brackish waters for community water service worldwide, electrodialysis, including its processing variants of electrodialysis reversal process and EDI, has potential for the management of growing produced water problems in areas of the United States where re-injection capacities are constraining energy development. Electrodialysis may be a good fit for CBM basins where produced waters contain less than 15,000 mg/L TDS, and where interest is growing in the use of produced waters for irrigation, watering of livestock and surface discharge for maintaining fish habitat.

Within its economical niche of application to produced water demineralization, electrodialysis has a number of potential advantages compared with reverse osmosis:

- electrodialysis does not require high feedwater quality and is less sensitive to pretreatment problems. Less pretreatment results in substantially lower preprocessing cost for the produced water demineralization system;
- in the processing of produced waters with a high bicarbonate alkalinity, the formation of precipitates, such as metal carbonates, that is a problem with reverse osmosis is not as much of a problem with electrodialysis because of its lower operational pressures. This means pretreatment using acidification and carbon dioxide degassing would not be needed for electrodialysis; and
- in single-pass processing, electrodialysis has the potential to achieve higher recoveries of demineralized water with a concomitant generation of lower volumes of brine requiring deep-well disposal. For each gallon of produced water processed, less than 0.1 gal of concentrated brine would be generated that would require

deep well-disposal vs. 0.3 gal generated with reverse osmosis.

Technology development needs

Future development of electrodialysis for produced water applications should emphasize the design of protective front-end processing and automated clean-in-place technology that ensures a 5-year to 7-year life for electrodialysis membranes with high dependability of performance, even with wide perturbations in produced water quality that can be encountered in the field. Initial development should continue to emphasize low- to moderate-strength produced water conversion to beneficial-use water streams to control electricity costs in the operation of the electrodialysis unit. Lastly, future development should aim to minimize solid-waste generation and maximize process-train automation. If the process train required little attention from on-site operators, water-treatment companies and other entities could participate in managing multiple treatment systems in each producing basin, thereby improving the economy of scale of operating such systems throughout the Rocky Mountain region. This business model may be particularly beneficial for the CBM industry because produced water output from each well is very high in the first 3 years, and tapers off during the next 10 years to minimal levels; and substantial savings would be realized through the strategic use of leased equipment. Electrodialysis treatment systems are highly modular by nature. The maximum number of modules would be in operation in the first years of CBM well operation, but up to 80% of the modules could be removed as produced water output substantially decreased.

Summary

Electrodialysis is a proven economical separations process in a number of industries and in the treatment of brackish waters around the world. The results of recent GTI pilot-scale tests in Wyoming on conventional gas-well produced water – using de-oiling and biological pretreatment followed by electrodialysis – show that such treatment is technically possible and economically attractive for the processing of produced waters with weak to moderate levels of TDS. Electrodialysis is at the pilot-ready stage of development for produced water treatment applications. A successful, cost-effective electrodialysis system could yield substantial benefits for the public, industry, agriculture and other stakeholders. Electrodialysis could help substantially expand the development of CBM reserves by reducing 10-fold the volume of brines requiring subsurface disposal, and also would generate substantial quantities of demineralized water for use as a supplemental source of water for agriculture and industry.

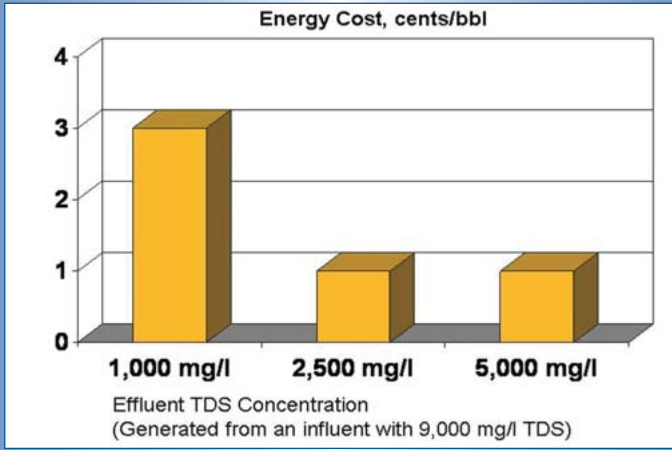

Figure 7. The power cost of electrodialysis.

For more information about this research, contact Tom Hayes, associate director, environmental engineering, Gas Technology Institute, at *tom.hayes@gastechnology.org* or (847) 768-0722. ✧

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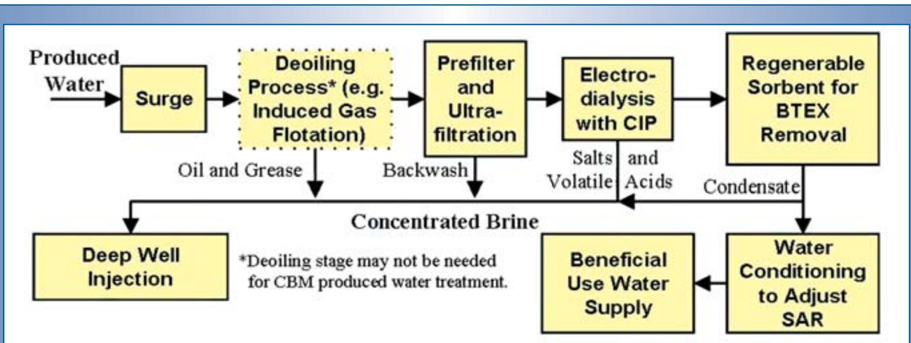

Figure 8. The electrodialysis processing scheme for the conversion of coalbed methane-produced water to beneficial-use water is shown above.

Consortium to Research U.S. Storage System

by Bob Watson and Dave Johnson,
Pennsylvania State University;
and Dan Driscoll,
U.S. Department of Energy/National Energy Technology Laboratory

First round of research projects have been selected to study the many ways natural gas can be stored to meet the nation's future energy needs.

Pennsylvania State University, in collaboration with the natural gas storage industry, has established a Gas Storage Technology Consortium (GSTC). The U.S. Department of Energy's (DOE) National Energy Technology Laboratory (NETL) is sponsoring the consortium. The consortium's mission is to provide a means to accomplish industry-driven research and development designed to enhance operational flexibility and deliverability of the nation's gas storage system and provide a cost-effective, safe and reliable supply of natural gas to meet demand. The consortium will address needs identified by the industry in conjunction with DOE's Strategic Center for Natural Gas 2020 Vision Report and industry-driven roadmapping sessions held in 2001 and 2004. The consortium is being administered by Pennsylvania State University and is signing up members, including universities, gas storage and delivery companies, and service companies.

Background

Gas storage is a critical element of the natural gas industry. Producers, transmission and distribution companies, marketers and end-users all benefit directly from the load balancing function of storage. Unbundling started a process that has fundamentally changed the way storage is used and valued. As an unbundled service, the value of storage in minimizing overall costs to consumers is increasingly being recovered at rates that reflect its value. Moreover, the traditional marketplace has differentiated between various types of storage services and has increasingly rewarded flexibility, safety and reliability.

The first carbon dioxide-sand frac in a gas storage field is shown above.

The total size of the natural gas market has increased and is projected to continue to do so toward 30 Tcf during the next 10 years to 15 years. Much of this increase is projected to come from electric generation, particularly peaking units. Gas storage, specifically the flexible services most suited to electric loads, is critical in meeting the needs of these new markets. The DOE, in collaboration with the Gas Technology Institute (GTI) and the Pipeline Research Council International (PRCI), has funded a number of projects to help storage operators maintain existing capacity and respond to the market's demand for flexible, safe and reliable services. A brief description of these programs and results achieved are provided in the following sections. These programs, along with objectives set forth by the DOE in support of the Strategic Center for Natural Gas 2020 Vision, will define the research funded through the GSTC.

Deliverability maintenance

Many natural gas storage wells suffer damage during normal storage operations. Storage operators spend upward of $100 million per year recovering lost deliverability. Significant savings are possible by properly diagnosing the causes of damage so effective remedial and/or preventive measures can be selected. New cost-effective techniques also are needed to prevent and repair this damage. This area has long been a priority for the DOE and the GTI/PRCI. Past and current projects identified the scope of the problem, defined the mechanisms responsible, defined diagnostic procedures, developed an expert system to help operators design effective treatments, identified non-damaging fluids for well work and examined non-damaging laser-based completion technology. Future work needed in this area includes improved fracture technology (with a focus on rock mechanics to ensure caprock integrity), fracture proppant stability and "smart well" technology to allow selective production/isolation via fiber-optic technology.

Increased flexibility

Changes in the natural gas marketplace have increased the need for flexible, high-deliverability storage services. The development of new storage facilities can fulfill part of this need, but re-engineering existing storage assets are a less expensive alternative to new construction. Most existing fields were designed for base-load service, but many can be re-engineered to provide some shorter-term flexible services. Past and current projects are pursuing improvements to tools operators can use to re-engineer existing facilities – novel stimulation techniques, inert base gas use and hydrate control – as well as defining technical and risk factors in the use of inert base gas, investigating the design and use of horizontal wells, examining the geomechanical and risk factors in the use delta pressure, and examining options for hydrate control. Future work needed in this area includes low-cost technologies to create small-diameter horizontal boreholes, improved control of water production at lower operating pressures, and water treatment and handling procedures.

Integrity

Storage services must be safe and reliable to serve current and future markets. Safety has always been a high priority within the natural gas industry, but the safety and integrity of underground storage facilities has been receiving increased scrutiny in public and regulatory communities. The program goals have been designed to maintain the industry's ability to adequately serve markets and provide the basis for prudent operational practices and scientifically based regulations. Current projects include a risk analysis of storage operations, and a combined effort to define the remaining strength of tubulars where metal loss has occurred and the development of a tool to better measure metal loss in those tubulars. Future work needed in this area includes investigation of cement degradation, cycling effects on casing strength, improved detection of annular leak sources, technical assessment of non-metallic tubulars and sleeves, and the development of integrated cavern mechanical integrity testing procedures.

Cavern storage/peak shaving

The need for flexible services has resulted in increased importance of cavern storage and peak shaving options. This type of storage, however, is generally expensive to build and is limited to areas with salt domes or relatively thick-bedded salt intervals. The ability to utilize thinner salt beds closer to market areas and maximize the use of caverns is extremely valuable to storage operators and consumers. Past and current projects have examined risk factors associated with converting existing caverns to gas storage, examined geomechanical factors influencing lower operating pressure limits, developed a thermal simulation package operators can use to help make inventory assessments and operational decisions, and examined design procedures for salt caverns in thin-bedded salts. Future work needed in this area includes improved inventory verification options, the development of evaporation options for brine disposal, development of tools to determine cavern interconnectivity and laser survey tool development.

Specifics about GSTC

The mission of the GSTC is 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 storage facilities.

The GSTC serves its members by guiding, stimulating and aiding their efforts to:

- formulate research, development and technology assessment goals;
- create a supporting infrastructure for conducting research and development that will increase knowledge of and expand the technological base for natural gas storage; and
- promote and enhance the dissemination of research results and technology transfer to storage operators for the benefit of the nation.

Any individual, firm, partnership, association, institution, university or corporation engaged in natural gas storage, research and development technologies associated with natural gas storage, or a user of natural gas storage services is eligible for GSTC membership, of which there are three levels. Full memberships are defined as those members from any individual firm, partnership, institution or corporation directly engaged in the production and service of the hydrocarbon industry, or individuals and institutions engaged in research and development associated with hydrocarbon or users of hydrocarbon services. Affiliate members are defined as those from associations and professional societies. University members are defined as any university or college engaged in research and development technologies associated with hydrocarbon storage.

Focus areas for research

The research funded through the GSTC will be consistent with the objectives set forth by the DOE in support of the Strategic Center for Natural Gas 2020 Vision. The main focus of R&D projects will be the demonstration of technologies to preserve and improve the deliverability and management of existing conventional underground storage reservoirs and salt cavern facilities. A secondary focus area will be on research to develop manmade storage systems and other non-traditional methods in close proximity to demand centers.

Proposals will be solicited in the following focus areas.

Mechanical—Examples of research topics in this area include, but are not limited to, investigations that address pipe and well casing integrity; cement bonding; delta-temperature effects on casing; use of "smart pipe" concepts for well casing; corrosion mitigation and quantification; removal techniques for scales, fines, salts and asphalts; and techniques to remediate damage through stimulation/recompletion/workover of existing wells.

Wellbore and reservoir—Examples of research topics in this area include, but are not limited to, investigations that address reservoir characterization, consider new approaches to modeling of gas cycling and inventory verification, develop techniques to maintain and improve injectivity and deliverability, and expand existing aquifers and reservoirs.

Operations—Examples of research topics in this area include, but are not limited to, investigations that address handling of produced water, techniques to minimize/mitigate water encroachment, cost-effective multiphase wellhead gas measurement systems, design criteria for facility sizing to meet variable demand and best-practices associated with product quality shipped/delivered.

Salt caverns—Examples of research topics in this area include, but are not limited to, investigations that address salt cavern stability and growth rates, interconnectivity and best-practices techniques for management of caverns.

Manmade and distributive storage—Examples include, but are not limited to, investigations that address methods for storage in abandoned mines and as gas hydrates, sorption of gas onto solids, mobile storage and end-used storage systems, cost-effective liners for mines and caverns, and identification of materials and construction protocols for manmade caverns.

2004-2005 funding cycle

Projects selected under the first request for proposals from the Natural Gas Storage Technology Consortium:

- **Correlations Co.**—"Smart Gas: Using Chemicals to Improve Gas Deliverability"
- **West Virginia University**—"Gas Storage Field Deliverability Enhancement and Maintenance"
- **Kinder Morgan**—"Deliverability Enhancement for Gas Storage Wells"
- **Colorado Engineering Experiment Station Inc.**—"Evaluation of Separators for Gas Storage Fluid Control"
- **Colorado School of Mines**—"Low-Cost Downhole Pressure Monitoring"
- **Clemson University**—"Produced Water Clean Up Using Hybrid Constructed Wetland Technology"

For more information, contact Dan Driscoll at *daniel.driscoll@netl.doe.gov* or (304) 285-4717. ✧

More about the GSTC

The director of the GSTC is Dr. Robert W. Watson, associate professor of petroleum and natural gas engineering and geoenvironmental engineering at Pennsylvania State University. For further information about the GSTC, visit its Web site at www.energy.psu.edu/gstc/ *or email the consortium at* gstc@ems.psu.edu

DOE's Gas Storage Program

The U.S. Department of Energy's Fossil Energy Gas Storage Program was initiated in 1995. Traditionally, research and development (R&D) projects have focused on two major areas – deliverability enhancement from existing fields, and alternative storage concepts, with a few projects related to gas measurement, liquefied natural gas (LNG) and reservoir management.

Past highlights

A 5-year field fracture stimulation project led to important findings that impact the application of stimulation technologies in gas storage fields. The project demonstrated that several new and novel fracture stimulation technologies can provide attractive deliverability enhancement while addressing the special concerns of gas storage operators. Highlights of this research effort include:

- the first liquid carbon dioxide and proppant fracture treatments in a storage field, which led to a seven-fold increase in deliverability in two of three wells;
- two tip-screenout fracture treatments, which led to an increase of nearly 50 MMcf/d in deliverability;
- a first-of-a-kind simulator developed to design and model extreme overbalanced fracturing; and
- a comprehensive dataset of multipoint deliverability and pressure transient tests that provided unique insight into the impact of stimulation of gas storage wells and the process of candidate well selection.

Studies of the technical and economic merits of four advanced storage concepts indicate alternatives to conventional storage can provide benefits in today's market:

- refrigerated-mined caverns and lined rock caverns were shown to be competitive with LNG for a single cycle and, for multiple cycles, can offer a substantially reduced unit cost of service. These facilities can be placed in market areas where conventional underground storage and salt caverns do not exist;
- lowering the minimum designed gas pressure can increase working gas volume in existing and new salt caverns. A new laboratory test matrix and an advanced model that determines the damage and healing that occurs in salt caverns were developed and have been successfully applied to a new and existing cavern in Mobile, Ala., indicating working gas can be increased by 8% and 18%, respectively; and
- a breakthrough in laboratory testing of storing natural gas as hydrates led to the design of a complete formation-storage-decomposition cycle in a 24-hour period of 2.25 MMcf of natural gas.

Current work

While several projects still focus on the traditional areas of R&D, deliverability enhancement and alternative storage, many projects were initiated to address the key challenges and barriers identified by gas storage operators at a 2001 Natural Gas Storage Workshop sponsored by the National Energy Technology Laboratory. Existing gas storage projects include:

- bedded-salt cavern stability modeling;
- hydrate formation control;
- identifying the timing and source of damage;
- novel LNG salt cavern storage;
- a carbonate dissolution process for creating cavernous storage;
- gas storage as hydrates;
- a sonic tool for scale removal;
- an energy meter development and testing;
- brine disposal in the Northeast; and
- thermal spallation of hard rock caverns

References:

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Safe Siting and Operation of Liquefied Natural Gas Facilities: Software Update

by Liese Dallbauman, Ph.D.,
Gas Technology Institute

Upgraded safety models will enable wider use of imported liquefied natural gas to help meet growing ga demand in the face of projected decreases in domestic production.

The Code of Federal Regulations (Title 49 Part 193, abbreviated as 49 CFR 193) defines safety standards for liquefied natural gas (LNG) facilities covered by federal pipeline safety laws. The code addresses protection in the vicinity of LNG storage and transfer systems by specifying methods used to calculate thermal and dispersion exclusion zones. The models specified – LNGFIRE3 for thermal radiation protection calculations and DEGADIS for dispersion protection calculations – are available in CD form. In addition, Gas Technology Institute (GTI) and the University of Arkansas (UA) recently have begun a U.S. Department of Energy (DOE)-funded effort to upgrade FEM3A, a sophisticated computational fluid dynamic model cited by 49 CFR 193 as an acceptable alternative to DEGADIS.

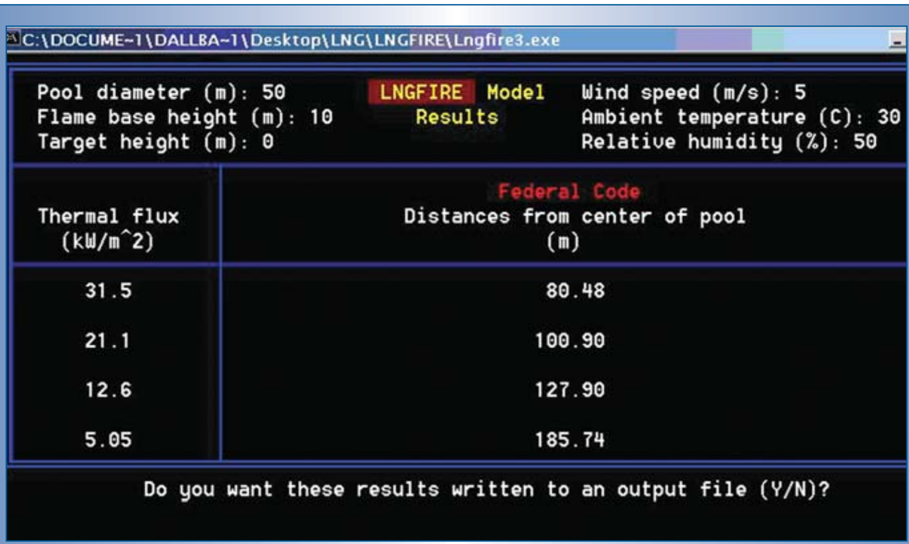


Figure 1. Results from the LNGFIRE3 software program.

LNGFIRE3

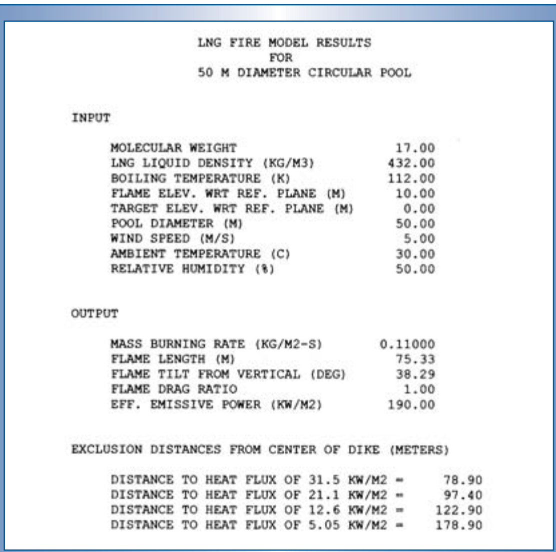
LNGFIRE3 calculates thermal exclusion zones surrounding LNG fires and has been validated through large-scale experiments. In addition to determining the distances corresponding to the four radiation flux levels specified by 49 CFR §193.2057, the program allows calculation of radiant flux reaching vertical and horizontal targets at up to 10 user-specified points downwind of an LNG fire. Wind speed, relative humidity and ambient temperature as well as parameters describing the LNG source are specified through a series of dialog screens. The model assumes the flame takes the shape of a cylinder or a parallelepiped, depending on the geometry of the fuel impoundment area, and accounts for wind-induced flame drag and tilt. Simple results (distance and flux) appear onscreen (Figure 1). More detailed results, including flame tilt and drag ratio, can be written to file (Figure 2).

Executable LNGFIRE3 code and documentation are available on a new CD, which can be ordered from the GTI Web site.

DEGADIS

Federal regulations governing LNG dispersion protection (49 CFR §193.2059) specify DEGADIS as an acceptable means of determining flammable vapor-gas dispersion distances. The program was originally developed for the U.S. Coast Guard and the Gas Research Institute (GRI) with the primary goal of simulating dispersion of cryogenic flammable gases. Subsequent work sponsored by the U.S. Environmental Protection Agency allowed simulation of vertical jet dispersion. Work funded by GRI and the American Petroleum Institute modified the VAX-based code for use on DOS machines. The current version runs in a DOS window within a Windows® environment. Liquefied natural gas dispersion profiles predicted by DEGADIS are consistent with field test data generated by the DOE and Shell U.K. Ltd.

Like LNGFIRE3, DEGADIS operates through a series of dialog screens, with the user supplying information on local conditions and the LNG spill. Table 1 lists the parameters the user must provide. The program generates one or more output files that describe in detail



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LNG FIRE MODEL RESULTS
FOR
50 M DIAMETER CIRCULAR POOL

INPUT

MOLECULAR WEIGHT                    17.00
LNG LIQUID DENSITY (KG/M3)         432.00
BOILING TEMPERATURE (K)            112.00
FLAME ELEV. WRT REF. PLANE (M)      10.00
TARGET ELEV. WRT REF. PLANE (M)      0.00
POOL DIAMETER (M)                   50.00
WIND SPEED (M/S)                     5.00
AMBIENT TEMPERATURE (C)             30.00
RELATIVE HUMIDITY (%)               50.00

OUTPUT

MASS BURNING RATE (KG/M2-S)        0.11000
FLAME LENGTH (M)                     75.33
FLAME TILT FROM VERTICAL (DEG)       38.29
FLAME DRAG RATIO                      1.00
EFF. EMISSIVE POWER (KW/M2)         190.00

EXCLUSION DISTANCES FROM CENTER OF DIKE (METERS)

DISTANCE TO HEAT FLUX OF 31.5 KW/M2 =     78.90
DISTANCE TO HEAT FLUX OF 21.1 KW/M2 =     97.40
DISTANCE TO HEAT FLUX OF 12.6 KW/M2 =    122.90
DISTANCE TO HEAT FLUX OF 5.05 KW/M2 =    178.90
```

Figure 2. Example of LNGFIRE3 output file.

Table 1. DEGADIS input parameters.

Release conditions	*Local conditions*
Source radius	*Wind speed*
Release rate	*Surface roughness*
	Ambient temperature and pressure
Case definition	
Upper and lower limits of concern	*Absolute or relative humidity*
Transient or steady state release	*Ground temperature*

Table 2. Examples of DEGADIS output information.

- *Summary of input parameters*
- *Density, enthalpy, and temperature of adiabatically mixed LNG and humid air*
- *Contaminant gas properties*
- *LNG vapor cloud radius, height, density and temperature*
- *Downstream concentration, density and temperature profiles*

the spatial and temporal evolution of the contaminant concentration profile. Table 2 is a partial list of the output file contents.

A CD available from GTI includes the Windows-compatible DOS version of DEGADIS, a new user manual and the detailed documentation cited in 49 CFR 193, (report GRI-89/0242). The report provides information on the development of the model, including equation derivations and solution descriptions.

FEM3A

While DEGADIS simulates dispersion over smooth, obstacle-free terrain, FEM3A is able to model dispersion over minimal obstacle arrays, such as a single tank and dike on smooth terrain. Flow visualization tests conducted in a specially designed low-speed wind tunnel at UA's Chemical Hazards Research Center (CHRC) have demonstrated that even simple barriers can have a major effect on dispersion (Figure 3). FEM3A simulations of the test conditions have been used to predict dispersion protection zones for LNG spills corresponding to the photo. The simulations have shown that these obstacles reduce the exclusion zone corresponding to a given LNG concentration.

Under the new DOE contract, UA and GTI researchers will refine the FEM3A model to make it applicable to more complex arrays. This will be achieved by improving the program that describes the turbulent mixing of the flammable cloud with the surrounding air. Measurements in the UA-CHRC wind tunnel will be used to verify the enhanced model. Wind tunnel data also will be used to validate the applicability of the model to complex scenarios, including such items as vapor fences, multiple obstacles and important terrain features.

For more information about GTI's LNG-related research, contact Dennis Leppin, associate director, gas processing, by email at *dennis.leppin@gastechnology.org* or via phone at (847) 768-0521. The CDs mentioned above can be ordered through the GTI Web site at *www.gastechnology.org*. Document numbers are GTI-04/0032 (for LNGFIRE3) and GTI-04/0049 (for DEGADIS). ✧

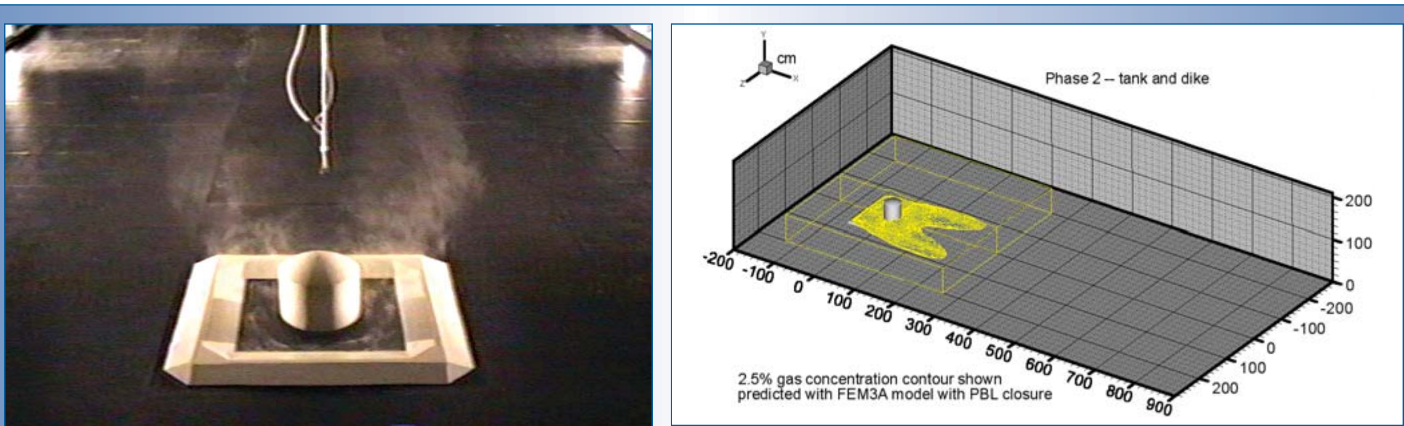

Figure 3. Wind tunnel dispersion with tank and dike (left), compared with FEM3A simulations of the associated hazard zones.

Critical Components of Salt Cavern-Based Liquefied Natural Gas Receiving Terminal Undergo Field Tests

by Michael M. McCall,
Conversion Gas Imports

Field tests of the mooring system, high-pressure pumps as well as a high-capacity, high-efficiency, water-warmed heat exchanger have been successfully completed.

Liquefied natural gas (LNG) receiving terminals combined with salt cavern gas storage is moving closer to commercial reality. The unique and previously unknown combination of gas storage in manmade salt caverns with LNG importation presents the possibility for LNG receiving terminals with large storage capacity and gas send out flow rates. In particular, the use of salt formations for cavern development and LNG receiving in the Gulf of Mexico has the potential for offshore facilities combining easy ship access, large storage and large send out to the gas pipeline grid. Technical validations through field tests of the critical components of a salt cavern-based LNG receiving terminal are part of a U.S. Department of Energy (DOE) cooperative research project commissioned by the National Energy Technology Laboratory (NETL) with cost sharing participants from an array of energy industry companies.

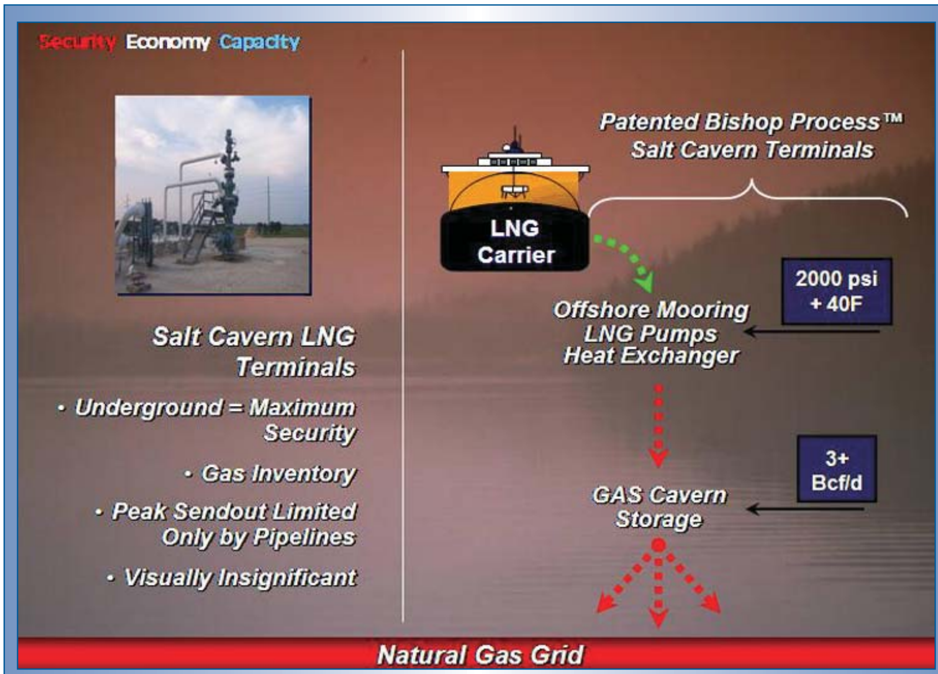

Figure 1. The Bishop Process salt cavern-based liquefied natural gas terminal.

LNG imports supply less than 2% of the current U.S. natural gas supply. Many predict that number will significantly increase during the next 20 years. This volume growth would require a number of new import terminals to augment the four existing LNG import terminals in the United States. There are more than 40 LNG import terminals in the world, all of which are designed around cryogenic liquid storage tanks. The LNG tanks are the most expensive and visible component of the facility. Significant scale increases have been introduced into the world's LNG business in liquefaction and shipping, but tank-based terminals are difficult to scale up because of the tank cost and space required to site them. Salt cavern-based terminals can provide the corresponding scale increases needed in LNG receiving terminals with storage capacity and send-out volumes exceeding the tank-based terminal model. Offshore mooring and unloading of the LNG ships into offshore salt caverns could reduce port congestion and avoid some of the not-in-my-backyard problems faced by facility siting in some coastal communities.

Salt caverns provide an answer

Manmade salt caverns are an integral part of the U.S. energy infrastructure. The entire Strategic Petroleum Reserve, totaling more than 650 million bbl of crude oil, is stored in salt caverns on the Gulf Coast. In addition, there are more than 600 million bbl of products owned by private industries including hydrogen, natural gas, natural gas liquids, olefins, refined products and crude oil stored in salt caverns in the United States and Canada. This high-deliverability storage is a critical logistical link between the natural gas, gas processing, petrochemical and refining industries. Salt cavern storage is a well-known technology and is well developed, acceptable to the community and low cost. Salt caverns, thousands of feet below the Earth's surface, have been used to store hydrocarbons for more than 60 years.

Salt caverns provide about 5% of the natural gas storage capacity in the United States but about 15% of the deliverability of natural gas into the gas grid. This ratio illustrates the high deliverability nature of natural gas

Figure 2. Bluewater Offshore's "Big Sweep" undergoing wave tank model testing.

Figure 3. Bluewater Offshore's "Big Sweep" illustration.

storage in salt caverns, and demonstrates their fundamental value in LNG receiving and natural gas distribution.

Salt formations will not tolerate direct LNG injection because of the low temperatures. The development of the patented Bishop Process™ LNG terminal, however, began with the basic premise that LNG technologies and salt cavern storage technologies can be combined in some form.

New "class" of LNG terminal

Phase 1 of the DOE research consisted of site research for locations that have salt formations, pipelines and water depths suitable for the approach of LNG ships. It also incorporated mathematical analyses about power requirements, necessary heat exchanges to warm the LNG, and preliminary cavern design and operating characteristics. Industry partners included BP, Bluewater Offshore and HNG Storage. The results, presented in April 2003, confirmed not only the feasibility of the process, but also illustrated that commercial applications would not be undertaken without further "proof" to a conservative energy industry and financial community. The incentive to develop this terminal technology is substantial, as salt cavern-based LNG receiving terminals, in the initial analysis, have material advantages to tank design terminals in lower capital and operating costs, greater volume of storage and rapid response to changes in send-out rate demand. **Vermilion Block 179** in the Gulf of Mexico was selected for the research because it is in shallow water (100ft) about 47 miles south of the Louisiana coast, has an ideal salt dome formation (top of the salt is less than 1000ft below water surface) and is adjacent to several major gas gathering pipelines.

Major portions of the equipment and systems being incorporated into this design have been well-proven in other applications. Other critical pieces of equipment have not been well proven and require field testing for industry acceptance.

DOE cooperative research expansion

In September 2003, the DOE, through the NETL, expanded the cooperative research agreement to include field tests of the critical components (high-pressure LNG pumps, Bishop Process™ Heat Exchanger, and off-

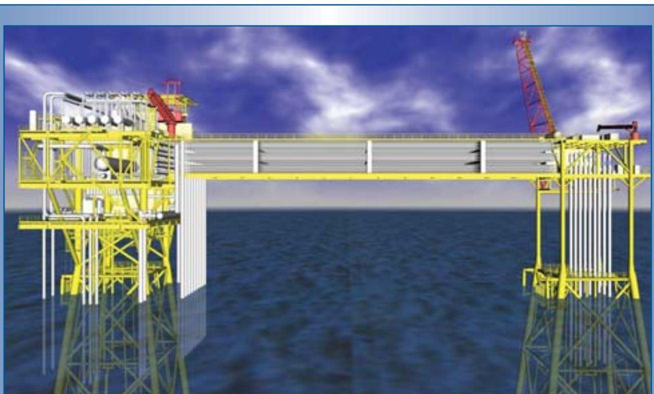

Figure 4. Paragon Engineering's liquefied natural gas process platform design.

Figure 5. SBM-Imodco Offshore's liquefied natural gas mooring system.

Figure 6. FMC Sofec Offshore's liquefied natural gas mooring system.

shore mooring and product transfer) and conceptual designs of their application in the Bishop Process™ salt cavern-based LNG receiving terminal (Figure 1). The goal of the DOE's cooperative research program is to move technology from concept to commercialization as rapidly as possible using the industry's joint financial participation with the DOE to fund the process and provide technical and operating expertise. These field tests are part of a DOE $2.7 million cooperative research project led by Conversion Gas Imports. The DOE is funding $1.8 million and the industry cost sharing of $0.9 million is provided by an expanded group of industry participants including, American Bureau of Shipping, A.D. Little, AGL Resources, Bluewater Offshore, BP, Carter Cryogenics, Credit Suisse First Boston, Det Norske Veritas, Dominion, Ebara, Ecology & Environment Inc., Encana, ExxonMobil, Fluor, FMC Sofec, Golar, HNG Storage, Hoegh LNG, International LNG Association, Marathon, Marsh & McLennan, Nikkiso Cryogenics, Northstar Industries, Paragon Engineering, PB Energy Storage Services, PEMEX, Remora Technology, RRS Engineering, SBM-Imodco and the U.S. Coast Guard.

The Bishop Process LNG import terminal works in the following manner: the LNG ship is offloaded through its internal pumps at its normal offload rates. The LNG cargo discharge from the ship is the inlet to a series of high-pressure LNG pumps, which receive the LNG at relatively low pressures from the ship and achieve cavern injection pressures at their discharge. The heat exchanger receives the LNG at high rates, high pressures and low temperatures and then warms it at discharge to cavern and pipeline compatible temperatures.

The gas can be directly injected into salt caverns without further compression or into the pipeline grid or a combination of the two. This one-step process converts the cold "exotic" LNG into warm "ordinary" natural gas. The ship can be turned around in the same amount of time as at a conventional cryogenic tank-based receiving terminal, but when it leaves, there is little LNG stored at the site – only enough to keep the cryogenic equipment cold between ship arrivals.

Designing the salt cavern-based LNG terminal

There are three distinct components to an offshore LNG receiving terminal: the LNG ship mooring and transfer systems; the process design and equipment; and the gas storage salt caverns. The DOE research has made considerable progress toward the goal of a workable and safe basis of design. Field tests of the mooring system; the high-pressure pumps; and a high-capacity, high-efficiency, water-warmed heat exchanger have been successfully completed. The field test results are being analyzed and will be incorporated into the mathematical models of these systems. The final product of the research project is the integration of the test results into designs, operability and maintainability studies, environmental studies, and cost analyses on the construction and operation of salt cavern-based LNG receiving terminals.

LNG ship mooring and transfer system

Offshore mooring and transfer of crude oil has been a well-established practice for more than 40 years with an excellent safety and environmental record. Building on this body of experience, Bluewater Offshore model tested in a wave tank facility a mooring system for offshore transfer of LNG in April (Figure 2). Bluewater's system transfers the LNG to a nearby platform containing the process equipment, power, pumps, heat exchanger, measurement, salt cavern wellheads and more (Figure 3). Paragon Engineering Systems provides the platform and process design and engineering (Figure 4). Other LNG ship mooring and transfer systems by SBM, FMC and Remora have been submitted as part of the research

Figure 7. Remora Technology's "Hi Load" liquefied natural gas mooring system.

Figure 8. Ebara's liquefied natural gas pump in assembly.

Figure 9. Nikkiso Cryo's liquefied natural gas pump undergoing tests.

Figure 10. The Bishop Process heat exchanger being field tested.

Figure 11. Research participants observing a test in progress.

(Figures 5, 6 and 7, respectively). High system availability and suitability for non-dedicated vessels characterize all designs.

High system availability—The investments made in the LNG production and transport chain are large, as are the costs associated with downtime of LNG production and/or demurrage of the carriers. High system availability is achieved by using weathervaning mooring systems, a robust flow path and a minimum number of cryogenic mechanical components.

Suitability for non-dedicated vessels—The current LNG fleet of more than 150 vessels and the more than 50 on order all have midship manifolds. Thus, transfer of LNG in all systems takes place at the midship manifold and only a minimum of adaptation of the LNG carrier is required.

High-pressure LNG pumps

LNG pumps in common use are of multistage centrifugal design. Those used in terminals receive LNG from the storage tanks at atmospheric pressures and discharge at pipeline pressures as high as 1,440psi. To obtain direct cavern injection, pumps must be capable of achieving discharge pressures in excess of 2,000psi. Ebara and Nikkiso Cryogenics, two of the largest LNG pump manufacturers, developed new designs with greater capability. Both manufacturers' designs have been field tested – Figures 8 and 9 – (Ebara – September 2003; Nikkiso Cryogenics – February 2004) with the results included in the research program.

High capacity LNG heat exchanger

There are several designs for LNG vaporizers or heat exchangers, but all those in use operate at maximum pressures below those necessary for direct injection of the warmed gas into salt cavern storage facilities. For the study, Northstar Industries designed and constructed a new design incorporating a cryogenic pipe within a water warmant pipe. This serial No. 1 Bishop Process Heat Exchanger was field tested April 12-16, at full scale, at the AGL Resources LNG plant near Canton, Ga. (Figure 10). Tests were performed at varying LNG rates, varying warmant water ratios and water temperatures. Flow rates as high as 170 MMcf/d were recorded, which in multiples can warm the LNG ship discharge at 10,000 m^3/hour or greater.

Initial observations were that the test results were similar to the mathematical predictions but with corrected models. A number of important design changes will improve operations in commercial applications. The patented Bishop Proccess LNG receiving terminal could utilized other vaporizer designs if modified to operate at higher pressures.

Preliminary research conclusions

The field work on the field tests of the critical components is complete. Commercialization of this technology requires a rigorous analysis of the test results, vetting of the conclusions by the industry participants and incorporation of what was learned into the process simulations. Then, the rating agencies and specialists in operability, maintainability, environmental impacts and safety can review the equipment and process designs, equipment lists and operating parameters (Figure 11). The total project completion is expected by year end.

No "show stoppers" have appeared in the field tests. Subsequent analysis will probe for workable solutions to move this technology forward to commercial applications. There have been several observations by the industry participants that the elimination of large volume cryogenic storage tanks makes the process design and operation simpler than those normally seen in the LNG industry. A startling contrast in a salt cavern-based terminal is that with permits in hand, it is estimated construction could be accomplished in about 2 years. This is at least 1 year less than tank-based designs and 2 years less than offshore tank-based gravity structure terminals.

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Superadiabatic Partial Oxidation for Hydrogen and Sulfur Production from Hydrogen Sulfide

by Dr. Rachid B. Slimane,
Gas Technology Institute

The Gas Technology Institute has been investigating superadiabatic partial oxidation concepts to not only develop novel, cost-effective processes to recover hydrogen and sulfur from hydrogen sulfide, but also produce hydrogen from natural gas and other liquid hydrocarbons, and gasify solid feedstocks, including waste materials with low calorific values.

Significant quantities of acid gases are generated each year (more than 200,000 tons/day of hydrogen sulfide – H_2S – processing capacity is in place worldwide), mainly as undesirable by-products of fossil fuel processing, including natural gas, petroleum and coal. Such gases are typically treated with the modified Claus process for sulfur (S_2) recovery; however, the hydrogen (H_2) component of H_2S is wasted as water in this process. In recent years, many approaches have been investigated to produce H_2, in addition to S_2, from H_2S. Despite the advances made, no method of H_2S decomposition can be considered commercially feasible today.

It is widely recognized that the most direct process of converting H_2S into H_2 and S_2 is through thermal decomposition – catalytic or non-catalytic. However, because of energy considerations, this approach has been considered impractical at temperatures exceeding about 1,700°F. In addition to being endothermic, the equilibrium of H_2S thermal decomposition at these temperatures is relatively low, and the reaction does not proceed to an industrially important extent. For example, based on thermodynamic equilibria, conversion of H_2S into H_2 is only about 20% at 1,831°F and 38% at 2,191°F. Temperatures exceeding 2,506°F are needed to drive the H_2S decomposition reaction to conversions greater than 50%.

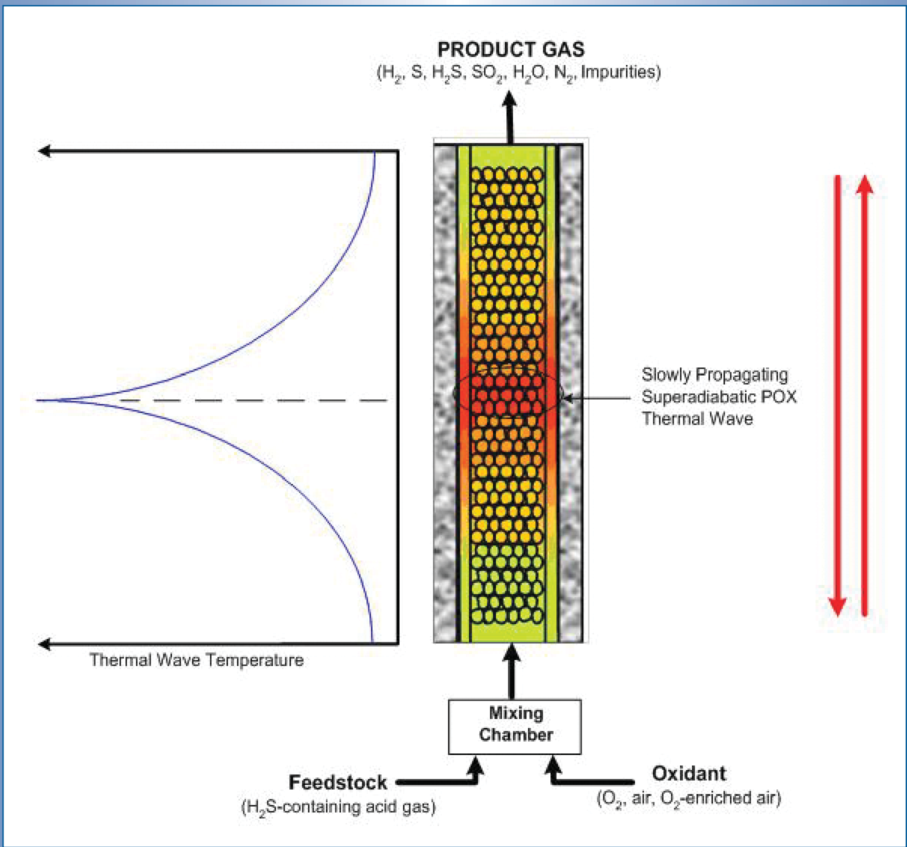

Figure 1. The superadiabatic partial oxidation concept for the thermochemical conversion of hydrogen sulfide into hydrogen and elemental sulfur is illustrated above.

Because of these limitations and other considerations, such as strict environmental regulations on S_2 emissions, any process for the recovery of H_2, in addition to S_2, from H_2S based on thermal decomposition or dissociation, has to overcome a number of technical

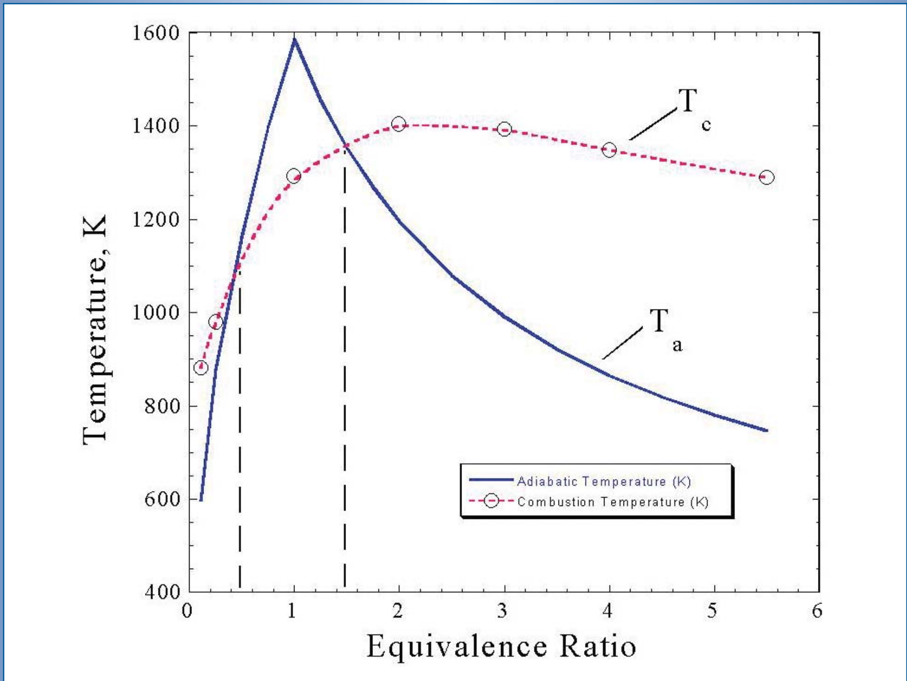

Figure 2. The superadiabatic partial oxidation temperature of hydrogen sulfide at different equivalence ratios. (Gas velocity =12 cm/s)

(and economic) hurdles, including:

- low yields even at high temperature (equilibrium-limited);
- to maximize H_2 production, it is necessary to separate the unreacted H_2S for recycle. Unless conversion is reasonably high, large recycle streams have to be dealt with;
- rapid quenching of product gas may be necessary to block any recombination of H_2 and S_2 (decomposition reaction is reversible); and
- fate of feed gas impurities has significant implications for emissions, tail-gas cleanup and purity of the H_2 product.

Recovering H_2 and S_2 from H_2S

The Gas Technology Institute (GTI), working with the University of Illinois at Chicago (UIC) and industrial advisors including UOP, has been developing a novel, potentially cost-effective process that promises to overcome the limitations of the non-catalytic thermal approach for producing H_2 and elemental S_2 from H_2S. The key feature of GTI's process is the superadiabatic reactor, where partial oxidation of H_2S in the H_2S-containing acid gas feed is carried out in a well-insulated, cylindrical vessel packed with an inert, porous ceramic medium with a high thermal capacity (Figure 1). The intensive heat exchange between the filtrating and burning gas mixture and the porous medium through the highly developed internal surfaces permits the accumulation of partial oxidation energy in the solid matrix. By coupling the partial oxidation of H_2S in the porous medium with the H_2S decomposition, very high temperatures (significantly higher than the adiabatic temperature for the feed mixture, Figure 2) can be achieved economically within a reaction zone – a slowly propagating thermal wave (Figure 3) – without the input of external energy, and therefore, no additional carbon dioxide emissions. In this self-sustaining reaction zone, conditions are favorable for the thermochemical conversion of H_2S into the desirable products, H_2 and elemental S_2, to proceed to an industrially significant extent.

Figure 3. Propagating superadiabatic partial oxidation thermal wave.

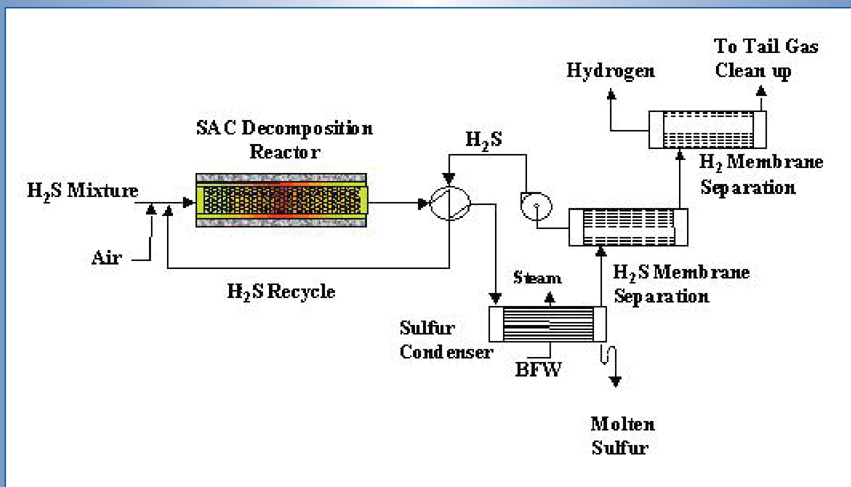

Figure 4. Gas Technology Institute's superadiabatic partial oxidation process for hydrogen and sulfur recovery from hydrogen sulfide.

GTI has envisioned a process comprising the superadiabatic partial oxidation (POX) reactor, product/byproduct separation schemes (such as membranes), H_2 purification and tail gas cleanup (Figure 4).

With funding from the U.S. Department of Energy – DOE – (Contract No. DE-FC36-99GO10450), GTI and UIC, work has focused on the superadiabatic POX reactor. A detailed numerical model has been developed to evaluate the effects of key process parameters and operating conditions on exit gas product yields. A bench-scale reactor system (Figure 5) has been designed, constructed and operated to demonstrate the technical feasibility of the superadiabatic POX concept, and address the effect of key variables on reactor performance. The experimental work has been supported by detailed thermodynamic and kinetic modeling studies, to evaluate the agreement between modeling predictions and experimental results, and optimize the superadiabatic POX process for H_2 and elemental S_2 production from H_2S-containing streams. Finally, the preliminary viability of the superadiabatic POX process was evaluated, within economic and market constraints.

Figure 5. A bench-scale test of Gas Technology Institute's superadiabatic partial oxidation reactor facility.

Summary of data/research results

Numerical modeling results showed that by optimizing the porous body reactor configuration, equivalence ratio and gas velocity, a maximum temperature of 2,475°F could be achieved in the superadiabatic H_2S POX reactor. Feed gases enter the reactor at ambient temperature, resulting in an overall H_2S conversion of 50%, with an H_2/water selectivity of 57/43 (for example, about 28.5% H_2 yield) and an elemental S_2/sulfur dioxide (SO_2) selectivity of 99/1. The overall process performance can be substantially improved, with respect to H_2 production, by membrane separation of product gases and recirculation of unreacted H_2S to extinction.

Experimental test results obtained in the recently completed, DOE-funded program (conducted mostly with gaseous feed mixtures simulating various – 20% H_2S and 80% nitrogen/oxygen – acid gas/oxidant combinations) are encouraging. The highest temperature achieved was about 2,194.5°F and the best estimated H_2 yield in a single pass amounted to 26% (for example, 26% of the H_2S in the feed to the superadiabatic POX reactor was converted into H_2 – Figures 6 and 7). By operating at a higher interstitial gas velocity[1] (greater than 45 cm/s), higher H_2S content acid gases (greater than 20% H_2S), and higher equivalence ratios[2], there is significant potential to achieve stable, self-sustaining superadiabatic thermal waves with much higher temperatures, leading to the expectation of improved H_2 yields. A superadiabatic POX temperature of 2,475°F and an H_2 yield of 28.5%, considered to constitute the optimum scenario (according to the numerical modeling results), appear to be within reach. The experimental test results indicate the beneficial effects of operating the superadiabatic POX reactor at a high interstitial gas velocity, to maintain a reasonably high H_2 yield, particularly as the equivalence ratio of the feed gas increases. The results also indicate operating conditions exist to optimize the H_2 yield and elemental S_2 yield in a single pass, while minimizing generation of SO_2.

1. The interstitial gas velocity is defined based on the feed gas flow rate in the interstitial space of the ceramic packing at ambient conditions (25°C, 1 atm.).
2. The equivalence ratio is defined as the ratio of the amount of O_2 that is stoichiometrically required to completely oxidize the H_2S in the fuel gas, to the amount of O_2 available.

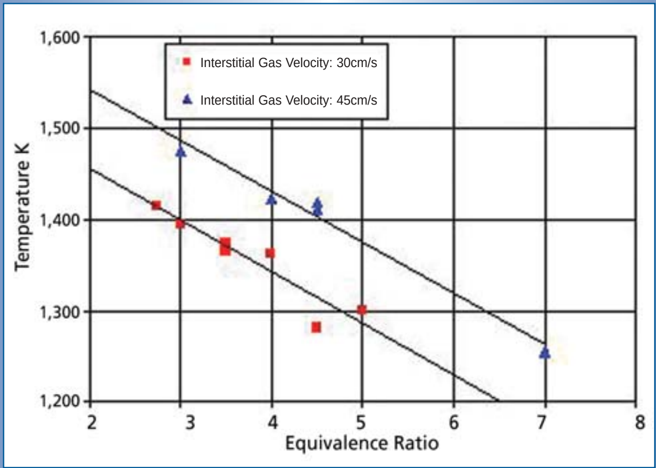

Figure 6. The above graphic shows temperatures from the superadiabatic partial oxidation of (20% H_2S-80%N_2)/O_2 at different equivalence ratios.

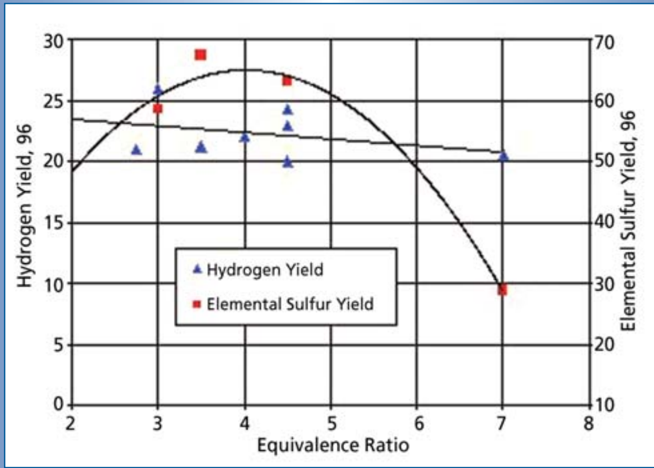

Figure 7. Hydrogen and elemental sulfur yields from the superadiabatic partial oxidation of (20% H_2S-80%N_2)/O_2 at different equivalence ratios.

GTI also has developed a preliminary estimate for the supply cost of H_2 generated through the superadiabatic partial oxidation process, by evaluating the economic potential of four selected process schemes. The selected configurations considered the superadiabatic POX process as a stand-alone process as well as in association with additional commercially available S_2 recovery and tail gas cleanup units. All four schemes were compared with natural gas-fired thermal dissociation of H_2S (a developing technology) and steam methane reforming (the industry standard for H_2 production). The superadiabatic partial oxidation process schemes were shown to have clear economic advantages over thermal dissociation of H_2S. In addition, with an efficient H_2/H_2S separation system, the superadiabatic H_2S decomposition process shows potential to produce H_2 at a cost approaching that for conventional steam methane reforming.

Future plans for H_2S-related research

The results developed so far indicate the superadiabatic POX concept can form the basis for a viable process to recover a significant portion of H_2 in acid gases (typical of Claus feeds), while recovering S_2 to the extent required by environmental regulations. GTI believes a combination of laboratory-scale and pilot-scale work is needed to address several issues, which are critical for successful demonstration and future commercialization of this technology:

- fate of feed gas impurities (including carbon dioxide – CO_2, and methane – CH_4) in the product gas, their effects on reactor performance and implications for tail gas cleanup;
- product/byproduct separation schemes to separate the unreacted H_2S for recycle (to maximize the overall H_2S conversion), the H_2 product for purification and the tail gas for cleanup;
- construction and operation of a pilot-scale superadiabatic reactor system to provide for a more practical evaluation of the process and develop large-scale data permitting more realistic engineering and economic analysis; and
- construction of an integrated superadiabatic H_2S POX reactor system for field-testing at an industrial site, such as a refinery.

Other applications

Distributed H_2 production from natural gas—GTI has submitted a proposal in response to the DOE Solicitation No. DE-PS36-03GO93007 Hydrogen Production and Delivery Research. GTI – in collaboration with UIC, Prof. Janet Ellzey from the University of Texas at Austin, and other industrial partners – proposed to confirm the viability of the superadiabatic reactor as a POX/autothermal reforming (ATR) reactor that can form the basis for developing an economical process for small-scale distributed H_2 production from natural gas. Such a process can replace a typical fuel processor using catalytic reforming.

The technology consists of the superadiabatic POX/ATR reactor as a syngas generator operating at high temperature without a catalyst, followed by one or two gas shift converters to reduce the carbon monoxide (CO) content of the reformer effluent below 1% and yield more H_2 (Figure 8). Because the superadiabatic POX/ATR product gases are rapidly cooled, it would be feasible to integrate a low- and/or high-temperature catalytic shift reaction zone into the superadiabatic POX/ATR reactor, allowing the water gas shift (WGS) reaction to proceed under favorable thermodynamic conditions. The steam required for the section can be excess steam fed with the reactants, steam produced by the superadiabatic POX reaction or steam introduced separately in the WGS reaction

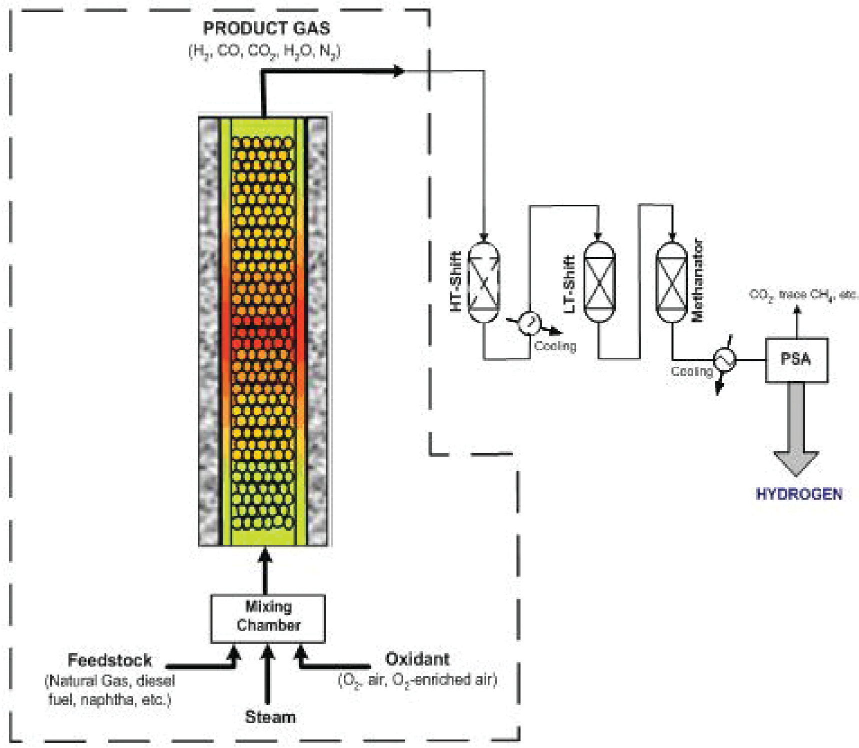

Figure 8. A proposed superadiabatic partial oxidation/autothermal reforming process scheme for low-cost hydrogen production.

zone. In this setting, the superadiabatic POX reactor can form the basis for a process combining reforming and shifting into a single integrated reactor design. Because of the high-temperature reforming reaction, little or no methane is present in the reactor effluent. Potentially, only H_2 separation and additional purification (CO removal) would be required to produce clean H_2 for broad-based applications in the emerging H_2 economy, including chemical and oil refineries, Fischer-Tropsch process and fuel cells.

Superadiabatic POX reactor as a replacement for Claus furnace—The major advantage of the superadiabatic POX process is the recovery of H_2 in addition to elemental S_2 from H_2S. Hydrogen production aside, another application for this process would be as a replacement for the Claus furnace, especially for acid gases containing contaminants such as benzene, carbonyl sulfide (COS), and CS_2, which add to the complexity and cost of tail gas cleanup in the Claus process. The high operating temperatures in the superadiabatic POX reactor should help crack benzene, and the excess H_2 can help hydrogenate COS, carbon disulfide (CS_2) and any unsaturates present. The superadiabatic POX process is less stringent than the Claus process from the point of view of the required feed gas conditioning. As indicated earlier in Figure 7, even with an acid gas containing less than 20% H_2S, more than 65% of the S_2 in the feed was recovered as elemental S_2 in a single pass through the superadiabatic POX reactor.

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