SUPPORT OF GULF OF MEXICO HYDRATE RESEARCH CONSORTIUM: ACTIVITIES TO SUPPORT ESTABLISHMENT OF A SEA FLOOR MONITORING STATION PROJECT

SEMIANNUAL TECHNICAL REPORT FOR THE 2ND QUARTER
1 MARCH, 2003 THROUGH 31 MAY, 2003

PREPARED BY THE MANAGEMENT TEAM,
CENTER FOR MARINE RESOURCES AND ENVIRONMENTAL TECHNOLOGY
220 OLD CHEMISTRY BUILDING, UNIVERSITY, MS 38677

MARCH 2004

DOE Award Number DE-FC26-02NT41628

This report was prepared with the support of the United States Department of Energy, under award No. DE-FC26-02NT41628. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the views of the DOE. DOE Award Number DE-FC26-02NT41628 is managed by the U.S. Department of Energy's National Energy Technology Laboratory.

Subcontractors:

Paul Higley, Specialty Devices, Inc., 1104 Summit Ave. #104, Plano, TX 75074

Task 1: Continuation of Work on the Vertical Line Array

J. Robert Woolsey, MMRI/CMRET, 220 Old Chemistry Building, University of Mississippi, University, Mississippi, 38677

Task 2: Construction of the Prototype Sea Floor Probe

Ralph Goodman, Department of Marine Sciences, University of Southern Mississippi, 1020 Balch Blvd., Stennis Space Center, MS 39529

Task 3: Acoustic System for Monitoring Gas Hydrates

Vernon Asper, Department of Marine Sciences, University of Southern Mississippi, 1020 Balch Blvd., Stennis Space Center, MS 39529

Task 4: Construction and Testing of an Electromagnetic Bubble Detector and Counter

Boris Mizaikoff, School of Chemistry and Biochemistry, Georgia Institute of Technology, Applied Sensors Laboratory, 770 State St, Atlanta, GA 30332

Task 5: Mid-Infrared Sensor Systems for Continuous Methane Monitoring in Seawater

Angela Davis, AUGER Geophysical Services, School of Ocean Sciences, University of Wales, Bangor, Menai Bridge, Anglesey LL59 5EY, Bangor, Wales, UK

Task 6: Seismo-Acoustic Characterization of Sea Floor Properties and Processes at the Hydrate Monitoring Station

ABSTRACT:
A Consortium, designed to assemble leaders in gas hydrates research, has been established at the University of Mississippi's Center for Marine Resources and Environmental Technology, CMRET. The primary objective of the group is to design and emplace a remote monitoring station on the sea floor in the northern Gulf of Mexico by the year 2005, in an area where gas hydrates are known to be present at, or just below, the sea floor. This mission necessitates assembling a station that will monitor physical and chemical parameters of the sea water and sea floor sediments on a more-or-less continuous basis over an extended period of time. Development of the station allows for the possibility of expanding its capabilities to include biological monitoring, as a means of assessing environmental health. Establishment of the Consortium has already succeeded in fulfilling the critical need to coordinate activities, avoid redundancies and communicate effectively among researchers in this relatively new research arena. Complementary expertise, both scientific and technical, has been assembled to innovate research methods and construct necessary instrumentation.

As funding for this project, scheduled to commence December 1, 2002, had only been in place for less than half of the reporting period, project progress has been less than for other reporting periods. Nevertheless, significant progress has been made and several cruises are planned for the summer/fall of 2003 to test equipment, techniques and compatibility of systems.

En route to reaching the primary goal of the Consortium, the establishment of a monitoring station on the sea floor, the following achievements have been made:

- Progress on the vertical line array (VLA) of sensors:
    - Software and hardware upgrades to the data logger for the prototype vertical line array, including enhanced programmable gains, increased sampling rates, improved surface communications,
    - Cabling upgrade to allow installation of positioning sensors,
    - Incorporation of capability to map the bottom location of the VLA,
    - Improvements in timing issues for data recording.

- Sea Floor Probe
    - The Sea Floor Probe and its delivery system, the Multipurpose sled have been completed.
    - The probe has been modified to penetrate the <1m blanket of hemipelagic ooze at the water/sea floor interface to provide the necessary coupling of the accelerometer with the denser underlying sediments.

- Electromagnetic bubble detector and counter
    - Initial tests performed with standard conductivity sensors detected nonconductive objects as small as .6mm, a very encouraging result,
    - Components for the prototype are being assembled, including a dedicated microcomputer to control power, readout and logging of the data, all at an acceptable speed.

- Acoustic Systems for Monitoring Gas Hydrates
  - Video recordings of bubbles emitted from a seep in Mississippi Canyon have been made from a submersible dive and the bubbles analyzed with respect to their size, number, and rise rate. These measurements will be used to determine the parameters to build the system capable of measuring gas escaping at the site of the monitoring station.
  - A scattering system and bubble-producing device, being assembled at USM, will be tested in the next two months, and the results compared to a physical scattering model.

- Mid-Infrared Sensor for Continuous Methane Monitoring
  - Progress has been made toward minimizing system maintenance through increased capacity and operational longevity,
  - Miniaturization of many components of the sensor systems has been completed,
  - A software package has been designed especially for the MIR sensor data evaluation,
  - Custom electronics have been developed that reduce power consumption and, therefore, increase the length of time the system can remain operational.

- Seismo-acoustic characterization of sea floor properties and processes at the hydrate monitoring station.
  - Adaptation of the acoustic-logging device, developed as part of the European Union-funded research project, Sub-Gate, for monitoring temporal variations in seabed acoustic responses has commenced. Electronics as well as hardware are undergoing development specific to this DOE project.

TABLE OF CONTENTS

PAGE

LIST OF GRAPHICAL MATERIALS

Graphical materials used to illustrate reports can be found in the individual reports submitted by the subcontractors.

INTRODUCTION/PROJECT SUMMARY

The Gulf of Mexico-Hydrate Research Consortium (GOM-HRC) is in its fifth year of developing a Gulf of Mexico-Sea Floor Observatory (GOM-SFO). The GOM-SFO is planned to be a multi-sensor station that provides more-or-less continuous monitoring of the near-seabed hydrocarbon system, within the hydrate stability zone (HSZ) of the northern Gulf of Mexico. It is anticipated that this station and associated studies will provide a better understanding of this complex hydrocarbon system, particularly hydrate formation/dissociation, fluid venting to the water column, and associated microbial/chemosynthetic communities. It is hoped that models can be developed from these studies that can provide a better understanding of gas hydrates and associated free gas as: 1) a geo-hazard to conventional deep oil and gas activities; 2) as a future energy resource of considerable significance; and 3) as a source of hydrocarbon gasses, venting to the water column and eventually the atmosphere, with global climate implications.

The GOM-HRC initially received funding from the DOI Minerals Management Service (MMS) in FY1998. Funding from the DOE National Energy Technology Laboratory (NETL) began in FY2000 and from the DOC NOAA-NURP in 2002. Some five industries and seventeen universities are involved at various levels of participation. Funded Investigations include a range of physical, chemical, and biological studies.

EXECUTIVE SUMMARY

A consortium has been assembled for the purpose of consolidating the efforts of leaders in gas hydrates research. The consortium, established at the University of Mississippi's Center for Marine Resources and Environmental Technology (CMRET), has, as its primary objective, the design and emplacement of a remote monitoring station on the sea floor in the northern Gulf of Mexico by the year 2005. The primary purpose of the station is to monitor activity in an area where gas hydrates are known to be present at, or just below, the sea floor. The goal necessitates assembling a station that will monitor physical and chemical parameters of the sea water and sea floor sediments on a more-or-less continuous basis over an extended period of time.

Development of the station allows for the possibility of expanding its capabilities to include biological monitoring. This option would facilitate the study of chemosynthetic communities and their interactions with geologic processes in addition to providing an assessment of environmental health. Central to the establishment of the Consortium is the need to coordinate activities, avoid redundancies and promote effective and efficient communication among researchers in this relatively new research arena. Complementary expertise, both scientific and technical, has been assembled to introduce collaborative possibilities, coordinate research methods and to construct necessary instrumentation.

The centerpiece of the monitoring station is a series of vertical line arrays of sensors (VLAs), to be moored to the sea floor. Each VLA will extend approximately 200 meters above the sea floor and will be comprised of hydrophones to record water-borne acoustic energy (and measure sound speed in the lower water column), thermistors to measure water temperature, tilt meters to sense deviations from the vertical induced by water currents, and compasses to indicate the directions in which the deviations occur.

The prototype VLA has been completed together with the associated data logging and processing systems. The system consists of 16 hydrophones spaced at 12.5 meter intervals with an overall length of 200 meters. The sensitivity and spacing of the hydrophones is critical to the data acquisition process with regard to the objective focus on near sea floor features such as hydrate bodies. The hydrophones will be sampled at a rate of 10,000 samples per second, which is compatible with high resolution imaging of geologic features.

Progress on the vertical line array of sensors for this reporting period includes both software and hardware upgrades to the data logger for the prototype vertical line array, directed at producing enhanced programmable gains, increased sampling rates, and improved surface communications. Cabling upgrades have been made to allow installation of positioning sensors. Incorporation of the capability to map the bottom location of the VLA has been added and improvements in timing issues for data recording have been made.

A fall cruise will include two separate deployments of the VLA in the northern Gulf of Mexico. The primary goal of the cruise is to test the adjustments made to the hardware and software systems since its initial sea trial in August, 2002.

The Sea Floor Probe (SFP) and its delivery system, the Multipurpose sled have been completed. The probe has been modified to penetrate the <1m blanket of hemipelagic ooze at the water/sea floor interface to provide the necessary coupling of the accelerometer with the denser underlying sediments. It is anticipated that a shallow-water test will be required prior to a deep-sea deployment of this system.

Video recordings of bubbles emitted from a seep in Mississippi Canyon have been made from a submersible dive and the bubbles analyzed with respect to their size, number, and rise rate. These measurements will be used to determine the parameters to build the system capable of measuring gas escaping at the site of the monitoring station. A scattering system and bubble-producing device, being assembled at USM, will be tested in the next two months, and the results compared to a physical scattering model.

Initial tests of the electromagnetic bubble detector and counter have been performed with standard conductivity sensors. The device detected nonconductive objects as small as .6mm, a very encouraging result. Components for the prototype are being assembled, including a dedicated microcomputer to control power, readout and logging of the data, all at an acceptable speed.

Laboratory tests will continue on the prototype. The system will be tested on a submersible and deployed at a gas vent.

Progress has been made toward minimizing system maintenance for the Mid-Infrared Sensor for Continuous Methane Monitoring through increased capacity and operational longevity. Miniaturization of many components of the sensor systems has been completed, and a software package has been designed especially for the MIR sensor data evaluation. Custom electronics have been developed that reduce power consumption and, therefore, extend the length of time the system can remain operational.

Further pressure testing in a laboratory setting will precede ocean tests.

Seismo-aoustic characterizarion of sea floor properties and processes is a priority for the hydrate monitoring station research effort. Adaptation of the acoustic-logging device, developed as part of the European Union-funded research project, Sub-Gate, for monitoring temporal variations in seabed acoustic responses has commenced. Electronics as well as hardware are undergoing development specific to this project.

Field trials are scheduled to test the performance of the device throughout its period of development.

EXPERIMENTAL

Experiments are described in the individual reports submitted by the subcontractors and included in the "Results and Discussion" section, which follows.

RESULTS AND DISCUSSION

Results and discussion of those results are described in the individual reports submitted by the subcontractors. Reports from the six subcontractors follow.

Gas Hydrate *In situ* Monitoring Station Vertical Array

Abstract

A near sea floor, 200 meter vertical acoustic array is being developed as part of a long term sea floor monitoring station to study gas hydrate deposits. This report addresses progress in the development of a vertical seismic array system specifically designed for 3-dimensional mapping of shallow gas hydrate deposits. The time frame covered in this report includes the first half of the second year of development of this vertical array. The report includes progress in the data logger, vertical array and software. The program includes production of 2 additional arrays and refurbishment of the year one array.

Introduction

The vertical array is comprised of an array of 16 hydrophones spaced 12.5 meters apart and extending approximately 200 meters up from the sea floor. A data logger and a pressure compensated battery pack are mounted at the bottom of the hydrophone array. The array is suspended via glass flotation and anchored with an expendable concrete weight. Recovery of the array with its battery pack and data logger is accomplished through activation of an acoustic release connecting the array to the anchor. The design is intended to allow several days of data collection using a near surface towed sound source, with shots fired and timed in sequence with the data collection regime programmed into the near bottom mounted data logger. An acoustic modem-based communication system allows the surface ship computer to reprogram and direct this data collection regime. This communications link to the sea floor equipment also provides an ability to recover sample data sets to assess and alter the data collection parameters.

The system developed during the first year of effort was successfully installed and recovered in 830 meters of water. The second year efforts include improvements and enhancements to the capability as well as construction of 2 additional vertical arrays capable of deployment in deeper depths. The refurbishment of the first year array is included in this effort.

Executive Summary

Progress during the first part of FY 2003 included further development of the data logger, the vertical array sensors and systems software.

- Software and hardware upgrades to the data logger for the prototype vertical array included enhanced programmable gains, faster sampling rates, and improved surface communications.
- The vertical array cabling was upgraded to allow installation of positioning sensors.
- SDI's Angulate program was adapted to use acoustic slant ranges and DGPS data to compute and map the bottom location of the vertical array. Progress was also achieved in T"0" delay and timing issues for improved control of data

recording.

Experimental

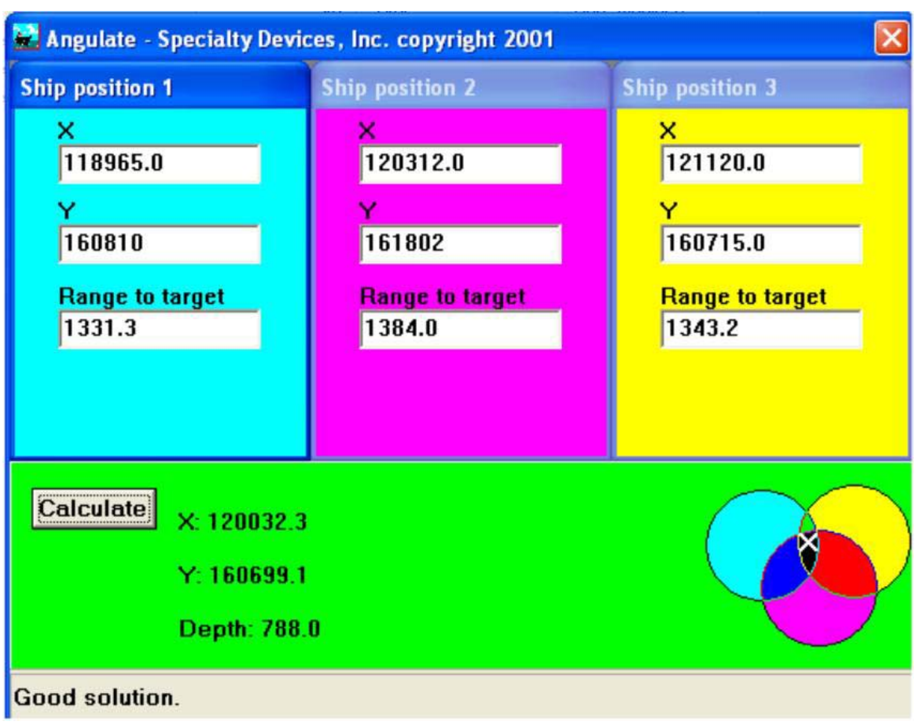
Positioning sensors

The positioning sensors include 2-axis inclinometers and a compass. The inclinometers and compass report using RS-485 protocol to a serial port on the data logger computer. The inclinometers and compass are to be included in a single housing with two such systems mounted to the vertical array. The first year vertical array cable is now equipped with connectors and wiring for these sensors. The sensors have been acquired and tested. The remaining tasks include designing the housings and modifying the data logger software.

Bottom Location Software

SDI's Angulate program computes the position and depth of fixed equipment on the seafloor assuming slant ranges to this equipment can be acquired from three positions on the sea surface. Changes and upgrades to this program include addition of a Latitude/Longitude computational capability and the ability to use acoustic release deck box ranges to computer bottom installed equipment. A graphic depiction of the results affords the operator the ability to asses the validity of the geometry used to compute a solution.

An example of the Angulate program results is displayed below:



Data Logger Software

The DATS data logger software now includes a capability to pre-program a sampling plan prior to deployment of the vertical array. This includes the sampling interval, the sampling period, the programmable gain setting, and the start delay.

Also added is an ability to sub-sample an individual channel of a data set and report this sub-sample to the surface via the acoustic modem. This sub-sampling routine includes statistical information that is used by the surface operator to determine the proper programmable gain settings of the individual channels. The sub-sampled data set also provides a visual representation of the sound source first arrival. The timing of the first arrival compared to the start of the recording interval for the shot can be used to check validity of the "T0" time.

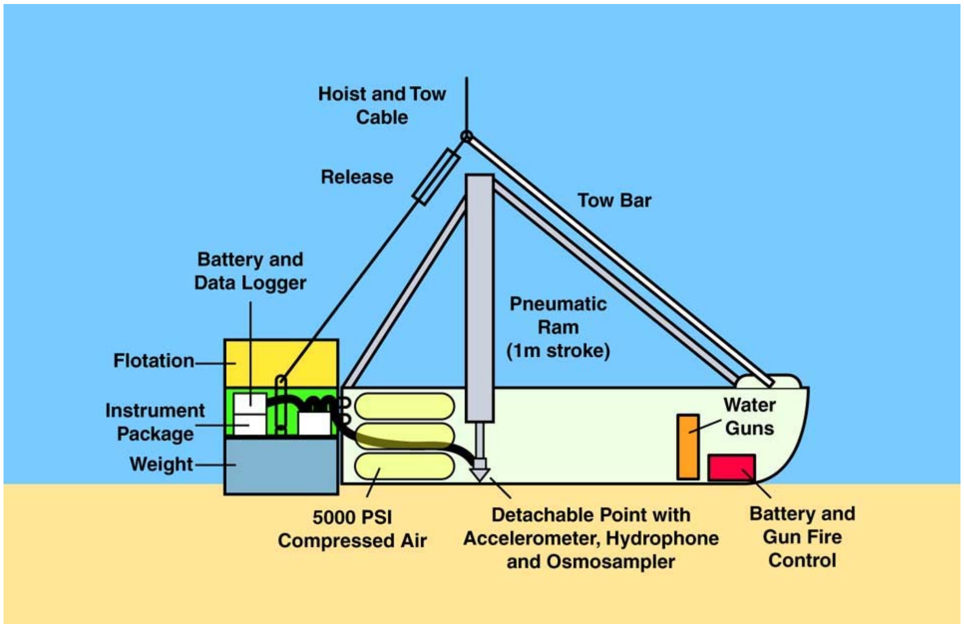
Remaining tasks on this software include adding the ability to measure propagation delays for timing pulses and correct the surface and sub-surface clock synchronization utilizing the smart modem range finding function. This will become a significant issue as clock drift becomes a significant issue as system deployments extend from the prototype deployments of a few days to semi-permanent deployments of months to years.

Conclusion

Although the second year effort was begun later than planned, progress has been significant. The majority of the planned changes to the data logger and surface system software are anticipated to be complete by the fall 2003 deployment cruise. This cruise will serve to further test and refine the hardware and software. The hardware design for the two additional deeper water-capable vertical arrays should be complete at this time. Hardware construction will initiate following incorporating refinements derived from this deployment.

Construction of the Prototype Sea Floor Probe

During the period of this report the Sea Floor Probe (SFP) and its mechanical delivery system; i.e. the Multi-Purpose Sled (MPS), have been completed (see figure). Some modifications to the original plan have been made to accommodate programmatic changes. Since project start-up the program has been expanded to include the interest of the JIP. Specifically, this involves the instrumentation of a test bore-hole with a multi-channel, 4-component, vertical line array (BVLA), approximately 400 meters in length, to accommodate the thickness of the hydrate stability zone at the station site. The BVLA will form the center of the acoustic section, together with the peripheral cluster of 5 water-column, vertical line arrays (VLA's). With this substantial installation, the emphasis of the seafloor probe/multipurpose towed sled (SFP/MPS) will shift more toward the s-and p-wave sound generation capability for the latter, for use as an energy source for the BVLA. The SFP has been modified to penetrate the less-than-one meter blanket of aqueous, hemipelagic ooze, so as to provide the necessary coupling of the accelerometer with the more dense underlying sediments. With the completion of the mechanical systems it remains to complete and install the necessary electronics for system command and control.



Multipurpose Towed Sled
Rigged For Single Point System Deployment

Acoustic Systems for Monitoring Gas Hydrates

Bubble clouds from the emission of gas hydrates into the sea can be observed directly by either optical or acoustical systems. It is the objective of this project to: (1) examine acoustic concepts for the detection and monitoring of bubble emission, (2) select the most promising method, (3) develop and test a measuring system, (4) deploy and retrieve the system and (5) analyze the data and evaluate the results.

Bubbles, because of their drastic differences in mechanical properties from those of seawater, cause significant effects on acoustic signals that pass through bubble clouds. These effects are dependent on the acoustic frequency, the sizes and number of bubbles, the geometry of the cloud, and the depth. The basic approaches for a monitoring system could be: (1) to measure the scattering strength from a collection of individual bubbles, (2) to measure the scattering that is caused by the change in sound speed of the bubble cloud itself, and (3) to measure the change in sound speed caused by the cloud. Each of these has its own caveats.

The measure of sound speed would be the most direct method because it only involves a measurement of time. But it would require the accurate placement of a source and a receiver on opposite sides of a bubble cloud. It also would require a low frequency source that would have the inherent problem of a wide beam width. This method was, therefore, dismissed as being impractical.

The scattering caused by the bubble cloud itself is highly dependent upon the size distribution, total bubble density, and acoustic frequency. Although, in principal, a system could be devised that would give the bubble properties, it would be more complex than envisioned for deployment in deep water. It would be worthy of further study in the longer term of research, but will not be considered further as part of this project.

Devising a system that uses the scattering from individual bubbles required some knowledge of the cloud size, bubble sizes, and number. During the deep submersible run last summer a video was made of a bubble seep at what is called the “shallow site.” Against a backdrop of a white board marked in inches it is possible to estimate the bubble sizes and number, and estimate their rise rate. At the time of this writing quantitative measures, although somewhat primitive, are being made on a short segment of the video. Sizes range up to about one half centimeter radii and have a rise rate of approximately 25 cm/sec, (which is consistent with other observations of bubbles of this size). From these measurements we will be able to determine the parameters for a measurement system that will be at a high enough frequency to be above the resonant frequencies of the bubbles. It appears from the video that most of the bubbles are on the order of a millimeter or larger. (The video has a low resolution so the smallest size is at best, a guess. At least the video does not seem to show a diffuse cloud of bubbles that are seen below breaking waves.) From the size and density measurements a scattering model will be developed to determine the appropriate system parameters.

At present a scattering system is being assembled at NRL utilizing existing transducers. To test the system a bubble-producing device has been built. This system will be tested within the next two months. The results will be compared to a physical scattering model.

Construction and Testing of an Electromagnetic Bubble Detector and Counter

A. Scope of Work:

In order to characterize activity at the hydrate sites, it is necessary to quantify the volume of gas being released into the water column, the temporal variability of this release, and the sizes of bubbles being generated. This proposal requested funds to build a bubble detector based on a technique which is used widely in the ocean to measure the conductivity of the water, but which can be adapted to measure bubbles as well because they lower the conductivity of the water in which they are entrained. This technique uses paired coils of wire, the dimensions of which can be tuned to suit the particular application. A current is induced in one coil of wire and a current is induced in the adjacent coil of wire, the magnitude of the induced current being dependent upon the electrical conductivity of the water which the coil pair surrounds. This technique is used by many manufacturers of *in situ* sensors to measure water conductivity because conductivity is directly proportional to the salinity of the water due to what is known as the "law of constant proportions". The widespread use of this technique indicates that it is well accepted and that its inherent sensitivity is appropriate for our application.

B. Status on Tasks to be Performed:

1. Design system: Before specifics of the design could be finalized, it was necessary to prove the concept. We acquired several standard conductivity sensors and performed initial tests; the results were quite promising. Using an Aanderaa conductivity sensor and water of salinity ~35, we were able to detect a non-conductive object as small as 0.12 mm^3. This equates to a bubble of 0.6mm diameter so it should be possible to detect, reliably, bubbles in the 1mm diameter target size range (volume of 0.52mm^3). We are continuing tests of the prototype system to determine its sensitivity to non-conductive objects placed at varying distances and azimuths from the sensing coil.

2. Construct system: Given the excellent results of the tests, we have decided to use a standard, OEM conductivity sensor instead of custom building our own. The only sensor available that is rated to >1,500m and which gives a pure analogue (0-5VDC) output is made by Falmouth Scientific Instruments and we have placed an order for one of these. The cost is over $4,000, but we feel that the reliability and unique nature of this application warrant this expense. We have also been evaluating Onset Tattletale model 8 microcomputers and working with preliminary code to drive the sensor. The Tattletale will be required to control power, select between temperature and conductivity readouts (temperature is required for calibration of the conductivity sensor) and logging the data. We will purchase a dedicated Tattletale for the project soon, but we are currently using a borrowed controller for evaluation to ensure that it will fulfill all of the appropriate functions at an acceptable speed.

3. Laboratory test system: As construction of the field system progresses, we will continue to perform detailed laboratory tests of the prototype system. Kevin Martin, the Master's student funded under this award, is developing a sensitivity map of the volume of water within and surrounding the loop. Preliminary tests have shown that objects outside of the sample volume do have an effect and it is important to evaluate the degree of sensitivity to these effects. Mr. Martin will be positioning a calibrated non-conductive sphere at various locations and azimuths from the sample volume and recording its effect on the measured conductivity. These tests will also be performed on the final system, once it is completed, in order to verify its function. Once the sensor is complete, we will expand to measurements using bubbles in the lab to ensure that the system is capable of responding quickly enough and to evaluate the effects of multiple bubbles.
4. Submersible test system: Once all system functions have been confirmed, and provided access can be obtained, we will mount the system on the Johnson Sealink submersible and deploy it on a suitable gas vent. During this exercise, we will obtain video of the bubbles being generated for comparison with the data collected by our sensor system.

C. Future Plans

From these preliminary experiments, from discussions with colleagues, and based on the results of other programs, it has become apparent that the detection and quantification capability provided by this system will be very useful, but that more information is also needed. This system will be able to accurately monitor the evolution of gas at a single vent and correlate this activity with changes in temperature. However, there is no guarantee that these results will be applicable to a wider range of vents and it is therefore imperative to develop hardware that is capable of surveying larger areas. To this end, we will be proposing to add a high-frequency sector scanning sonar and a digital camera to this package to monitor the overall evolution of gas across the vent field and to acquire images of specific bubbles for verification. These results will be coordinated with those of other researchers working in the area to provide an overall monitoring capability.

Mid-Infrared Sensor systems for Continuous Methane Monitoring in Seawater: Methane detection using attenuated total reflection (ATR) spectroscopy.

ABSTRACT/SUMMARY

This technical report summarizes the progress towards development of spectroscopic methane sensing systems based on mid-infrared (MIR) attenuated total reflection (ATR) spectroscopy for operation in deep-sea environments. Representative figures are included.

- The prototype of a miniaturized control system for the 'sphereIR' has been developed, encompassing integration of spectrometer system control, data storage and retrieval, and multivariate data evaluation into a single-board PC.
- A chemometric data evaluation software package ('deepSniff') for evaluating complex spectra including corrections for baseline drifts and spectral anomalies resulting from matrix substances has been developed and incorporated into the miniaturized control system of the deep-sea device.
- The miniaturized control system including the data evaluation package has been successfully integrated with the optical components of 'sphereIR'; full control of the optical bench has been achieved.
- Mid-infrared detection based on a miniaturized Stirling-cooled MCT detector has been optimized and integrated with the spectrometer.
- The fundamental components of the spectrometer capable of operating at depths > 3,000 m have been designed along with design concepts of sensor head.
- The deep sea glass housing for the sensor module has been equipped with penetrators for power supply and data transmission suitable for operational depths >3,000 m.
- High-pressure multireflection ATR measurements simulating deep-sea conditions evaluating environmental impact on the sensor system and multivariate data analysis have commenced and will continue throughout the following project period.

Based upon current results, we anticipate finalizing a first prototype of a miniaturized, multicomponent IR sensor system ready for field deployment as component of the gas hydrates observation platform in the Gulf of Mexico during continuation of this project in late 2004.

Miniaturized control system for 'sphereIR'

The miniaturized control system for 'sphereIR' is an essential integral component for the successful operation of the IR methane sensing system during field deployment. The control system is based on a single-board PC and a miniature 60 gigabyte hard disk drive. During the reporting period we have developed a robust combination of both hardware and software to enable and maintain independent sensing operation in harsh deep-sea environments. The control system is capable of entire sensor system rebooting (incl. hard- and software start up) in case of short-term or long-term power loss, or in case of software or hardware lockups (Figure 1). The developed system minimizes hands-on system maintenance and increases operational longevity during sensing campaigns where unforeseen events such as power failures are likely to occur. The miniature 60 gigabyte hard disk drive allows the storage of data from multivariate data analyses as well as the raw data, which enables additional data reevaluation after system retrieval. A multifunctional data evaluation software package ('deepSniff') has been developed, additionally providing the ability to selectively power down various components of the sensing system (i.e. IR light source, interferometer, Stirling-cooled MCT detector, and HeNe laser) in an effort to minimize power consumption during off-peak operational periods, while sustaining the system's long-term operational goals (Figure 2). Details of the hard- and software will be provided in the final report.

Data retrieval with this system can be achieved by using a PC on-site (ship with appropriate link) and is readily adaptable for any kind of data up-link e.g. if a fiberoptic communication loop is available near the station site. Data retrieval does not require any disassembly of the system housing thus reducing the amount of operational down time during data retrieval campaigns. Using the same software and connection for data retrieval, measurement series can be defined on-site without sensor disassembly. Currently, data retrieval requires resurfacing of the sensor; however, in the case of availability of a direct fiberoptic connection at the measurement site, data retrieval can be setup such that retrieval could be completed virtually anywhere in the world via internet connection.

Chemometric data evaluation package for 'deepSniff'

In the previous reporting period the fundamentals of a novel chemometrics software concept for deep sea spectroscopic data analysis has been developed. This package has now been converted into a Windows-controlled data evaluation package and incorporated into the multifunctional software 'deepSniff' specifically designed for the control of 'sphereIR', which is now also capable of automated multivariate data evaluation. Chemometric data evaluation is a robust approach for unattended evaluation of complex spectroscopic data sets enabling automated detection and correction of baseline drifts and successful identification and exclusion of spectroscopic anomalies arising from matrix interferences that can be both expected and unexpected. Operational details and screen shorts will be provided in the final report.

Mid-infrared detection based on a Stirling-cooled MCT detector

A Stirling-cooled MCT detector was successfully integrated with the spectrometer components to be used in the 'sphereIR' (Figure 3). The Stirling-cooler provides several thousand hours of maintenance-free detector cooling operation (77 K) ideal for long-term deep-sea monitoring. Custom electronics were developed and integrated into 'deepSniff' providing software control of the detector power supply to reduce power consumption during measurement downtimes and prolonging the lifetime of the cooler itself by switching the detector on and off when appropriate (Figure 4). These electronics also provide a hardware/software system for determining the Sterling-cooler state by monitoring the current drawn by the cooler to ensure proper data acquisition during unattended measurement campaigns. Furthermore, control on the power cycle of the detector is provided enabling to set measurement times taking into account a nominal time delay between powering the cooler and achieving the desired operational temperature for the MCT element.

First tests evaluating the long-term signal stability of the Stirling-cooled MCT detector were conducted measuring water with an uncoated germanium crystal over a period of 24 h (Figure 5). Results from the stability evaluation and long-term operation capabilities of the detector corroborate that this detector scheme is a feasible solution for long-term deep-sea sensing in conjunction with multivariate chemometric data evaluation.

Fundamental spectrometer components and design concepts

The complete electronics of the ‘sphereIR’ have been developed and interfaced with the spectrometer components (Figure 6). 3D computer modelling of each component of the Bruker IRcube spectrometer providing the fundamental spectroscopic components of the system and the additional components (i.e. Stirling-cooled MCT detector, custom control electronics, and optical components) confirm that all required parts can be arranged to fit inside the spherical deep sea housing (17’ diam.) produced by Benthos. The sensor housing unit has so far been equipped with penetrators for communication and power; future adaptations and additional penetrators will be added for the optical transducer, which is a primary focus of project phase 2003/2004. Our collaborator Bruker Optics (Billerica/MA and Ettlingen/Germany) has ensured continuous support of this project during the ongoing development phase.

First design concepts for the ‘sphereIR’ have been finalized. Two 1/2 inch aluminum baseplates will be constructed as platforms for mounting both optical and electronics components. Along with each baseplate two 1/8 inch arches will provide additional support for the internal platforms and will serve as vibration dampening elements (Figure 7). Considerations for glass housing compression at projected operational depths have been incorporated into the structural design of the internal platforms. Construction of the platforms will commence as soon as ACAD modeling of all components is finalized and final construction schematics are completed during the early stages of the next project period.

High-pressure multireflection ATR measurements

Initial high-pressure ATR measurements to investigate the behavior of the developed methane sensor principle at simulated deep-sea conditions have started. These measurements aim at determining the influence of hydrostatic pressure on the obtained spectroscopic results. Furthermore, the influence of pressure on multivariate data evaluation methods will be investigated. These measurement series are essential for finalizing the algorithms of chemometric data evaluation to insure data integrity as well as providing comparable results between different operational environments and variations of the background matrix. Furthermore, information on the influence of increasing water pressure on the enrichment process and polymer membrane integrity will be accessible, in order to optimize the sensor performance.

First results indicate that hydrostatic pressure has an influence on the dynamic equilibrium of water diffusion into a Teflon AF membrane (Figure 8). The results suggest that increasing hydrostatic pressure affects the dynamic equilibrium at approx. 150 psi, which corresponds to a depth of approx. 100 meters. At a pressure of 200 psi the effect further increases suggesting pressure dependence of the enrichment behavior. The tailing effect observed when recording water absorbance versus time and the corresponding pressure data suggest a leak in the pressure assembly and will be investigated during commencing measurement series. Current efforts focus on recording repeatable and verifiable data sets over broader pressure ranges for proper evaluation of the observed behavior, which allows subsequent integration into the multivariate data evaluation concept. Further measurements will focus on the roles of the membrane thickness and membrane properties in order to optimize methane enrichment for deep-sea environments.

FIGURES

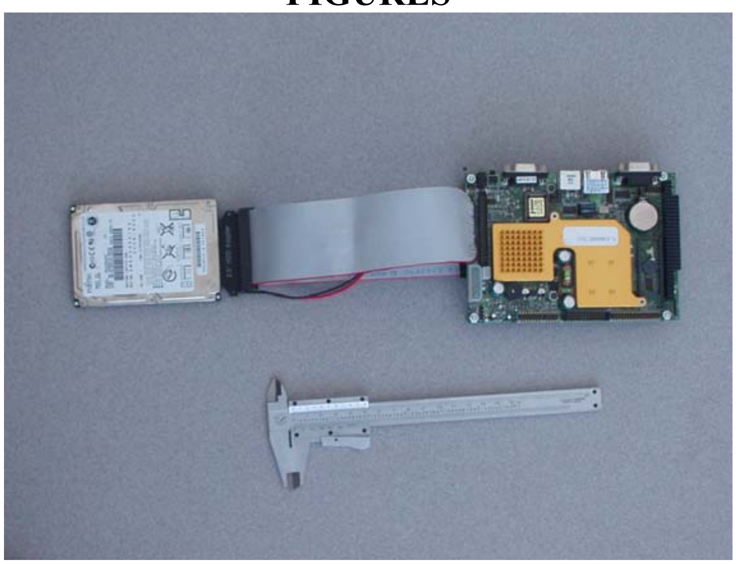


Figure 1: *Single-board PC and miniature hard disk drive for system control, data storage, and data evaluation.*

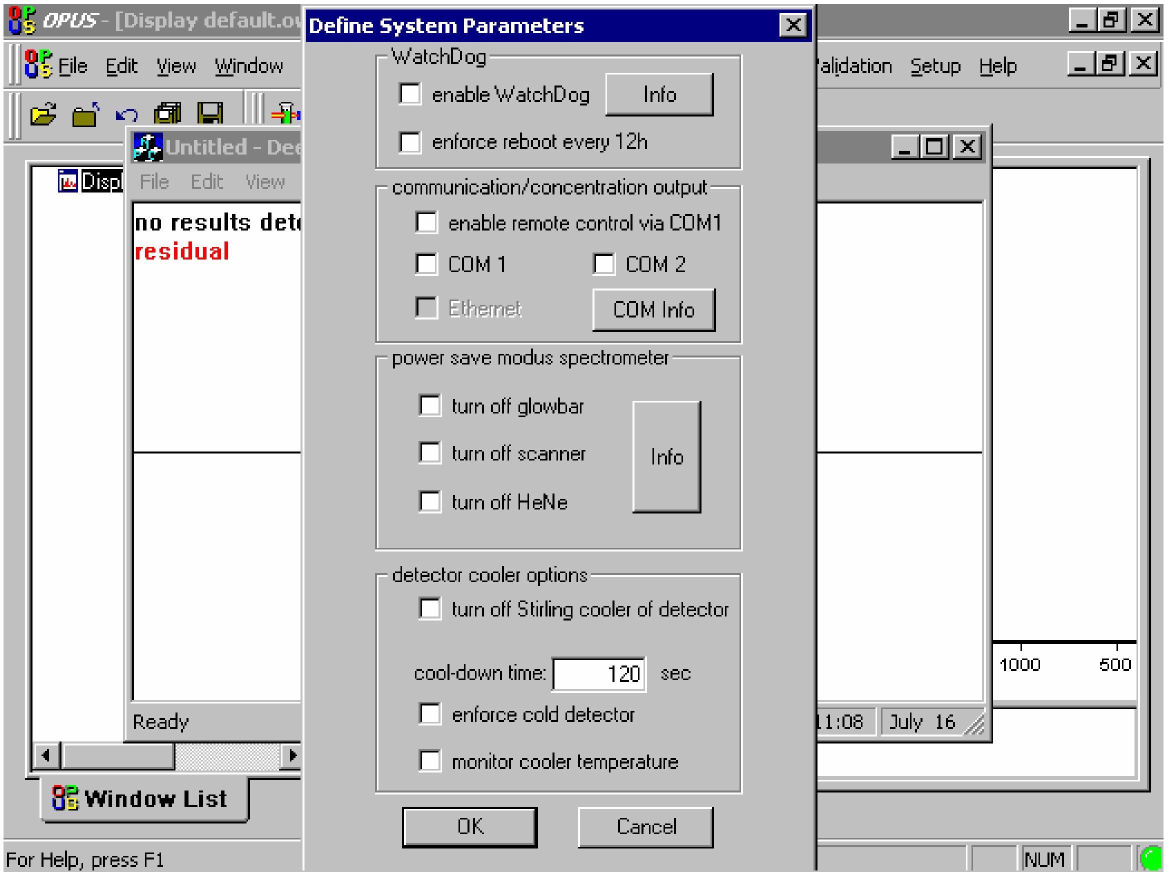


Figure 2: *Screen capture of multifunctional software 'deepSniff' for powering down selected spectrometer components.*

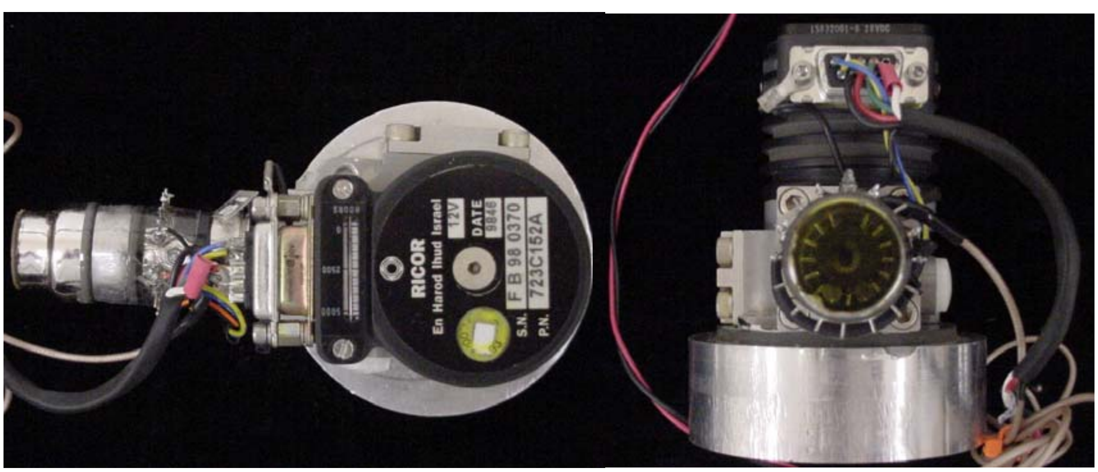


Figure 3: *Stirling-cooled MCT detector.*

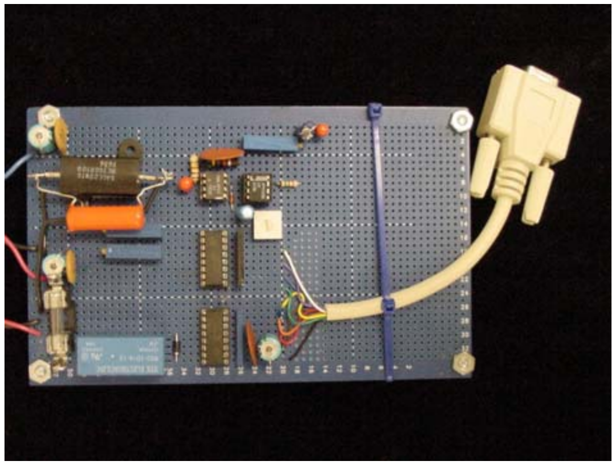


Figure 4: *Custom electronics for controlling and monitoring the Stirling-cooled MCT detector.*

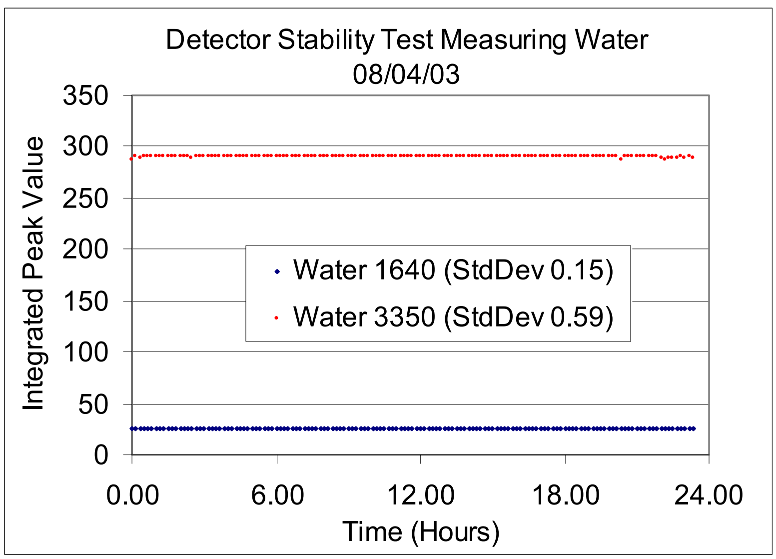


Figure 5: *Detector stability test measuring water with uncoated germanium ATR crystal.*

Electronics Schematic

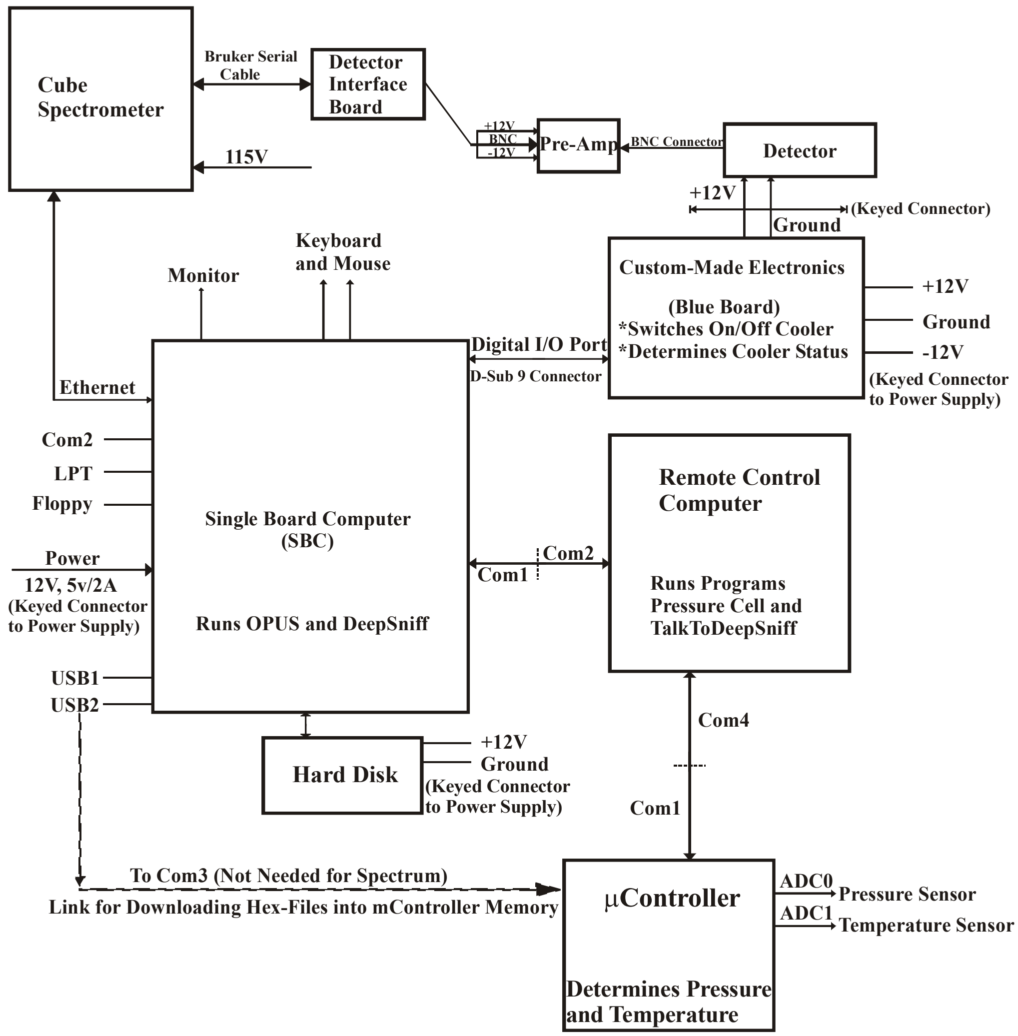


Figure 6: *Electronics schematic for control of 'sphereIR'.*

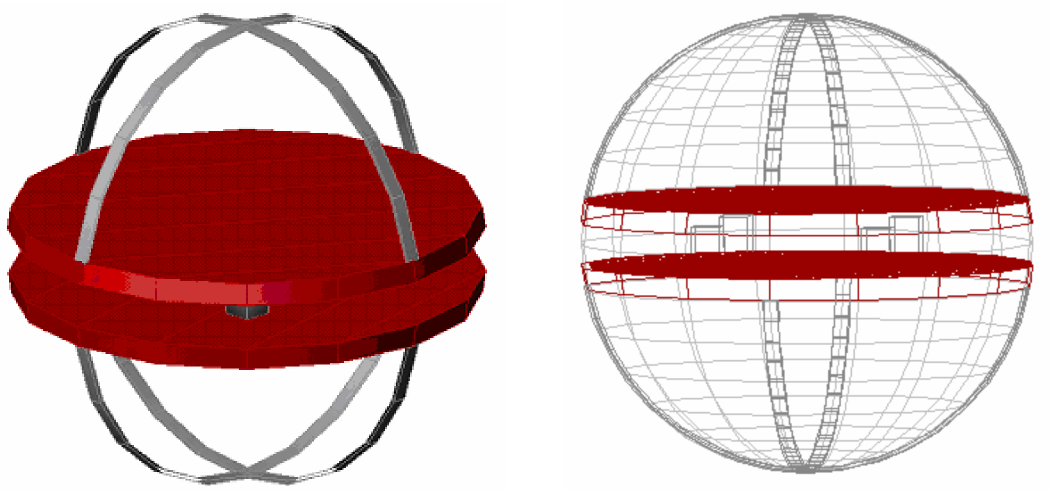


Figure 7: *'sphereIR' construction concepts.*

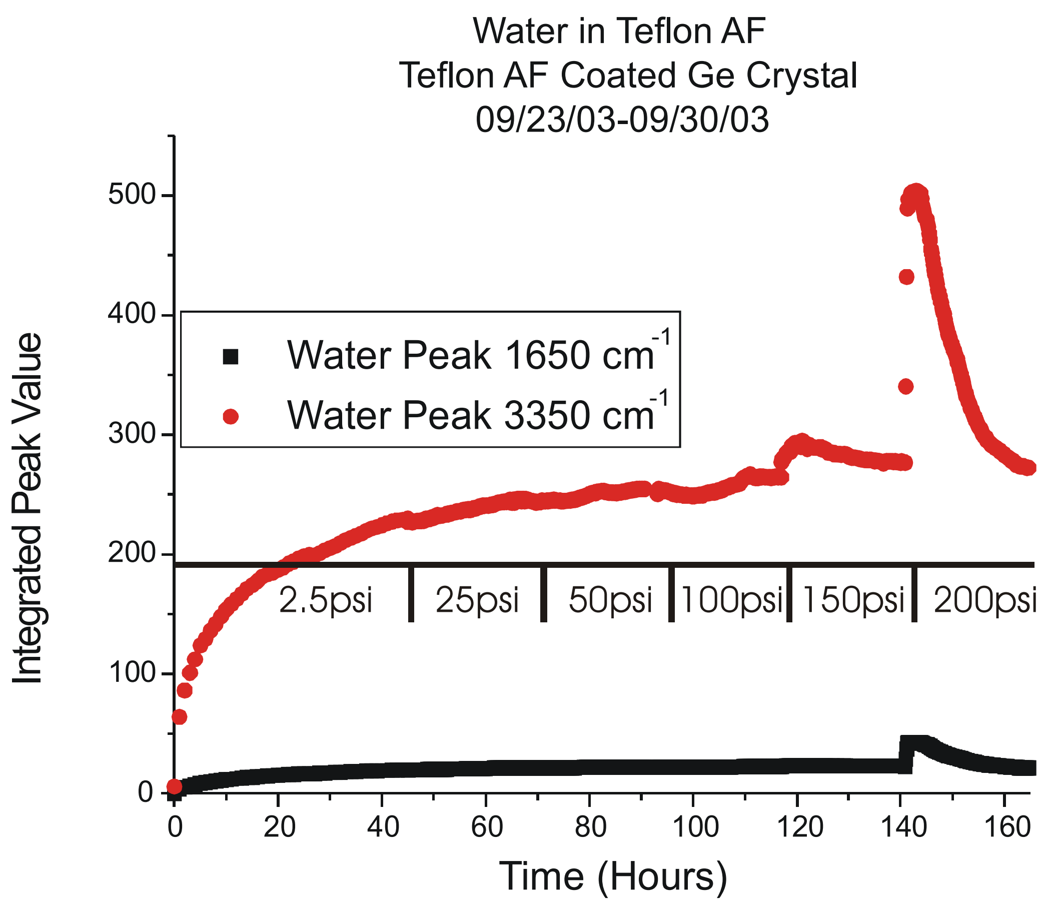


Figure 8: *First results investigating the influence of hydrostatic pressure on water diffusion into a polymer membrane.*

Seismo-acoustic characterization of sea floor properties and processes at the hydrate monitoring station

As part of a European Union-funded research project (Sub-GATE Project, 1998-2001), the Geophysics Group at the University of Wales Bangor designed and developed a prototype acoustic logging device for monitoring temporal variations in seabed acoustic responses. The aim of the EU project was to study fresh water and methane fluxes at the sediment-water interface. The instrument was developed specifically for shallow water operations, and worked through an antenna and radio modem system providing a telemetric link to a remote laptop PC for data storage. The acoustic device was developed and successfully deployed at a shallow vent site in the southern Baltic during a series of multi-disciplinary experiments aimed at studying submarine groundwater fluxes and transport-processes from methane rich coastal sedimentary environments. The rationale underpinning the research development and experimental trials was recognition of the value of the acoustic reflection signature for monitoring physical changes at the sediment-water interface and within the subsurface structure.

Within this DOE funded project, the intention is to further develop this acoustic logging instrument so that it is able to be pre-programmed for remote operation whilst under long-term deployment in the deeper water environment of the Gulf of Mexico. The development work in the current phase of this DOE-funded project aims to extend the capability of the electronics to allow remote operation on the seabed for periods of up to 3 months at a time. On completion this will enable temporal changes in sea floor acoustic reflection responses to be investigated at the gas hydrate monitoring station.

Development work on the electronic system has commenced based on design decisions reached during a series of meetings involving all members of the project team. Operational requirements have been specified and work has commenced on the hardware development. A work program has been drawn up, to include field trials to test the performance of the electronic components during the instrument's staged development.

CONCLUSIONS

Funding for this Cooperative Agreement was in place several months into the fiscal year. As a result, projects are somewhat behind an optimal schedule. However, all projects are progressing toward the goal of incorporation into the permanent sea floor monitoring station. The VLA is assembled, modified and will be ready for testing in late summer. Likewise, the sea floor probe and multipurpose sled, the bubble detector and counter and the MIR sensor are nearing field-testing status and should be tested prior to the end of the funding cycle. The studies of the acoustic properties of vent bubbles and the seismo-acoustic characterization of sea floor properties at the site of known hydrate occurrence promise to add immeasurably to available information relating to the impact/influence of hydrates on their surroundings.

REFERENCES

References cited by individual researchers/subcontractors can be found in their individual reports, included in this document as Appendix A.

LIST OF ACRONYMS AND ABBREVIATIONS

ACAD - AutoCAD
ATR - attenuated total reflection
BVLA – borehole vertical line array
CMRET - Center for Marine Resources and Environmental Technology
DGPS – Differential Global Positioning System
DOC – Department of Commerce
DOE - United States Department of Energy
DOI – Department of the Interior
EU – European Union
FT-IR - Fourier transform infrared (spectroscopy)
GOM - Gulf of Mexico
HRC – Hydrates Research Consortium
HSZ - hydrate stability zone
IR - Infrared
JIP – Joint Industries Project
MFP - matched field processing
MIR - mid-infrared
MMRI – Mississippi Mineral Resources Institute
MMS – Minerals Management Service
MPS – multi-purpose sled
NETL – National Energy Technology Laboratory
NOAA – National Oceanic and Atmospheric Administration
NRL – Naval Research Laboratory
NURP – NOAA's Undersea Research Program
PC – personal computer
PCA, PCR - principal component analysis, principal component regression

PI - principal investigator
SDI – Specialty Devices, Incorporated
SFO – sea floor observatory
SFP - sea floor probe
USM – University of Southern Mississippi
VLA - vertical line array (of sensors)