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

SEMIANNUAL TECHNICAL REPORT FOR THE 6th QUARTER
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DISCLAIMER

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 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 promote innovative research methods and construct necessary instrumentation.

Noteworthy achievements six months into the extended life of this cooperative agreement include:

Progress on the vertical line array (VLA) of sensors:

- Analysis and repair attempts of the VLA used in the deep water deployment during October 2003 have been completed.
- Definition of an interface protocol for the VLA DATS to the SFO has been established.
- Design modifications to allow integration of the VLA to the SFO have been made.
- Experience gained in the deployments of the first VLA is being applied to the design of the next VLAs; One of the two planned new VLAs being modified to serve as an Oceanographic Line Array (OLA).

Progress on the Sea Floor Probe:

- The decision to replace the Sea Floor Probe technology with the borehole emplacement of a geophysical array was reversed due to the 1300m water depth at the JIP selected borehole site. The SFP concept has been revisited as a deployment technique for the subsea floor array.
- The SFP has been redesigned to include gravity driven emplacement of an array up to 10m into the shallow subsurface of the sea floor.

Progress on the Acoustic Systems for Monitoring Gas Hydrates:

- Video recordings of bubbles emitted from a seep in Mississippi Canyon have been analyzed for effects of currents and temperature changes.
- Several acoustic monitoring system concepts have been evaluated for their appropriateness to MC118, i.e., on the deep sea floor.

- A mock-up system was built but was rejected as too impractical for deployment on the sea floor.

Progress on the Electromagnetic Bubble Detector and Counter:

- The initial Inductive Conductivity Cell has been constructed from components acquired during the previous reporting period.
- Laboratory tests involving measuring bubble volume as a component of conductivity have been performed.
- The laboratory tests were performed in a closed system, under controlled conditions; the relationship between voltage and bubble volume appears to be linear.

Progress on the Mid-Infrared Sensor for Continuous Methane Monitoring:

- Designs and construction schematics for all electronic mounting pieces and an electronics system baseplate were finalized after extensive modeling to facilitate the successful fabrication and implementation of electronic components into the deep-sea, glass instrument housing.
- Construction schematics and fabrication of an electronics system baseplate have been completed with successful integration of all currently fabricated electronic mounting pieces.
- Modeling and design of an optics platform complementary to the constructed electronics platform for successful incorporation into 'sphereIR' has commenced.
- A second generation chemometric data evaluation software package for evaluating complex spectra including corrections for baseline drifts and spectral anomalies resulting from matrix substances has been developed and will be incorporated into an optimized 'deepSniff' program upon completion of initial systems tests of the 'sphereIR'.
- Continuation of spectroscopic investigations of the highly permeable polymer, poly(trimethylsilyl)propyne (PTMSP), as a potential sensing membrane for methane have continued and will continue in the following project period.
- High-pressure multireflection ATR measurements simulating deep-sea conditions for evaluating environmental impact on the sensor system and multivariate data analysis continue.

Progress on the Seismo-acoustic Characterization of Sea Floor Properties and Processes at the Hydrate Monitoring Station:

- Work has continued on developing the electronic part of the acoustic logging system designed for investigating fine-scale temporal changes in sea floor acoustic reflection responses at the Gas Hydrate Monitoring Station.
- The hardware has been built and extensively tested. Final testing and commissioning are anticipated in the very near future.

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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 Hydrates Monitoring Station, 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 fourteen industries and fourteen universities, the USGS and the US Navy and Naval Research Laboratory 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 and administered by 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. 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.

Development of the station allows for the possibility of expanding its capabilities to include biological monitoring. A portion of funding recently acquired from the Department of the Interior's Minerals Management Services has been directed toward this effort. This option will facilitate the study of chemosynthetic communities and their interactions with geologic processes in addition to providing an assessment of environmental health.

The centerpiece of the monitoring station, as originally conceived, is a series of vertical line arrays of sensors (VLAs), to be moored to the sea floor. Each VLA was to have been approximately 200 meters above the sea floor and 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. Although still being discussed, it now appears that the project may be better served if some vertical arrays are converted to horizontal line arrays (HLAs). The prospective horizontal water-bottom arrays, will consist of hydrophones and 3-component accelerometers and will be laid upon, and pressed into, the soft sediment of the sea floor. They will be arranged into a cross so that they simulate two perpendicular arrays. Their deployment will be accomplished by means of a sea-floor sled designed to lay cable and deploy probes into shallow, unconsolidated sediments. This sled will also be used as a seismic source of compressional and shear waves for calibrating the subsurface seismo-acoustic array commissioned by the Joint Industries Project (JIP).

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. This system was tested in Atwater 14 and Mississippi Canyon 798 in October, 2003. Vertical Array data were retrieved successfully from both sites. Processing techniques continue to be developed for these data by consortium participants who are currently funded by the Minerals Management Service. Adjustments to the original array have now been completed following careful evaluation of its performance in October. Additional vertical arrays are being built for use in the water column monitoring chemical parameters of the hydrate environment.

Radio telemetry and fiber-optic link are being designed to remedy the problem of real time communications from the surface ship to the VLA recording system. This development includes modifications to the VLA DATS computer. Positioning sensors have been completed that will be used to define the offset of the acoustic sensors (due to water column disturbances including currents) during acquisition of geophysical data.

The Sea Floor Probe (SFP) in its original design has been revived as a delivery system for the subsurface sensor arrays. This development is the result of the decision by the JIP to locate their hydrate drilling operations in Atwater Valley and Keathley Canyon, both in water depths of 1300m, a depth beyond the housing and operational capabilities of many of the sensors developed within the Consortium. The new design for the probe includes using it to deploy a 10m geophysical array into the shallow subsurface. This array will be the initial borehole array component of the monitoring station until access to a long borehole can be arranged.

An acoustic system has been designed that will estimate bubbling activity and characteristics at gas hydrate vents. A system was built but found to be impractical for deep sea environments.

The electromagnetic bubble detector and counter field unit has been built using information gained through tests of the prototype. Laboratory tests have been performed. In a closed system, results show that the relationship between voltage and bubble volume appears to be linear. A field test should be possible in the near future.

Design for all and construction of many of the components for the miniaturized Mid-Infrared Sensor System for continuous methane monitoring have been accomplished. Modifications to the software package as well as to the device itself have been made and experiments made using simulated data. This unit is nearing readiness for field testing.

Significant progress has been made in the development of both hardware and support software for the Seismo-acoustic characterization of sea floor properties and processes instrumentation. A laboratory-tested electronic instrument designed to log, remotely, high resolution acoustic reflection signatures is ready for final testing prior to sea deployment. The device will measure variations in seabed acoustic responses as a measure of stability or instability of the hydrate stability zone.

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.

CONTINUATION OF WORK ON THE VERTICAL LINE ARRAY
Gas Hydrate In situ Monitoring Station Vertical Array

Abstract

The sea floor moored, 200 meter vertical acoustic line array (VLA) has been developed and several test installations were made during 2003. The development of this array technology has evolved and been integrated into a part of a larger Sea Floor Observatory (SFO) to be installed in the Gulf of Mexico. The SFO is intended to provide a long term means to study characteristics of gas hydrate deposits. This report addresses progress in the development of the VLA and the integration of this technology into the SFO. The time frame covered in this report includes the first half of this program in FY 2004. The report discusses the analysis and refurbishing efforts following the 2003 deployments and modifications in the array technology to facilitate integration into the SFO. Redesign efforts are underway to convert one of the two additional VLA arrays into an Oceanographic Line Array (OLA).

Introduction

The design for the vertical array includes an array of 16 hydrophones spaced 12.5 meters apart and extending approximately 200 meters up from a point just above the sea floor. A data logger was designed for the first version of the VLA which was self timed to record during the arrival of the acoustic signal of interest. Communication to the data logger was via an acoustic modem. Recovery of the array with its battery pack and data logger was accomplished through activation of an acoustic release connecting the array to the anchor. The design was intended to allow several days of data collection using a near surface towed sound source.

The need for longer term deployments, more precise timing between surface source firing and bottom recording, and the need to recover larger data sets required integration of the VLA into a SFO. This SFO is to be equipped with a real time communications link to the surface ship and a longer term power source. Modifications are required to interface the VLA data recorder to the SFO and to increase deployment durations from weeks to years.

Executive Summary

Progress during the first 6 months of FY 2004 included analysis and repair attempts of the VLA used in the deep deployment during October 2003, definition of an interface protocol for the VLA DATS to the SFO and design modifications to allow integration of the VLA to the SFO.

Experience gained in the deployments of the first VLA is being applied to the design of the next VLAs. One of the two planned new VLA arrays is being modified to serve as an Oceanographic Line Array (OLA).

Experimental

Repair efforts to the VLA

Further analysis of the VLA beyond the design depth showed some damage to the vertical array cable. The cable was opened and it was determined that repair of this cable could not be accomplished due to salt water leakage into the cable. An engineering effort is underway to improve the cable design. The acoustic modem failure however was repairable and repairs were made. Deeper capability acoustic modems were purchased along with the appropriate surface communications units for the deeper modems.

Development of the Sea Floor Observatory

The anticipated cure for the need for real time communications from the surface ship to the VLA recording system is now to being designed to include a radio telemetry and fiber optic communications link. A hard wired cable connection will be used from the seafloor mounted DATS to a sea floor fiber optic cable which will extend to the surface. At the surface, a radio telemetry buoy will provide the link to the surface ship. To accomplish this task, the VLA computer is being modified to include three forms of communications to the termination of a sea floor fiber optic link. The acoustic modem serial communications capability is being modified to function as a hard wired link to the fiber termination, a “T-0” timing link and dedicated interface computer is being added to provide an external “T-0” pulse to start data acquisition, and a high speed Ethernet communications capability is being added to provide a high speed method to recover to the surface, data stored in the VLA DATS. The development includes hardware and software modifications to the VLA DATS computer. Once completed, the pop-up buoy will bring the end of the fiber optic to the surface and a telemetry buoy can be added to provide real time communications and data recovery capability during seismic data acquisition.

VLA Positioning sensors

The positioning sensors, including the compass and tilt sensors, were completed. These sensors are to be used to define the offset of the acoustic sensors due to water currents during acquisition of geophysical data. The sensors and housings were completed and pressure tested. The pressure rating for the housings is twice that of any anticipated deployment.

Oceanographic Line Array

One of the VLAs has been re-designated to serve as a sensor platform for the collection of near sea floor oceanographic parameters. Possible sensors to be included on this array include temperature distribution, flourometers, transmissometers, mass spectrometers, conductivity and current flow profiling. The OLA will be designed to be integrated into the SFO power and data recovery system.

Results and Discussion

The majority of this reporting period was devoted to the engineering and design efforts to implement these changes.

The oceanographic array resulted from requests for oceanographic sensors to be included on the VLA and a discussion at the March 2004 program review. The sensor interface has been defined and includes options for various serial communications, optional power levels and voltages, power drain monitoring, power and communications control, and a mechanical protocol and in-water weight limits.

Other efforts during this time period included improving the design of the array connection, developing methods to lengthen the design life of components of the VLA, and investigation of power sources for the VLA and SFO energy requirements.

Conclusion

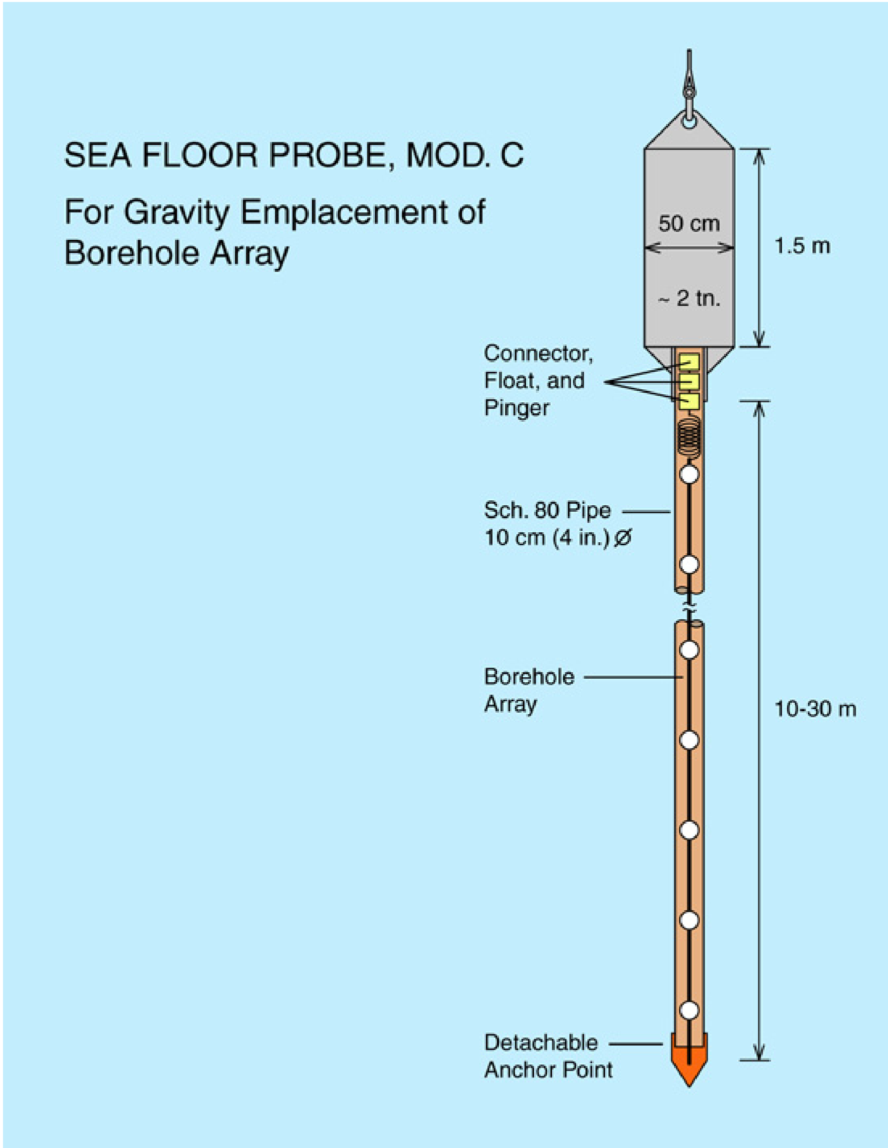
The FY 2004 year effort started with evaluation of the year end 2003 deployments and development of methods to implement improvements. The demise of the VLA cable led to changes in the construction of the cable intended to make this critical element more robust. Material and construction methods have been developed and pending an evaluation of these new techniques will be implemented in the new array construction.

CONSTRUCTION OF THE PROTOTYPE SEA FLOOR PROBE

During the period from 1 December 2003 through 30 May 2004 work continued on the evolving conceptual designs and technology of the Sea Floor Probe (SFP) as determined by changing circumstance; i.e., changes in site location and opportunities for access to a borehole for installation of a multi-sensor array (reducing the need for a SFP). As noted in the previous reporting period, priority was given to the deployment of a multi-sensor borehole array (see Figure 1) to be installed in cooperation with the JIP, utilizing for this purpose, one or more core-holes to be drilled in Atwater Valley Block 14. Toward the end of the reporting period, it became apparent that two problems with this plan were becoming increasingly difficult to surmount. One, ownership of the lease in MC 798 made access for long term seafloor monitoring activities problematic; and two, it was becoming increasingly apparent that the 1300m water depth at AV 14 was going to be insurmountable for the 1000m instrument depth limitation of our Bio-Geochemistry Team. Although hope remained high for an eventual opportunity to install a bore-hole array at a suitable hydrate site (in less than 1000m water depth), a return to the original SFP concept, conceived before hope of a bore-hole array, would again be appropriate, at least as a viable, low cost interim measure. Factored into the design of the new SFP was the recent experience with the mega coring technology of the French ship, Marion Defresne which had consistently succeeded in gravity- driving core barrels to depths greater than 10m in the Mississippi Canyon area. Based on this experience, modification to the SFP would include a simplified means for gravity drive, capable of array emplacement to 10m. The system would provide valuable multi-sensor data at low cost, of considerable value to the Monitoring Station as well as in the development of the final bore-hole array design (see Figure 2).

The basic design of the Gravity SFP will use a channel beam with a detachable point to deliver the array in the penetration drive. The channel beam is fitted with a 1 ton releasable, concrete weight. The array is attached to the detachable point and following impact and penetration of the channel beam into the sediment, the weight with the recoverable integrated data/power unit attached is remotely released and the channel beam retracted. The recoverable data/power unit mounted on top of the weight can be remotely recovered/exchanged using a manned vehicle or ROV.

Figure 1. Sea Floor Probe for emplacement of Borehole Array



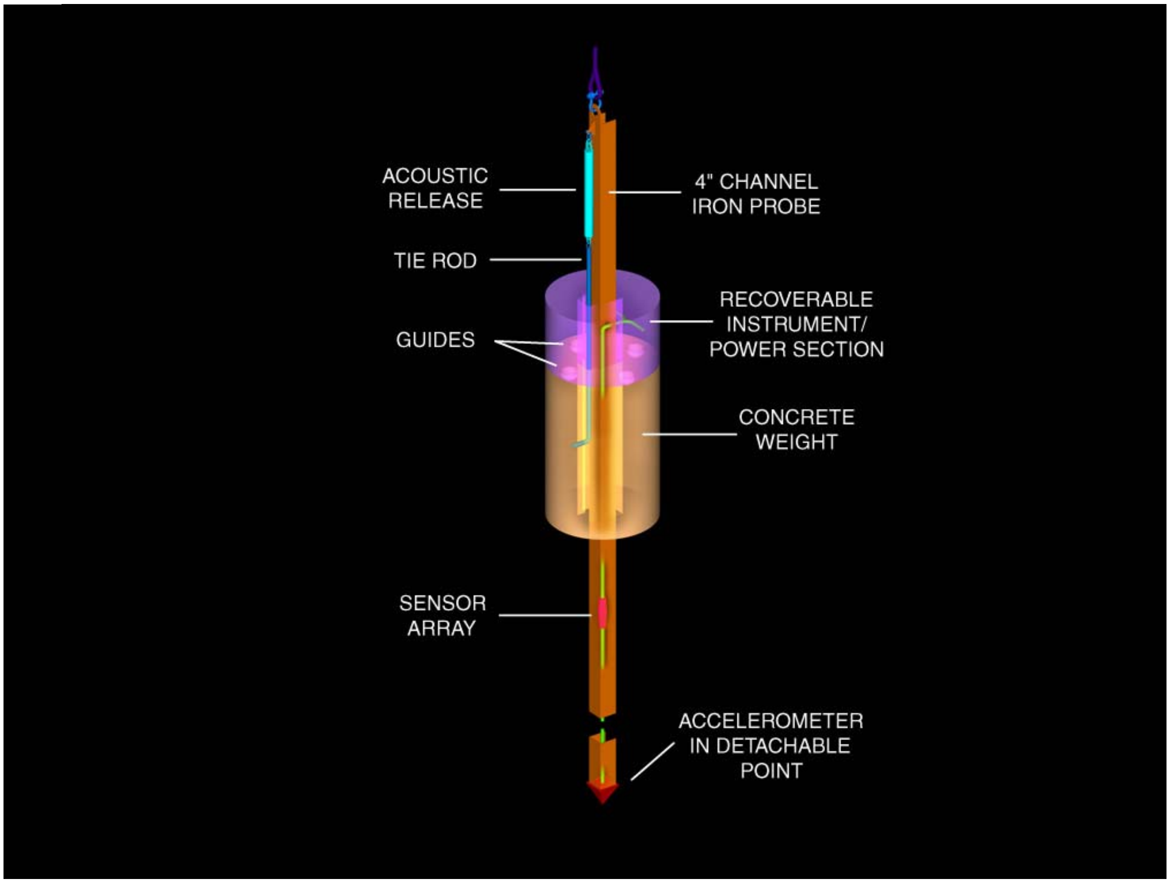


Figure 2. Advanced Borehole Array design

ACOUSTIC SYSTEM FOR MONITORING GAS HYDRATES

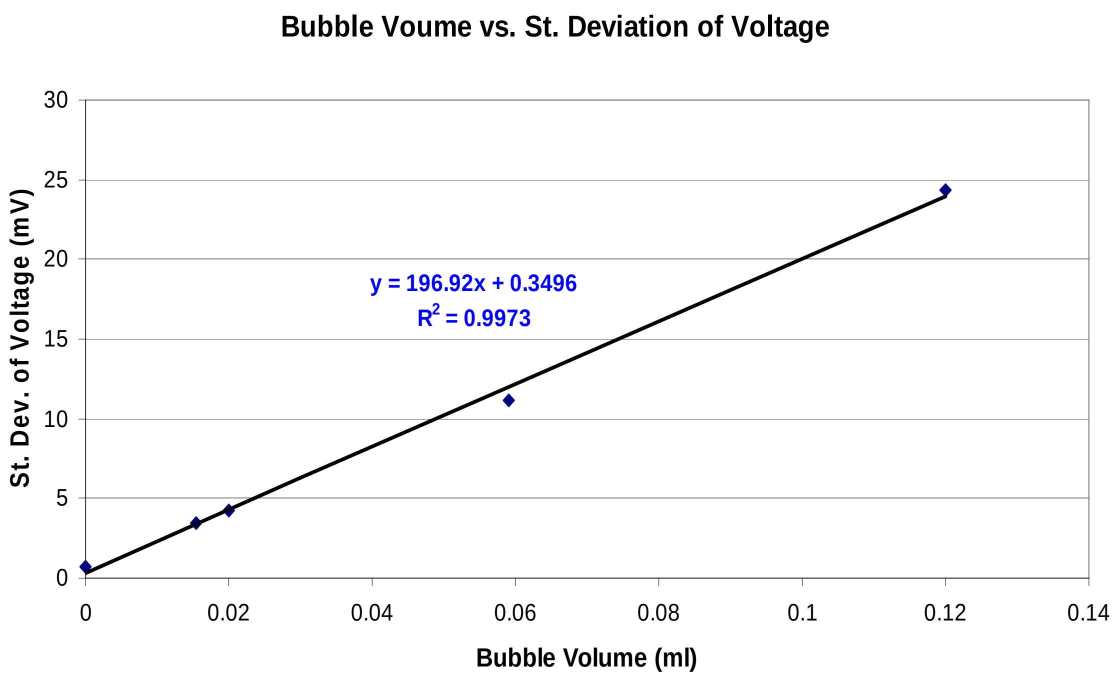
Our recent efforts on the Acoustic Monitoring System project were centered on two activities: (1) Estimation of bubbling activity and characteristics at gas-hydrate vents and (2) Design of an acoustic monitoring system that could address those characteristics. In earlier periods we reported on the physical phenomena of acoustic propagation and scattering by individual bubbles and bubble clouds, the expected state of bubbling at gas vents and the physical character of the bubbles that are emitted. We have used TV clips to determine a possible rate of bubbling, bubble sizes emitted, and rate of rise. This, however, was for one, possibly typical vent and under physical oceanographic conditions that prevailed at the time and place of the TV monitoring. We have engaged in efforts to understand the effects on the bubbling vents of the deep currents and warm waters brought in by eddies that move into the northern Gulf and ride up on the shelf in the Consortium's planned monitoring station in the region south of the Mississippi Delta. We will report more extensively on that effort in the final report. We have evaluated several acoustic monitoring system concepts. Most system candidates were rejected as impractical for deep-seafloor operations. A candidate system design was proposed and a mock-up was built by the Naval Research Laboratory. It also was rejected as a system that would be difficult to implement in real environments. During this reporting period we began thinking about a new system based on existing transducer modules we have in hand and will report on that design and propose the implementation of that system in the next reporting period.

Construction and Testing of an Electromagnetic Bubble Detector and Counter

The initial Inductive Conductivity Cell has been constructed from components acquired during the previous reporting period. These include the Richard Brancker Research sensor system, a dedicated Tattletale model 8 microcomputer and a third party (Persistor) data storage module. We also acquired and modified a pressure housing rated for 5,000m as well as the necessary cables to connect the data logger to the conductivity sensor.

Laboratory tests involving measuring bubble volume as a component of conductivity have been performed. The concept is, basically, that as bubbles rise through the water column, they displace ions and this produces a change in conductivity. If this change can be measured, it should be possible to relate it to the volume of the water column occupied by bubbles, thereby providing a measure of gas venting/seep activity on the seafloor.

The laboratory tests were performed in a closed system with salinity of 35ppt and temperature of 20^{o}C. With varying voltages, the following data were collected.



Under these controlled conditions, the relationship between voltage and bubble volume appears to be linear.

Future work includes expanding the experiments to include variations in the environment and *in situ* testing of the device.

Mid-Infrared Sensor Systems for Continuous Methane Monitoring in Seawater – Methane detection using attenuated total reflection (ATR) Spectroscopy

ABSTRACT/SUMMARY

This semiannual 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 accompany the text.

- Designs for all electronic mounting pieces and an electronics system baseplate were finalized after extensive modeling to facilitate the successful fabrication and implementation of electronic components into the deep-sea, glass instrument housing.
- Construction schematics for all electronic mounting pieces for 'sphereIR' have been completed. This includes mounting pieces for all electrical components from the Bruker IRcube FT-IR spectrometer and the miniaturized control system developed at the Applied Sensors Laboratory (ASL). Fabrication of all mounting pieces is near completion and will be completed early in the next project period.
- Construction schematics and fabrication of an electronics system baseplate have been completed with successful integration of all currently fabricated electronic mounting pieces.
- Modeling and design of an optics platform complementary to the constructed electronics platform for successful incorporation into 'sphereIR' has commenced.
- A second generation chemometric data evaluation software package for evaluating complex spectra including corrections for baseline drifts and spectral anomalies resulting from matrix substances has been developed and will be incorporated into an optimized 'deepSniff' program upon completion of initial systems tests of the 'sphereIR'.
- Continuation of spectroscopic investigations of the highly permeable polymer, poly(trimethylsilyl)propyne (PTMSP), as a potential sensing membrane for methane have continued and will continue in the following project period.
- High-pressure multireflection ATR measurements simulating deep-sea conditions for evaluating environmental impact on the sensor system and multivariate data analysis have been continued and will continue throughout the following project periods.

Based upon current results, we anticipate finalizing the first prototype of a miniaturized, multicomponent IR sensor system ready for field testing at the end of the next project period.

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Finalized design of electronics compartment for 'sphereIR'

Design of the electronics compartment for 'sphereIR' was finalized after extensive modeling to facilitate successful fabrication and integration of all electronic components into the deep-sea, glass instrument housing (**Figure 1**). The electronics compartment consists of a robust ½ inch aluminum alloy 6061 platform (electronics baseplate) for mounting all electrical components required for autonomous operation in a deep-sea environment. This includes all electrical components from the commercially available Bruker IRcube FT-IR spectrometer as well as the miniaturized control system developed at the ASL. In order to successfully mount all electrical components in the deep-sea instrument housing, 39 aluminum mounting pieces were designed. In addition, two aluminum structural beams were designed to aide vibration dampening and to prevent slippage of the internal platform when deployed.

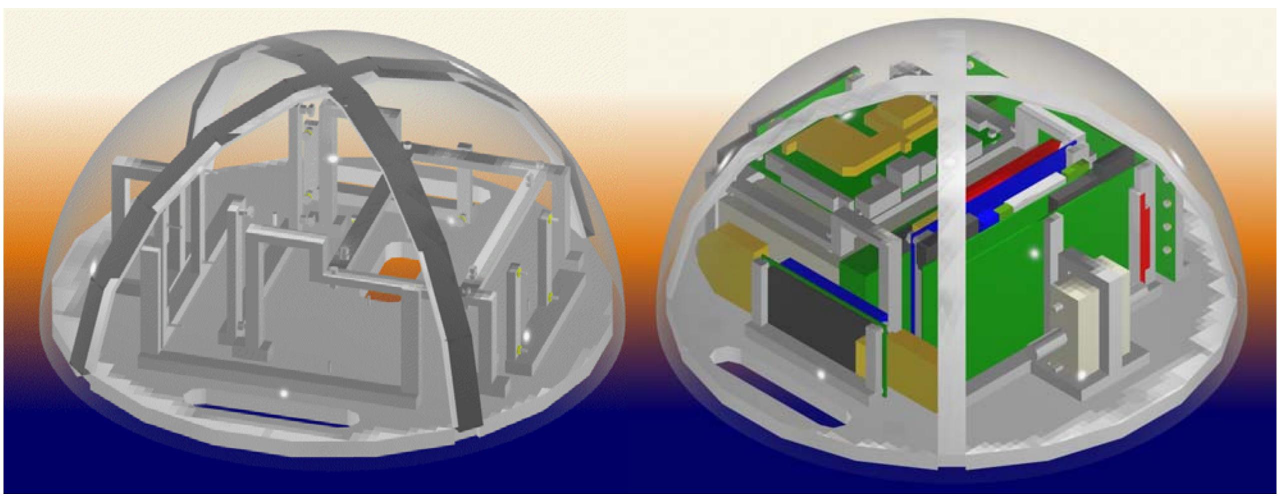

Figure 1: *Modeling of designed electronics compartment and modeling of designed electronics compartment with system components.*

A number of concerns were considered and incorporated into the design of the electronics compartment. First, the diameter of the electronics baseplate is 15.37 inches. This allows ample room for compression of the instrument housing in a deep-sea environment without compromising the structural stability of the instrument housing. The design provides room for the addition of shock-absorbing materials to be placed between all metal components that will be in contact with the instrument housing. The electronics compartment also provides attachment points and wiring slots for a complimentary optics compartment to be constructed during the second term of this project period. The modular design should allow for the internal platforms to remain secure and stable over the anticipated operational depth ranges. The construction materials also provide the means for heat distribution away from heat sensitive components and dissipation from the internal compartments.

Construction of electronic mounting components and baseplate

Once design of the electronics compartment was completed, construction schematics for all mounting pieces and baseplate were developed with AutoCAD software. Construction schematics for the electronics baseplate were submitted to the Georgia Tech College of Sciences Machine Shop for fabrication with construction tolerances ≤ 0.002” (high-end tolerances of commercially available optics baseplates). Construction schematics for the 39 mounting pieces were used during fabrication at the ASL with a Minitech CNC Mini-Mill/3 with tolerances ≤ 0.005”. All components were fabricated from standard aluminum alloy 6061. All construction schematics are available upon request with exemplary schematics provided (**Figure 2**). A photograph of the fabricated pieces of the electronics system is provided (**Figure 3**).

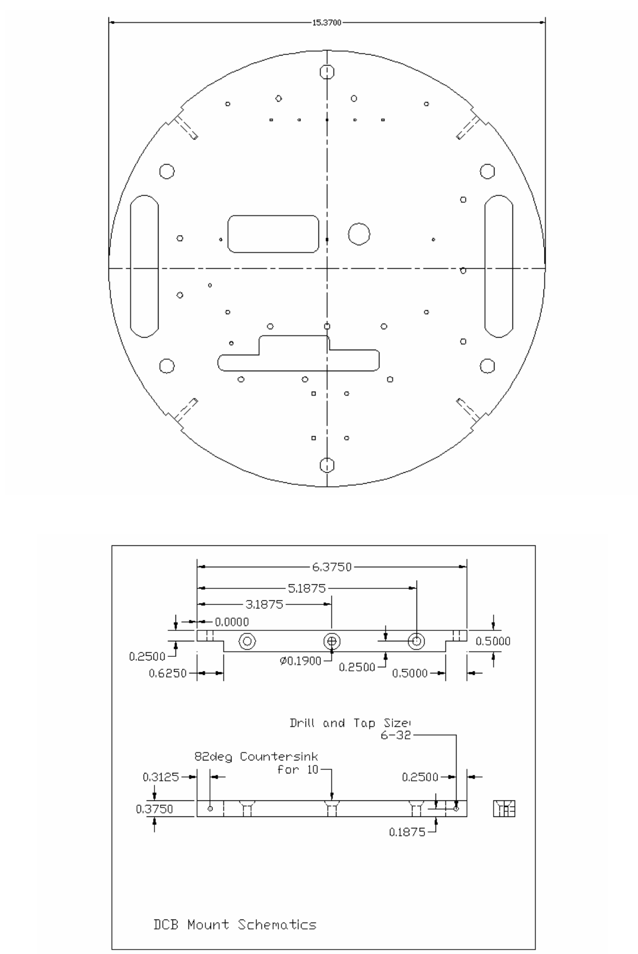

Figure 2: *Exemplary construction schematics for electronics baseplate and electronics mounting components.*

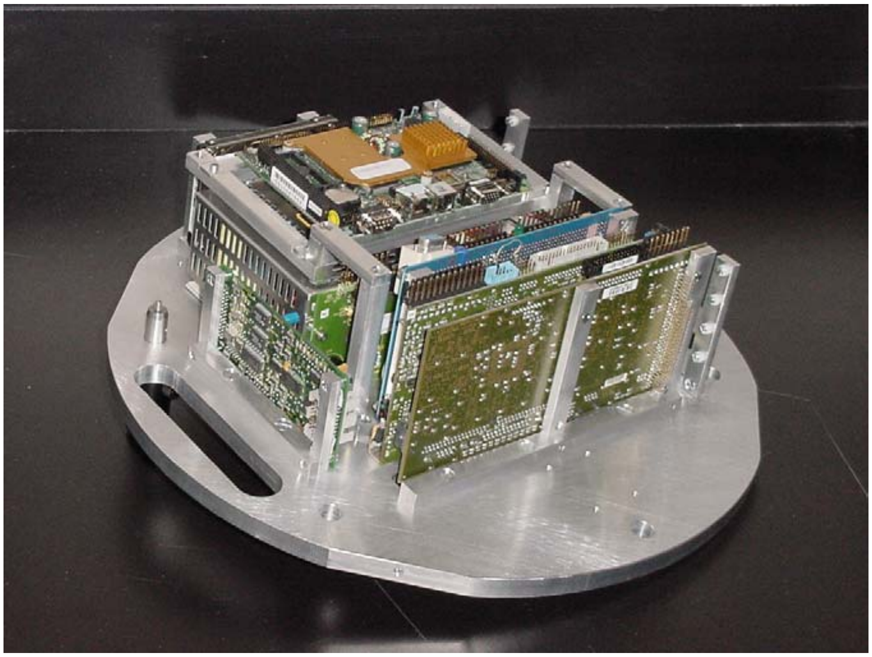

Figure 3: *Fabrication of electronics compartment with electronics baseplate, electronic mounting pieces, and electronic components.*

Modeling and design progress of optics compartment for 'sphereIR'

The modeling and design for the optics compartment of 'sphereIR' have begun **(figure 4)**. The optics baseplate form factor will be identical to that of the electronics baseplate and be constructed with ½ inch aluminum alloy 6061 and tolerances ≤ 0.002". Complementary attachment points and wiring slots will be incorporated into the finalized design. The ultimate design and construction of the optics compartment is contingent upon finalizing the sensor head configuration for appropriate selection and placement of necessary optical components (i.e. lenses and/or mirrors). The sensor head configuration should be determined early in the next project period and final construction completed during the late stages of the next project period.

Second generation chemometric software package

The development of a second-generation chemometric software package for 'sphereIR' has been completed using the Microsoft Visual Basic programming language. The development of this package was to increase the robust performance of the data evaluation system and incorporating more user-friendly features. Currently, the package is available for use in desktop data analyses. After initial systems testing, the second-generation chemometric software package is to be incorporated into an optimized, user-friendly 'deepSniff' program described in previous technical reports. Representative screen shots are provided (**Figure 5**).

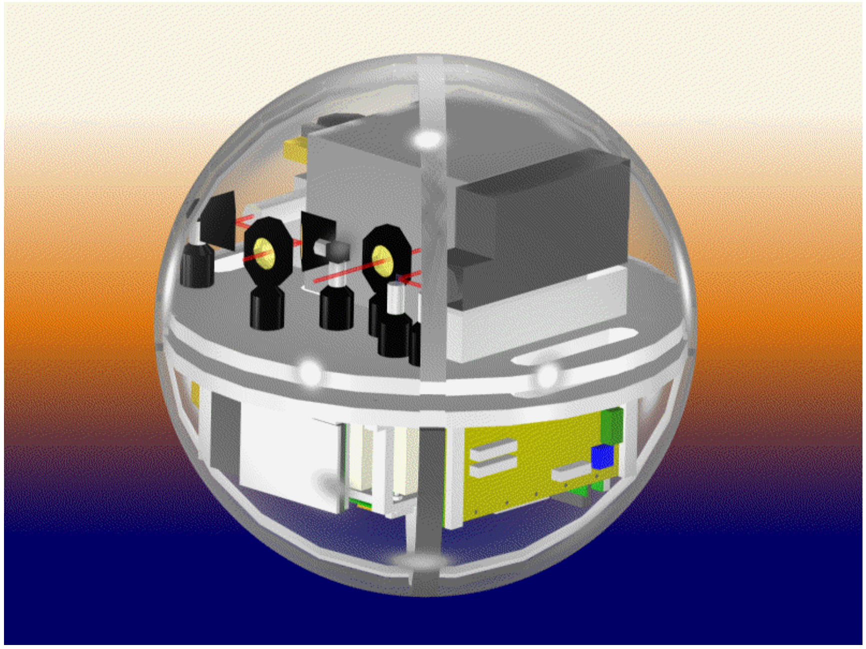

Figure 4: *Modeling of working design for complementary optics compartment with finalized design of electronics compartment.*

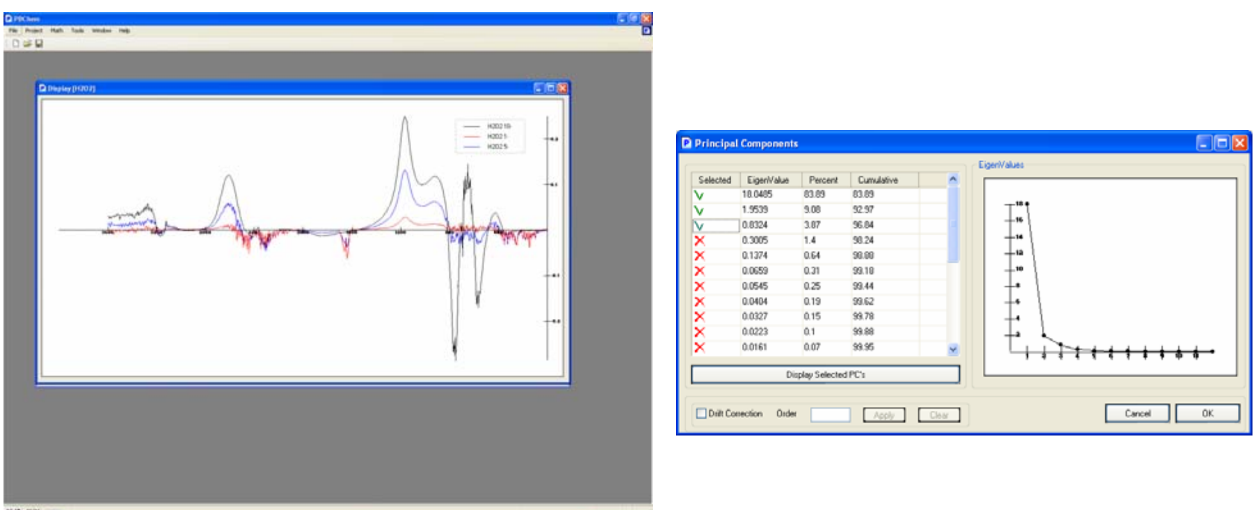

Figure 5: *Screen shots of second-generation chemometric software package including representative infrared spectra and principle component analysis.*

Spectroscopic investigations of poly(trimethylsilyl)propyne (PTMSP) as a methane sensitive enrichment membrane

Spectroscopic investigations of the highly permeable polymer, poly(trimethylsilyl)propyne (PTMSP), have continued. ATR crystal coating strategies established in the previous project period were incorporated for measurements performed during this project period. An ATR-IR spectrum for PTMSP collected during the last project period is provided (**Figure 6**). Evaluation measurements of PTMSP coated zincselinide (ZnSe) crystals were carried out to compare the enrichment behavior for a representative analyte, tetrachloroethylene (TeCE), in PTMSP and Teflon AF, a widely used polymer coating at the ASL. Initial calibration results indicate PTMSP to be a more sensitive enrichment membrane than Teflon AF (**Figure 7**). Further measurements are ongoing to corroborate these initial findings and will be available shortly. One interesting note of the measurements made thus far is that the T_{90} value for TeCE (time that 90% of analyte enrichment has occurred) into PTMSP is approximately 140 percent greater than that for TeCE into Teflon AF. Typical behavior would be for the T_{90} value to be smaller for more sensitive membranes. Additionally, the TeCE absorbance in PTMSP is always greater than in Teflon AF which corroborates that the enrichment factor for TeCE in PTMSP is greater than TeCE in Teflon AF. It has been found that flow conditions can play a crucial role in sensor response (i), and it is hypothesized that the flow conditions for the current measurements are responsible for this observation. We hypothesize that the flow velocity is slower than the mass transfer rate for TeCE into PTMSP and therefore there is not a sufficient replenishment of analyte molecules in the flow channel to achieve the optimum enrichment rate. Thus, a longer T_{90} value is expected for TeCE in PTMSP because the rate of enrichment is analyte limited unlike the case of TeCE in Teflon AF. Although flow conditions can influence the sensor response behavior, the equilibrium value for analyte enrichment should remain unchanged; however, in optimal flow conditions, the T_{90} value for TeCE in PTMSP should be shorter than that for TeCE in Teflon AF. Investigations looking into these results are ongoing with the first measurements of methane enrichment into PTMSP anticipated to begin early in the next project period.

High-pressure multireflection ATR measurements

High-pressure ATR measurements investigating the behavior of the methane sensor principles at simulated deep-sea conditions have continued in this project period. These measurements aim at determining the influence of hydrostatic pressure on the obtained spectroscopic results. First results reported in the last semiannual report indicated that hydrostatic pressure might have an influence on the dynamic equilibrium of water diffusion into a Teflon AF membrane (**Figure 8**). However, repeated measurements have shown evidence that results displayed in Figure 8 may be influenced by mechanical instabilities in the experimental setup such as leakage and gasket swelling. Current results show little or no influence of pressure on obtained spectra with the same experimental setup used to obtain data displayed in Figure 8 (**Figure 9**). The lack of repeatability between measurements and pressure variations

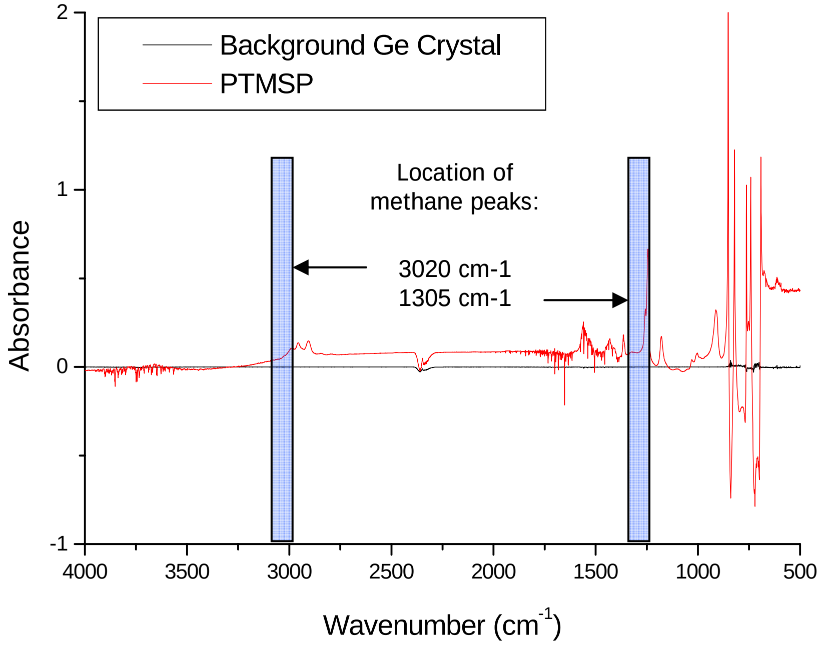

Figure 6: *ATR-IR spectra of a poly(trimethylsilyl)propyne coated germanium ATR crystal.*

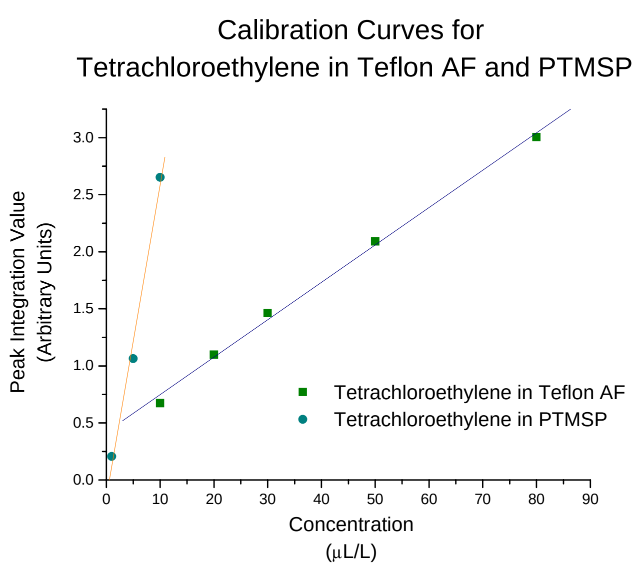

Figure 7: *Initial calibration curve results for enrichment of tetrachloroethylene into Teflon AF and PTMSP coated ATR crystals.*

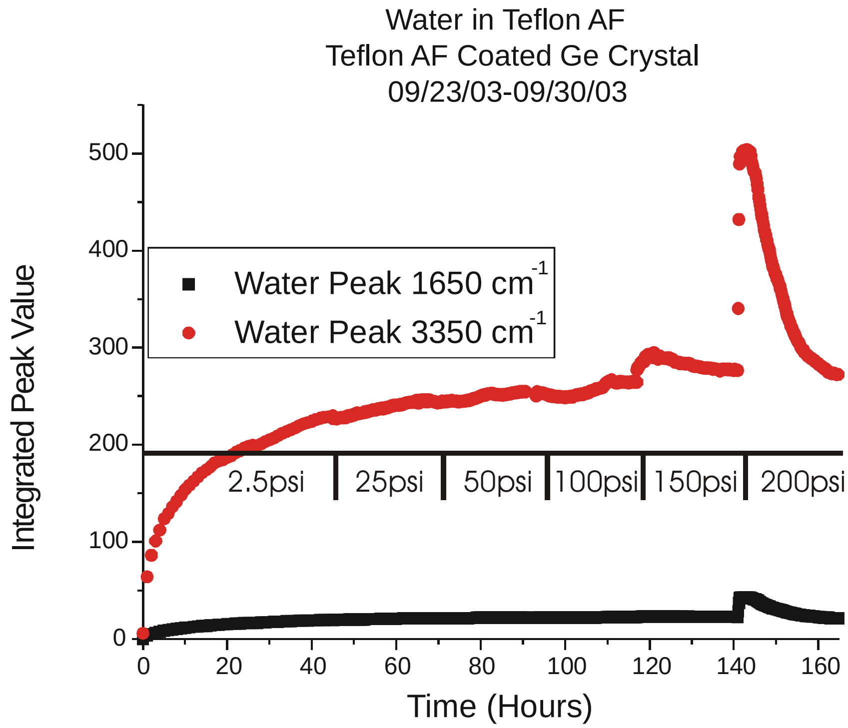

Figure 8: *First results investigating hydrostatic pressure influences on water diffusion into a polymer membrane.*

observed during the measurement series displayed in Figure 9 support the hypothesis that there are mechanical instabilities in the experimental setup. However, in Figure 9 there is no evidence of mechanical changes influencing the obtained results. Repeating the previous measurements using an indium-ATR crystal interface as opposed to a polymer-ATR crystal will be performed during the next project period to minimize the potential for mechanical influences in the spectroscopic measurements. It is still unknown if increasing hydrostatic pressure affects the dynamic equilibrium of water diffusion into Teflon AF membranes. Ongoing efforts are aimed at obtaining repeatable and verifiable data sets over broader pressure ranges for proper evaluation of hydrostatic pressure influences. Future measurements will focus on the roles of membrane thickness and membrane porosity in order to optimize methane enrichment membranes for deep-sea environments pending the results of hydrostatic influences on spectroscopic measurements.

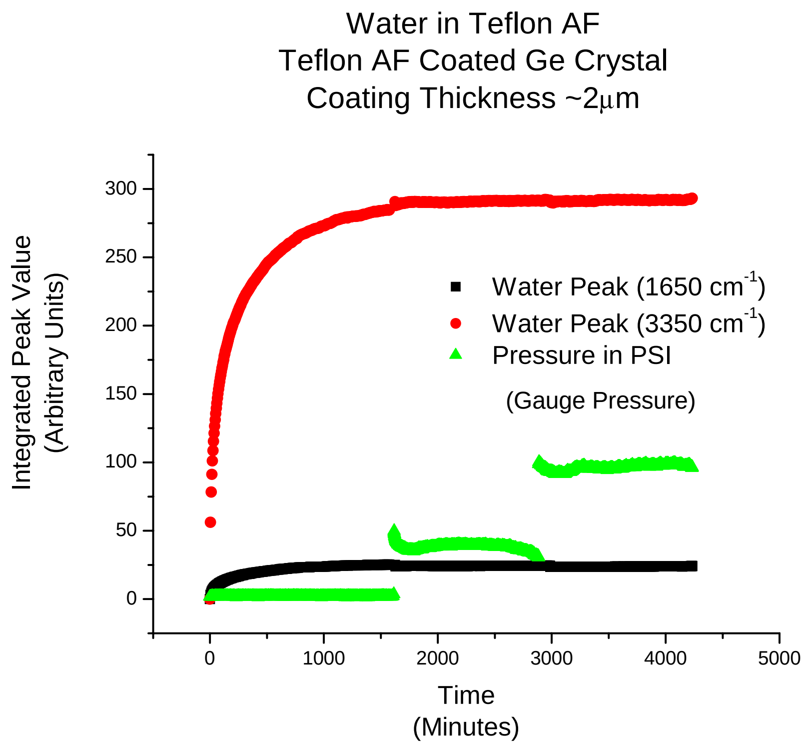

Figure 9: *Latest results investigating the influence of hydrostatic pressure on water diffusion into a polymer membrane.*

ABBREVIATIONS

MIR	mid-infrared
ATR	attenuated total reflection
IR	infrared
FT-IR	Fourier transform infrared (spectroscopy)
ASL	Applied Sensors Laboratory
CNC	Computer controlled
PTMSP	poly(trimethylsilyl)propyne
ZnSe	Zincselinide
TeCE	Tetrachloroethylene
CAD	Computer assisted design

SEISMO-ACOUSTIC CHARACTERIZATION OF SEA FLOOR PROPERTIES AND PROCESSES AT THE HYDRATE MONITORING STATION

ABSTRACT

Work has continued on developing the electronic part of the acoustic logging system designed for investigating fine-scale temporal changes in sea floor acoustic reflection responses at the Gas Hydrate Monitoring Station.

While the project has suffered a series of unforeseen delays, virtually every element of the specification has now been met. The hardware has been built and extensively tested along the way. Final testing and commissioning are anticipated in the very near future.

CONTENTS

INTRODUCTION

The intention within this DOE funded project has been to design and construct an electronic instrument able to operate a fixed station, acoustic logging device that will ultimately be deployed at the Gas Hydrates Monitoring Station. The primary requirement is for an instrument that is able to be pre-programmed for remote operation whilst under long-term deployment in the deep water environment of the Gulf of Mexico. The development work is being carried out under a collaborative agreement between the University of Wales Bangor and Scimar Engineering Ltd. (as subcontractor to the University).

EXECUTIVE SUMMARY

The rationale underpinning the research development and experimental trials in this DOE funded project is recognition of the value of the acoustic reflection signature for monitoring physical changes at the sediment water interface and within the subsurface sediment structure. To this end, a research prototype acoustic system previously developed for an EU project is being further developed in readiness for deployment at the Gulf of Mexico Gas Hydrates Monitoring Station.

While the project has suffered some delays (initial delays with the issue of the contract and some unforeseen developmental problems), the main project deliverable (a laboratory-tested, electronic instrument designed to remotely log high-resolution acoustic reflection signatures; supplied in the form of a working board set ready for insertion in a pressure tube) is almost complete.

EXPERIMENTAL DEVELOPMENTS

Significant progress with the hardware development and operational software has been made in the past 6 months resulting in an instrument with the following specification:

- Two channel impulsive transmitter, capable of putting 400V clamped voltage spikes onto one of two transmitters
- Two channel selectable receiver, with selectable gain of 6, 18, 30, 42, 54, 66, 78 db of gain, 8 pole high pass filter with selectable knee frequency in 500 Hz steps to 255 kHz, 16 bit A-D conversion with selectable sampling rates to 320 kHz, 512 kBytes of RAM and 128 Mbyte (expandable to 1 Gbyte) of FLASH memory.
- Four channel temperature and pressure sensing auxiliary functions, and battery supply voltage monitoring.
- Fully integrated switched mode power supplies requiring single wide-range DC input, 9-30V DC, allowing use of very high capacity alkaline battery packs.
- Board set mounted in a custom housing ready for pressure tube mounting, and with bench test lead set, and host computer program for data stripping and manual mode control.
- Autonomous and umbilical controlled modes are possible. Virtually all parameters (pulse length, sampling rate, record length, TX and RX channel selection, gain, filter setting, recording dead time) are software selectable and can either be controlled from a surface umbilical (or used in a bench mode for testing) or set into a 4 deep configuration stack so that mixed mode autonomous operation is possible with almost infinite parameter variability.
- Data stored in FLASH ram can be replayed over the umbilical or by physical removal and reading in a standard PC card reader (MCC format). A PC utility to strip the data directly out of the FLASH memory will be supplied

The final phase of system testing is underway and commissioning is expected to be in the very near future.

RESULTS AND DISCUSSION

The challenges of the system development can best be described in two parts: the design stage and the implementation and testing stage.

The seabed autonomous operation of the instrument offered several elements that had to be combined, making this device quite different to many sonars, and definitely at this stage making it a scientific rather than `run of the mill` instrument.

The instrument has a highly programmable structure so that parameters can be changed in response to field experience (e.g., knowledge of the exact nature of the signals to be received, optimization of the measurement process).

For deployment at the Hydrates Monitoring Station, it is proposed that the electronic instrument be interfaced with transmitting and receiving transducers on a fixed frame. The whole will be deployed on the seabed with a recommended 2 m (approx.) clearance between the transducers and the sediment surface. Given the short water path travel time, the electronic system has been designed to produce a very short duration clamped source and very fast settling time. It will provide for high accuracy, high frequency and high resolution (16 bit) data recording, with filter responses with little ringing, optimized for impulsive signals. The instrument will allow very high volume and secure data recording. In addition, power management will provide for optimal bottom battery life.

CONCLUSIONS

The chosen electronic instrument design integrated many state of the art technologies, and tests so far have shown the data recording and source quality to be excellent. It should though be pointed out in this final stage of the development that aspects of the project have proved far harder than originally expected and that the development team has experienced some severe problems along the way meaning that overall bench development time has been at least twice that originally estimated. However, despite time over-runs, the electronic instrument is nearing completion and fully meets hopes set at the project outset.

Subject to the successful outcome of a follow-up proposal (submitted to DOE; for 2004-05 funding period), future efforts will be concentrated on optimizing transducer specifications and packaging for deep water operations.

CONCLUSIONS

This report covers the accomplishments of the third six-month period funding of Cooperative agreement Project #DE-FC26-02NT41628, between the Department of Energy and the Center for Marine Resources and Environmental Technology, University of Mississippi. The efforts of the Hydrates Research Consortium are reviewed and plans for the final phases of the project presented. This cooperative agreement has been extended to November 30, 2004, so that the subcontractors can complete their contracts while dovetailing their individual project goals with one another as well as with the overall goals of the monitoring station project. As addressed in the introduction to this document, the evolution of the vision for the station has produced significant changes in its design. These changes necessarily affect the subcontractors and their progress though to unequal extents. The decision to break from the JIP program was a necessary one from a scientific perspective though a costly one for the Consortium. The group is making every effort to economize on both funding and time in order that the monitoring station becomes a reality in 2005. Project summaries of the subcontractors' efforts appear in their reports contained within this document.

The initial components of the station are due to be emplaced on the sea floor in the spring of 2005. Additional components will be added during subsequent visits to the station site with completion of the station expected in 2006.

REFERENCES

Relevant references appear following the contributions by the individual subcontractors.

ACRONYMS

AF	amorphous fluoropolymers
ASL	Applied Sensors Laboratory
ATR	attenuated total reflection
BHA	borehole array
CAD	Computer Assisted Design
CMRET	Center for Marine Resources and Environmental Technology
DOC	Department of Commerce
DOE	Department of Energy
DOI	Department of the Interior
DRS	Data Recovery System
EU	European Union
FT-IR	Fourier transforms infrared (spectroscopy)
FY	Fiscal Year
GOM	Gulf of Mexico
HLA	Horizontal Line Array
HRC	Hydrates Research Consortium
HSZ	Hydrate Stability Zone
IDP	Integrated Data Power Unit
IR	infrared (spectroscopy)
JIP	Joint Industries Project
MC	Mississippi Canyon
MIR	mid-infrared
MMRI	Mississippi Mineral Resources Institute
MMS	Mississippi Minerals Management Service
NETL	National Energy Technology Laboratory
NIUST	National Institute for Undersea Science and Technology
NOAA	National Oceanographic and Atmospheric Administration
NURP	NOAA's Undersea Research Program
OLA	Oceanographic Line Array
PC	personal computer
PCB	Pressure Compensated Battery
PTMSP	poly(trimethylsilyl)propyne
ROV	remotely operated vehicle
SFO	Sea Floor Observatory
SFP	Sea Floor Probe
SSD	Sation Service Device
T-O	Time Zero
TeCE	tetrachloroethylene
US	United States
USGS	United States Geological Survey
VLA	vertical line array
ZnSe	Zinc selinide

APPENDIX

GULF OF MEXICO HYDRATE RESEARCH CONSORTIUM: ESTABLISHMENT OF A SEA FLOOR MONITORING STATION, AN UPDATE

INTRODUCTION

Since the Gulf of Mexico Gas Hydrates Research Consortium (GOM-HRC) was organized in 1999, it has made considerable progress toward establishing a sea-floor observatory (SFO) to monitor and investigate the hydrocarbon system within the hydrate stability zone of the northern Gulf of Mexico. The intention has been to equip the SFO with a variety of sensors designed to determine a steady-state description of physical, chemical and thermal conditions in its local environment as well as to detect temporal changes of those conditions.

In the original design, the heart of the SFO was a network of five vertical line arrays (VLAs), each of which would consist of 16 channels of hydrophones spaced over the lower 200m of the water column. Each VLA would be suspended from glass floats and be anchored to the sea floor. Since water currents would cause the VLAs to deviate from vertical, each would also include inclinometers and compasses for determining the location of each hydrophone within the water column.

The intention was to use standard surveying techniques to determine the configuration of sub-bottom strata and to monitor that configuration by applying Matched Field Processing (MFP) to the acoustic energy received by the VLAs. The source of the energy could be either the intentional firing of conventional seismic devices or the opportunistic noise of passing ships.

In either case, MFP would require knowledge of the source location. In the former, the location would be measured directly. In the latter, it would be estimated relative to the known location of the VLAs by triangulation. The net of five VLAs would provide 20 independent estimations that would be analyzed statistically to minimize error in the final determination.

Significant disagreement between the MFP results and the sub-bottom configuration determined previously would indicate that a change had occurred within the sea floor. A new survey could then be carried out to determine the structural nature of the change and the output of other sensors examined to determine chemical and thermal changes.

This original strategy came under question during 2003, however, due to a number of external factors that had become apparent. Discussions arose among some Consortium members as to whether or not the design of the SFO could be modified to accommodate, and perhaps even to capitalize on, those factors. There was agreement to explore a number of modifications but not to alter the original intention or basic mission of the SFO. This update documents that exploration and other developments.

MODIFICATIONS

CHANGE 1: ARRAY TYPE

One external factor affecting the establishment of the station is the recent development of an ocean acoustics technique by which the sound of waves at the sea surface can be used to image the sea floor. The method requires that at least two horizontal line arrays (HLAs) be deployed on the sea floor perpendicular to each other. Each HLA should be as long as the water is deep and contain as many hydrophones as is feasible. If each hydrophone comprises a separate data channel, the cross of HLAs will also be capable of triangulating on ship noise. One VLA would still be required to separate the up-going and down-going wave-fields, but the sound of waves could be utilized as an energy source by redeploying the other four VLAs as two HLAs. This would allow the sound of wind-driven waves to be used without forfeiting the use of either intentional seismic sources or ship noise.

A second external factor is the opportunity to deploy an array of sensors in a borehole that will be drilled by the Department of Energy/Joint Industry Project (DOE/JIP) Consortium. The borehole array (BHA) will consist of hydrophones, three-component accelerometers and temperature sensors that would remain in the hole after the drill stem is recovered, letting the hole collapse and making the installation permanent. It would provide long-term monitoring from within the hydrate stability zone. If it were located at a suitable site, it would comprise a valuable addition to the SFO.

If both these array modifications were to be incorporated, the seismo-acoustic components of the SFO would comprise three mutually perpendicular axes of a Cartesian coordinate system. One VLA would be the vertical axis in the water column and the horizontal axes would consist of the other four VLAs deployed horizontally. The BHA would comprise the sub-bottom portion of the vertical axis.

A second VLA has been constructed to accommodate geochemical sensors: off-the-shelf thermistors, CTDs, fluorometers and transmissometers. This array will provide the capability of studying hydrate-related hydrocarbon fluids in the water column. It will be possible to deploy this array either in an autonomous mode or as a component of the SFO.

The original design of the SFO calls for each of the VLAs to be equipped with a sea-floor data logger. The five data loggers were to be connected to a central integrated data/power (IDP) module that would collect data from, and supply power to, the individual loggers. The change to using HLAs would not affect this arrangement.

The BHA has been funded separately by DOE/JIP and it would not represent a cost increase to the SFO. The only cost increase would be associated with increasing the length of the four VLAs so they could be re-deployed as two HLAs with lengths equivalent to the water depth. This could be a factor in whether or not the BHA becomes an integral part of the SFO.

Since the Consortium's break from the JIP plan, it appears likely that the placement of a BHA will not happen in the near future. For this reason and because the

BHA concept adds so much to the overall station capability, the idea of emplacing shorter arrays via the Sea Floor Probe has been revived. Ten meter arrays, both geochemical and geophysical have been added to the plan for the station.

CHANGE 2: DATA RECOVERY

External factors have also impacted the way SFO data will be recovered. For some time it has been thought that a commercial service would be available in 2004 which would allow the IDP to stream data onto an optic-fiber link for near-to-real time transmission to shore. It was learned in the autumn of 2003, however, that the service would not become available until 2006 or later.

The use of a remotely operated vehicle (ROV) to download data directly from the SFO's data loggers was found to be prohibitively expensive due to the depth of water and the weight of the battery packs that would need to be exchanged. Therefore, until such a link becomes available, the IDP module will stream data onto an optic-fiber data recovery system (DRS) which will be connected via optic fiber to an access connector. Whenever downloading is required, a system of buoys will bring the DRS access connector to the surface so that the data can be downloaded onto computer in a boat. The system has been used successfully before and involves far less expense than repeated use of a deep-water ROV. The system has been dubbed the "Big M" and is illustrated in Fig.1.

CHANGE 3: POSITIVE SYNCHRONIZATION OF TEST SIGNALS

The DRS will serve yet another need. While surveying to determine the configuration of sub-bottom strata in the vicinity of the SFO, the towed sea-floor sled will be used to generate shear waves for recording by the SFO's arrays. During the course of that survey, an access connector will be brought to the surface and connected to a radio telemetry buoy that will synchronize the firing and receiving of signals.

CHANGE 4: ELECTRICAL POWER FOR THE SFO

The Gulf of Mexico Hydrates Research Consortium funds the development of microbial batteries but it will be some time before they can provide electrical power to the SFO. In the meantime, the IDP module will supply electricity to the SFO by exchanging the pressure compensated battery (PCB) component about once a year. This will involve unplugging the depleted PCB from the IDP and plugging in a fresh one. The emplacement and exchange of PCBs will be accomplished by a station service device (SSD) especially designed for the task.

A docking station will be incorporated into the IDP module to facilitate changing the PCB. The SSD will carry the recharged PCB unit to the sea floor and return with the depleted unit. In addition, the SSD will be capable of recovering pore-fluid samples at *in situ* pressures. Perhaps most significantly, the SSD will be the means by which all station systems are connected to the IDP for data recovery and electrical power.

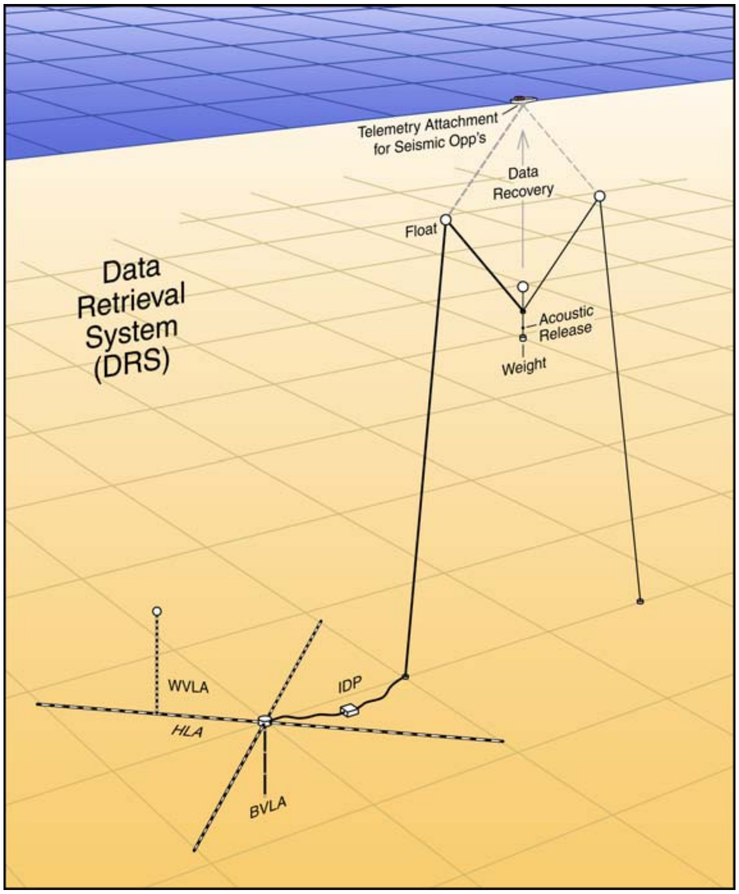

Figure 1. Diagram of the component parts of the sea floor observatory

CONCLUSION

Modifications discussed herein are not intended to change the basic concepts, overall plans and mission for the SFO. Instead, they are expected to enhance the accomplishment of that mission.

Funding has been requested for the supply of components and construction of the new systems in order to adapt to the changing circumstances, as well as, for the continuation of the, all-important, on-going studies and systems development projects. On the positive side, the SFO will gain a significant degree of autonomy, provide time on the learning curve to deal with the large data sets generated by the station, provide an ROV-like SSD capable of conducting a wide range of support activities, and, probably most important, keep on task towards station operation by 2006.

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