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

ANNUAL TECHNICAL REPORT FOR THE 8th QUARTER
1 JUNE, 2004 THROUGH 30 NOVEMBER, 2004

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NOVEMBER, 2005

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.

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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 one year into the extended life of this cooperative agreement include:

- Progress on the vertical line array (VLA) of sensors:
  - Repair attempts of the VLA cable damaged in the October >1000m water depth deployment failed; a new design has been tested successfully.
  - The acoustic modem damaged in the October deployment was repaired successfully.
  - Additional acoustic modems with greater depth rating and the appropriate surface communications units have been purchased.
  - The VLA computer system is being modified for real time communications to the surface vessel using radio telemetry and fiber optic cable.
  - Positioning sensors – including compass and tilt sensors – were completed and tested.
  - One of the VLAs has been redesigned to collect near sea floor geochemical data.

- Progress on the Sea Floor Probe:
  - With the Consortium's decision to divorce its activities from those of the Joint Industries Program (JIP), due to the JIP's selection of a site in 1300m of water, the Sea Floor Probe (SFP) system was revived as a means to emplace arrays in the shallow subsurface until arrangements can be made for boreholes at >1000m water depth.
  - The SFP penetrometer has been designed and construction begun.
  - The SFP geophysical and pore-fluid probes have been designed.

- 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:
    - Laboratory tests were performed using bubbles of different sizes in waters of different salinities to test the sensitivity of the. Differences were detected satisfactorily.
    - The system was field tested, first at the dock and then at the shallow water test site at Cape Lookout Bight where methane bubbles from the sea floor, naturally, in 10m water depth. The system successfully detected peaks in bubbling as spike decreases in conductivity.

- Progress on the Mid-Infrared Sensor for Continuous Methane Monitoring:
    - Modeling and design of an optics platform complementary to the constructed electronics platform for successful incorporation into 'sphereIR' continues. AutoCAD design and manual construction of mounting pieces for major optical components have been completed.
    - Initial design concepts for IR-ATR sensor probe geometries have been established and evaluated. Initial evaluations of a horizontal ATR (HATR) sensing probe with fiber optic guiding light have been performed and validate the design concept as a potentially viable deep sea sensing probe.
    - Ray tracing simulations have been performed to evaluate light propagation through HATR elements to facilitate the optimal design of both the sensing probe and optical configuration of 'sphereIR'.
    - The highly permeable polymer, polydimethylsiloxane (PDMS), was investigated as a potential methane enrichment membrane for IR-ATR sensors.

- Progress on the Seismo-acoustic Characterization of Sea Floor Properties and Processes at the Hydrate Monitoring Station:
    - All system components underwent extensive testing in preparation for determining sea floor acoustic reflection responses at the Gas Hydrate Monitoring Station.
    - Final testing and commissioning have been completed.

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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 sea floor station to monitor a mound where hydrates outcrop on the sea floor. This Monitoring Station/Sea Floor Observatory (MS/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 (GOM). It is anticipated that this station and associated studies will provide a better understanding of this complex hydrocarbon system, particularly hydrate formation and dissociation, fluid venting to the water column, and associated microbial and/or chemosynthetic communities. Models developed from these studies should 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 gases, 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 Department of Commerce National Oceanographic and Atmospheric Administration's National Undersea Research Program (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, most recently, biological studies.

EXECUTIVE SUMMARY

A consortium has been assembled for the purpose of consolidating both laboratory and field 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. In order to meet this goal, the Consortium aims to assemble 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 current funding 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. In addition, the NOAA-NURP has, as a focal point, investigations of the effects of deep sea activities on world atmosphere and therefore, weather. Two projects currently funded through NURP's National Institute for Undersea Science and Technology support this effort in collaborations with the Consortium.

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. After some two years of discussion, it now appears likely 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 Program (JIP).

The prototype DOE-funded 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 Valley Block 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 deployments in August 2004 proved the modifications to be successful. 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 data recording system (DATS). 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. These have been pressure-tested successfully with pressure ratings for the housings twice that of the expected 900m deployment.

Further modifications to the VLA data recorder are being implemented in order to increase deployment duration from days/weeks to years. Acoustic modems with greater depth ratings have been purchased. Hardware and software modifications to the VLA DATS computer are being made to lock in firing time for the signal fired from the sea floor while high speed Ethernet communications capability is being added to enable the system to handle large quantities of data.

Modifications to the original design of the Sea Floor Probe (SFP) include a simplified means for gravity drive capable of array emplacement at approximately 10m. This system will provide valuable, multi-sensor data at low cost and aid in the development of the final bore-hole array design when a deep borehole can be accessed.

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

The electromagnetic bubble detector and counter field unit has been built and laboratory tests have been performed. Field testing of the system in the shallow water environment, Cape Lookout Bight, offshore North Carolina, produced very positive results. The system is ready for testing in deep water.

Final selection, modeling, design and construction of the remaining components of the ‘sphereIR’ including optimized sensor probes and the complementary optics baseplate are underway. Mounting pieces for the aperture/optics block and inferometer block have been designed and constructed as have 8 mounting pieces for the laser. A probe redesign is under investigation for extending sensor deployments with reduced maintenance requirements. Tests were performed to evaluate feasibility of using a mid-IR sensing probe with a horizontal ATR crystal as the sensing element with fiberoptic light guiding. Tests were also performed to verify the capability of generating evanescent field spectra with fiberoptic light coupling into a horizontal attenuated total reflection crystal probe (as opposed to mirror coupling). Tests were also performed involving ray tracing simulations of light propagation through these HATR elements. Investigations of methane enrichment capabilities of polydimethylsiloxane typically used as introduction membrane material in underwater mass spectrometers were continued and the conclusion reached that it does not represent significant interference in the spectral regions of interest for IR-ATR methane sensing.

Hardware for the Seismo-acoustic characterization of sea floor properties and processes instrumentation has been completely assembled. Despite difficulties in debugging the circuitry, and cumbersome hardware modifications, the final device meets all design specifications. Field testing in shallow water has been done but has proven extremely time-consuming; optimizing transducer specifications and packaging for deep water operations must be completed prior to deep sea deployment. The device will measure variations in seabed acoustic responses as indicators 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. Annual Reports from five of the six subcontractors follow.

CONTINUATION OF WORK ON THE VERTICAL LINE ARRAY

DOE Award Number: **DE- FC26-02NT41628**

Annual Report covering the period

June 2004 – November 2004

Submitted by

Paul Higley

Submitted September 22, 2005

CONTINUATION OF WORK ON THE VERTICAL LINE 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 12 months effort from November 2003 through October 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. Other technology testing opportunities were undertaken and design efforts to convert one of the two additional VLA arrays into a Oceanographic Line Array (OLA) now renamed a Benthic Boundary Layer Array (BBLA).

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. Communications to the data logger was via an acoustic modem. Recovery of the array with its battery pack and data logger was accomplished through activation on 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 FY 2004 included analysis of the vertical Line Array (VLA) used in the 2003 deployments, improvements to the VLA construction, definition of the interface of the VLA Data Acquisition System (DATS) to the Sea Floor Observatory (SFO) and design modifications to allow integration of the VLA to the SFO.

Experience gained in the deployments of the first VLA were applied to the new VLA design. One of the two planned new VLA arrays is being modified to serve as an Oceanographic Line Array (OLA). An application of this technology to a site in Italy provided valuable test and verification of VLA design and is now incorporated in the SFO VLA.

Experimental

Repair efforts to the FY 2003 VLA
Further analysis of the VLA deployed beyond the design depth showed that repair of this cable could not be accomplished. An engineering effort was initiated and a cable was built for an application in Italy using this new design. Five deployments were performed in the Italy site without damage to the cable. This experience verified the improved design and is being incorporated in the additional vertical arrays for the SFO.

The acoustic modem depth damage was repairable and repairs were made. Additional acoustic modems were purchased with a deeper depth rating, along with the appropriate surface communications units for the deeper modems.

Development of the Sea Floor Observatory
A design is under development for real time communications from the surface ship to the VLA DATS using radio telemetry and fiber optic cable. A hard wired cable connection will be used from the seafloor mounted DATS to a sea floor fiber optic cable. The fiber optic cable can reach a surface buoy where radio telemetry 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. A "T0" timing pulse is needed for the coordination of the gun firing with the bottom VLA DATS. A serial command line will provide control and house keeping functions and a high speed Ethernet communications capability is being added for large volume data recovery from the VLA DATS. The development includes hardware and software modifications to the VLA DATS computer.

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 these housing is twice that of any anticipated deployment. Similar heading and tilt sensors were also deployed on the Italy installations and functioned well.

Oceanographic Line Array
One of the VLA arrays 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 provide a data recovery system for OLA data.

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, a mechanical protocol and in-water weight limits.

Other efforts 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. Extending the deployed life of the SFO components to achieve five to ten year deployed life has been part of the efforts during this year. Corrosion protection of most exposed metal components has been addressed by enclosing these components in neoprene jackets with an oil fill providing a barrier to sea water. Remaining metal components are being addressed with anodes and new coating methods to inhibit corrosion.

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 lead to changes in the construction of the cable intended to make this critical element more robust. These improvements were tested due to a fortunate opportunity to use similar application of this technology at a site in Italy. Alterations of the early VLA were made to allow integration of the VLA array into the SFO.

CONSTRUCTION OF THE PROTOTYPE SEA FLOOR PROBE

DOE Award Number: **DE- FC26-02NT41628**

Annual Report covering the period

June 2004 – November 2004

Submitted by

J. Robert Woolsey

Submitted October 12, 2005

ABSTRACT

The Sea Floor Probe (SFP) was recently revived as a deployment option for the probes components of the monitoring station. Although deep boreholes are still being planned, they will not be available at the monitoring station site in MC118 until 2006 at the earliest. Until then, the SFP will serve to provide access to the shallower subsurface for collection of geophysical and geochemical information from the site at a fraction of the cost of borehole data and at a much earlier date. A penetrometer, to determine maximum penetration at the deployment site, has been designed and is under construction. Once maximum penetration has been determined construction of the already-designed probe can commence. Sea tests are scheduled for early 2005.

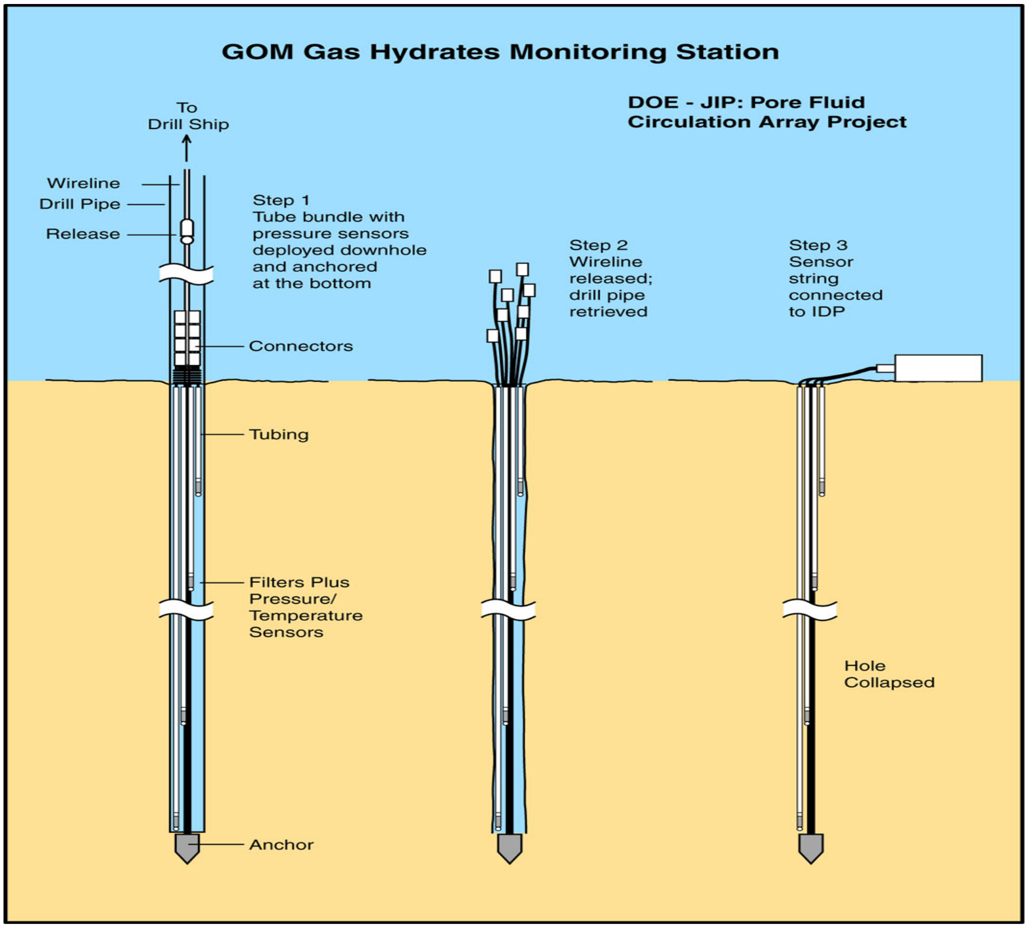
INTRODUCTION

Work continued on the evolving conceptual designs and technology of the Sea Floor Probe (SFP) as determined by changing circumstances; 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 Joint Industries Program (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 facets with this plan were becoming insurmountable; uncertainties of lease owner plans for MC 798 (not conducive to long term sea floor instrumentation planning/operations) and the 1300m water depth at AV 14 would be too much for the 1000m instrument depth limitation of the Biogeochemistry 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, (which predated hope of a bore-hole array), would again be appropriate, as a viable, low cost interim measure. Factored into the design of the revived SFP plan 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, SFP modifications should include a simplified means for gravity drive, capable of array emplacement to approximately 10m. The system should provide valuable, low cost, multi-sensor data and aid in development of the final bore-hole array design (Figure 2).

EXECUTIVE SUMMARY

Conceptual designs and technology of the Sea Floor Probe (SFP) has evolved over the course of the project 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 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. Uncertainties in lease owner plans for MC 798, candidate for the station site, made choice of this block not conducive to long term sea floor instrumentation planning/operations; and secondly, it was becoming

Figure 1. Borehole/Sea Floor Probe design



increasingly apparent that the 1300m water depth at AV 14 was too much for the 1000m instrument depth limitation of the 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 existed), would again be appropriate, at least as a viable, low cost interim measure. Factored into the design of the revived SFP plan 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 could include a simplified means for gravity drive, capable of array emplacement to approximately 10m. The system should provide valuable multi-sensor data at low cost, and aid in the development of the final bore-hole array design.

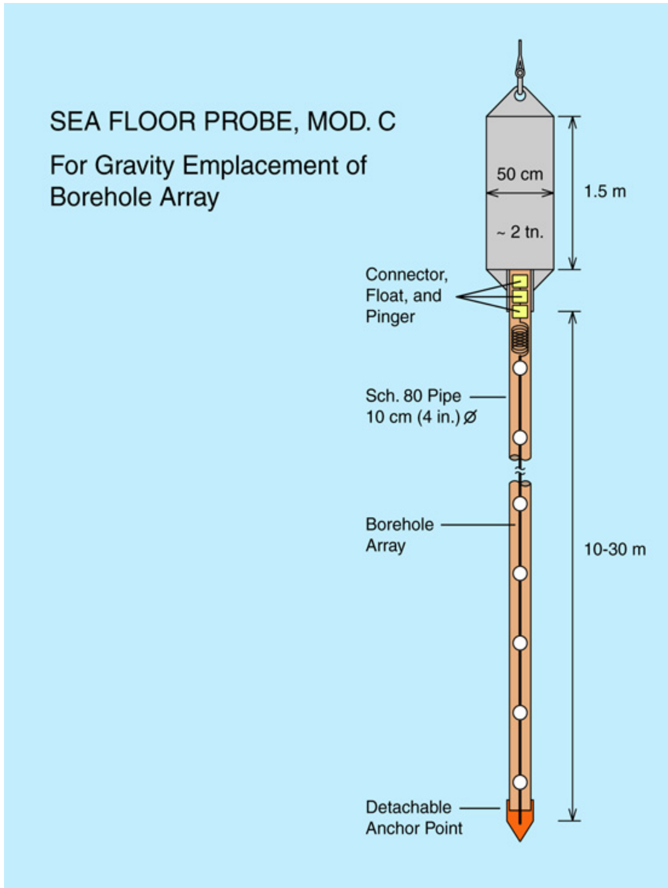


Figure 2. Sea Floor Probe

EXPERIMENTAL

Experimental work planned around the Gravity SFP will consist of two parts. First a SFP penetrometer will be constructed more or less identical to the design shown in Figure 2 only without the array and with a fixed point. The purpose of the penetrometer will be to determine the depth to which the instrumented SFP may be expected to penetrate into the bottom sediments of the study area. Once maximum expected penetration is determined, maximum barrel length can be determined and more importantly, the maximum depth of array emplacement. The second experiment will involve the design of the multi-sensor Gravity SFP, both for geophysical and geochemical applications. The basic SFP concept will incorporate a channel beam with a detachable point to deliver the array in the penetration drive. The channel beam will be fitted with a concrete weight of approximately 1 ton, which can be released by an acoustic release. The array is attached to the detachable point and, following impact and penetration of the channel beam into the sediment, the weight, with a recoverable integrated data/power unit attached, is released remotely 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.

RESULTS

Results achieved during the reporting period include design and initiation of construction of the SFP penetrometer and conceptual design of the Geophysical and Pore Fluid Gravity Probes (see Figure 3).

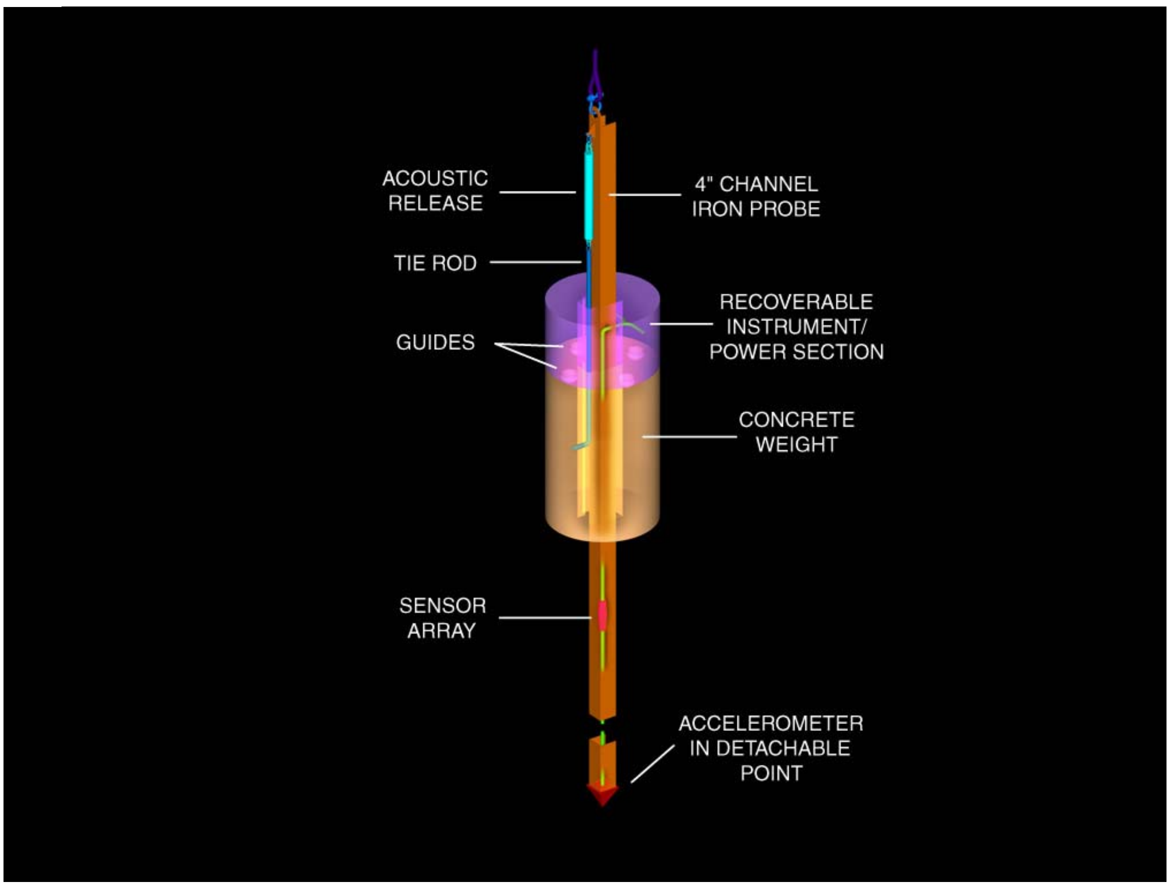


Figure 3. Conceptual Multi-Sensor SFP

ACOUSTIC SYSTEM FOR MONITORING GAS HYDRATES (latest update)

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

Start Date: 01/01/02
End Date: 11/30/2004

DOE Award Number: DE-FC26-02NT41628
Vernon L. Asper
Kevin M. Martin
University of Southern Mississippi
Department of Marine Science

Final Report

October 24, 2005

Abstract

In order to characterize the 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 project involved the design and construction of a bubble detector based on a technique which is used widely in the ocean to measure the conductivity of the water. The conductivity sensor was able to measure bubbles because they lower the conductivity of the water in which they are entrained and this signal was recorded as the bubbles rise through the sensor. Although this type of sensor has seen widespread use, there were concerns regarding its responsiveness and inherent sensitivity. To address these concerns, the sensor was tested rigorously in the laboratory using a calibrated volume of air that served as a standard. In most cases, the error between the actual gas volume and that detected by the system was less than 5%. The system was field tested over an area where natural methane is seeping from the seafloor near Cape Lookout in North Carolina with excellent results. Future plans call for the system to be deployed over a deep methane seep in the Gulf of Mexico to evaluate the potential for hydrate formation inside the funnel and to compare its results with those of other techniques.

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Introduction

Hydrocarbon seeps are locations where gas bubbles (vents) naturally from the marine sediment. The gas at these seeps is formed either thermogenically under high temperature and pressure or by microbial respiration. Large quantities of gas hydrates form in marine sediments mainly along continental margins and in permafrost in polar regions. Gas hydrates can be comprised of several gases, such as, ethane, propane, and carbon dioxide, however, methane (~99.9%) forms the most prevalent gas hydrate (Kvenvolden, 1988). At locations where the thermodynamic conditions are not met or are interrupted, the gas is released directly from the sediment into the water. The small bubbles dissipate in the water column but large bubbles have the potential to reach the atmosphere; highly active seeps can actually be observed by bubbling at the surface.

Kvenvolden (2002) estimates that between 500-24,000 Gt of methane are associated with gas hydrates. Even if the estimates were just 10,000 Gt, this is still twice as large as fossil fuel reservoirs, which contain 5,000 Gt of carbon. This makes gas hydrates currently the largest reservoir of organic carbon in the global carbon cycle. However, the role of gas hydrates in the global organic carbon cycle is not completely understood. MacDonald et al. (1994) propose that gas hydrates work as a pressure release system. They state that the accumulation of gas hydrates traps oil and free gases, which are released from below the hydrates when the "plug" of gas hydrates is dislodged due to excess buoyancy force or the rise in water temperature.

A great deal of interest in information on the extent of the gas release from hydrates and hydrocarbon seeps has been brought forward in recent years. Leifer et al. (2000) conducted a study that showed greater than 108 times more methane in the water column around hydrocarbon seeps than atmospheric equilibrium values in the Santa Barbara Channel (SBC), indicating that the release of gas plays an important role in the marine environment. However, due to the lack of a reliable technique, only estimates exist for the quantity of gas released into the environment. Several papers (Max and Miles, 1999; Dickens, 2003) have stated that both regional and global estimates of gas output vary significantly and that it is necessary to find the total flux of gas from venting hydrates. This suggests a need for comprehensive surveys and the development of an accurate but simple technique to quantify gas release. This study hopes to bridge that gap by incorporating an extensively used concept in oceanography, conductivity, to quantify the gas release.

Background

Gas hydrates are formed, at low temperatures and high pressure, from the incorporation of gas and water into a solid cage-like configuration, known as a clathrate (Zaptsepina and Buffett, 1998). A saturated clathrate structure of methane contains 5 ¾ molecules of water for every molecule of methane present. In theory, due to expansion factors, 1 m^3 of pure methane hydrate contains ~ 164 m^3 of methane gas at standard conditions (Kvenvolden, 1993).

Hydrate formation is normally confined to continental margins due to the adequate supplies of organic matter to generate the gas; even though temperature and pressure conditions required to form gas hydrates occur elsewhere in the ocean (Hyndman and Davis, 1992). The free gas (gas not associated with any other substituent) under excess pressure will react with ice or liquid water to form hydrates (Enns et al., 1965).

Furthermore, the temperature and pressure conditions suitable for hydrate stability in the seafloor are dependent upon the composition of the gas and the presence of salt and other constituents in the surrounding seawater (Zatsepina and Buffett, 1998). The physical properties and surface chemistry of deep marine sediments may also affect the thermodynamic state, growth kinetics, and spatial distribution of hydrates (Clennell et al., 1999). In oceanic sediments gas hydrates occur when the bottom temperature approaches $0^{o}C$ and the depth of the water exceeds 300m; the lower limit is determined by the geothermal gradient (Figure 1) (Kvenvolden and Lorenson, 2001). Wherever the geothermal gradient is interrupted, either by a decrease in pressure or an increase in temperature or salinity, the hydrate dissociates, releasing gas into the surrounding environment (Dickens, 2003).

The Gulf of Mexico (GOM) is one area where the presence of gas hydrates has been well-documented (MacDonald et al., 1994; Sassen et al., 2003; Brooks et al., 1984; Leifer and MacDonald, 2003). In the GOM, Leifer and MacDonald (2003) observed three separate seepages with total gas flux of 62.3 $x10^{-3}$ mol s^{-1}; however, rates at each of the vents were completely different, with one venting ~7 times more gas than the others. Bubble radii ranged from 1 to 2 mm for the small bubbles and larger bubbles up to 2 cm with bubbles with average radii of 5.5 mm. They also observed that the larger bubbles more closely resemble spheres and broke apart into smaller bubbles almost instantly. Furthermore, they noted that the larger bubbles were more contaminated with oil, a condition that may have led to the spherical shape. Upwelling velocities were calculated to be 1-15 cm s^{-1}.

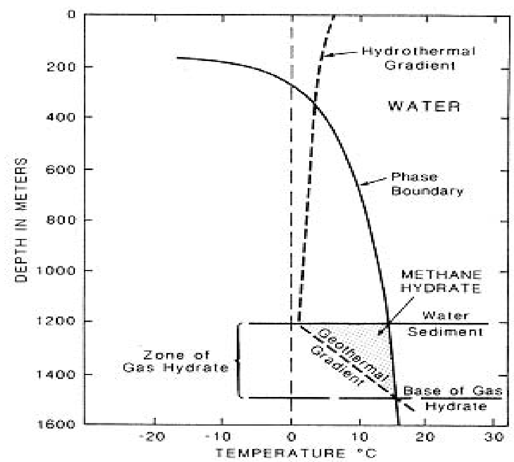

Figure 1. Examples of depth-temperature zones for hydrate stability; outer continental margin adapted from Kvenvolden (1988).

There are also locations in the marine environment where gas hydrates are never formed because the conditions needed are not met; yet, substantial gas is formed and vented from the sediment. These seeps are usually located shallower than gas hydrates therefore more observations exist. One well-documented area of hydrocarbon seeps is in the SBC (Hornafius et al., 1999; Leifer et al., 2000). The SBC seeps are shallow (20-70m) and are probably the most active seeps, with an estimated 1.5x105 m^{3} d^{-1} gas release with a bubble radius of 1-15 mm (Hornafius et al., 1999). At the surface of the SBC, upwelling rates were observed to be 30-100 cm s^{-1} (Leifer et al., 2000).

There have been a few different techniques used to estimate the gas flux from hydrocarbon seeps and hydrates. One of these techniques is the use of acoustical sonar (Hornafius et al., 1999). Sonar observations of bubble size are useful for large-scale observation but may lack the resolution to observe the smaller bubbles. Sonar also lacks the capabilities for long-term studies. Another technique being used is imaging (Leifer and MacDonald, 2003). This technique is applicable for observing all bubbles sizes; however, due to memory constraints has a limited application time, usually several hours. Leifer and MacDonald (2003) also note that errors occur when the plumes are too large and encompass a large portion of the camera's field of view. In addition, they state that errors can occur if a bubble is not in the narrow plane of focus. Other techniques have included a rotating wheel (MacDonald et al., 1994) and-a tipping bucket (Roberts et al., 1999). These methods have to be coupled with other sensors creating a large and bulky sensor package to deploy. The technique being proposed, using an electromagnetic sensor, would allow for a simple and small sensor package and for long term monitoring of gas emissions.

The proposed technique utilizes a fundamental concept in oceanography, conductivity. Conductivity is the capability for a material to pass an electrical current. Therefore, in this application, the ion in solution carries an induced electrical current, meaning the greater number of ions the higher the conductivity and vice versa. In oceanography, this concept has been used to infer salinity using the law of constant proportions. The development of this technique will take it one step further. Using the concept that a rising bubble acts like a large void in the seawater that removes a quantity of ions within the conductivity cell as it passed through creating a drop in conductivity (Figure 2). After the bubble exits the cell, the surrounding seawater will replenish the cell with ions returning conductivity to the original value. Furthermore, the drop in conductivity should be proportional to the volume of the bubble.

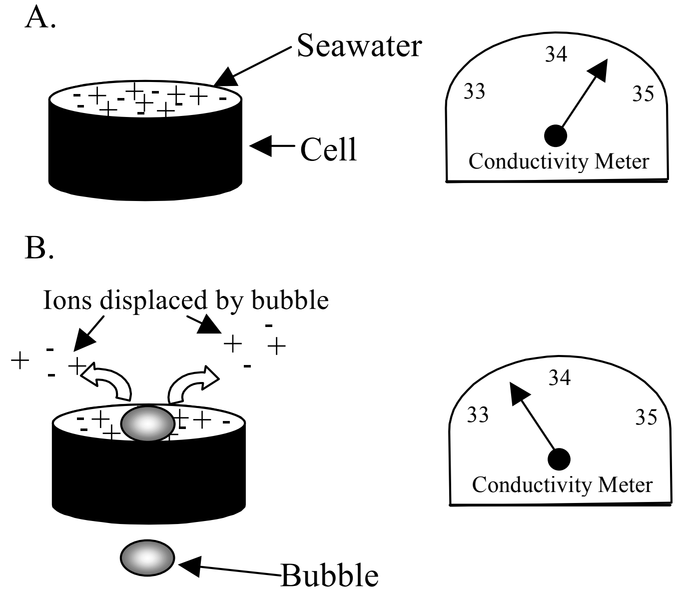

Figure 2. A dramatization of the purposed concept. A) Conductivity cell in seawater. B) Bubble in the cell displacing seawater ions causing a reduction in conductivity.

Experimental

An RBR XR-420-CT Conductivity and Temperature sensor was used as the experimental inductive conductivity cell. This particular CT is a one-off sensor with a pigtail connected to the sensor before the factory A-D converter allowing direct access to the unfiltered analogue signal. The reason for accessing the analogue signal directly is that the factory A-D converter does not sample at a high enough speed (1Hz). The signal from the sensor was supplied to a Tattletale Model 8 data logger with a 12-bit A-D converter with maximum sampling speed of 100kHz. High sampling rate was necessary in order to capture the bubble as many times as possible within the cell.

A test tank (figure 3) was constructed using clear 6-inch PVC pipe and Plexiglas. The tank was maintained at a salinity of 35 using table salt and temperature of ~20^{o}C (room temperature). An air hose was inserted into the tank to create the bubbles, and by varying the orifice size at the submerged end, different bubble sizes were created. Bubbling rates were controlled by varying the air pressure into the air hose using a regulator. A series of bubbling rates and bubble sizes were generated to find the limits of the sensor. A funnel was placed at the bottom of the sensor to ensure the bubbles pass through the cell.

The complete analogue signal of voltage changes (i.e. conductivity changes) for each bubble size was compiled for statistical analysis. Once the data were compiled, they were graphed in MATLAB and/or Excel and comparisons were developed. Using MATLAB a mathematical correlation between bubble size and conductivity change was developed. The complete mathematics behind this correlation are still being developed as part of Martin's thesis research, but preliminary observations show that curve fitting for each bubble may be necessary.

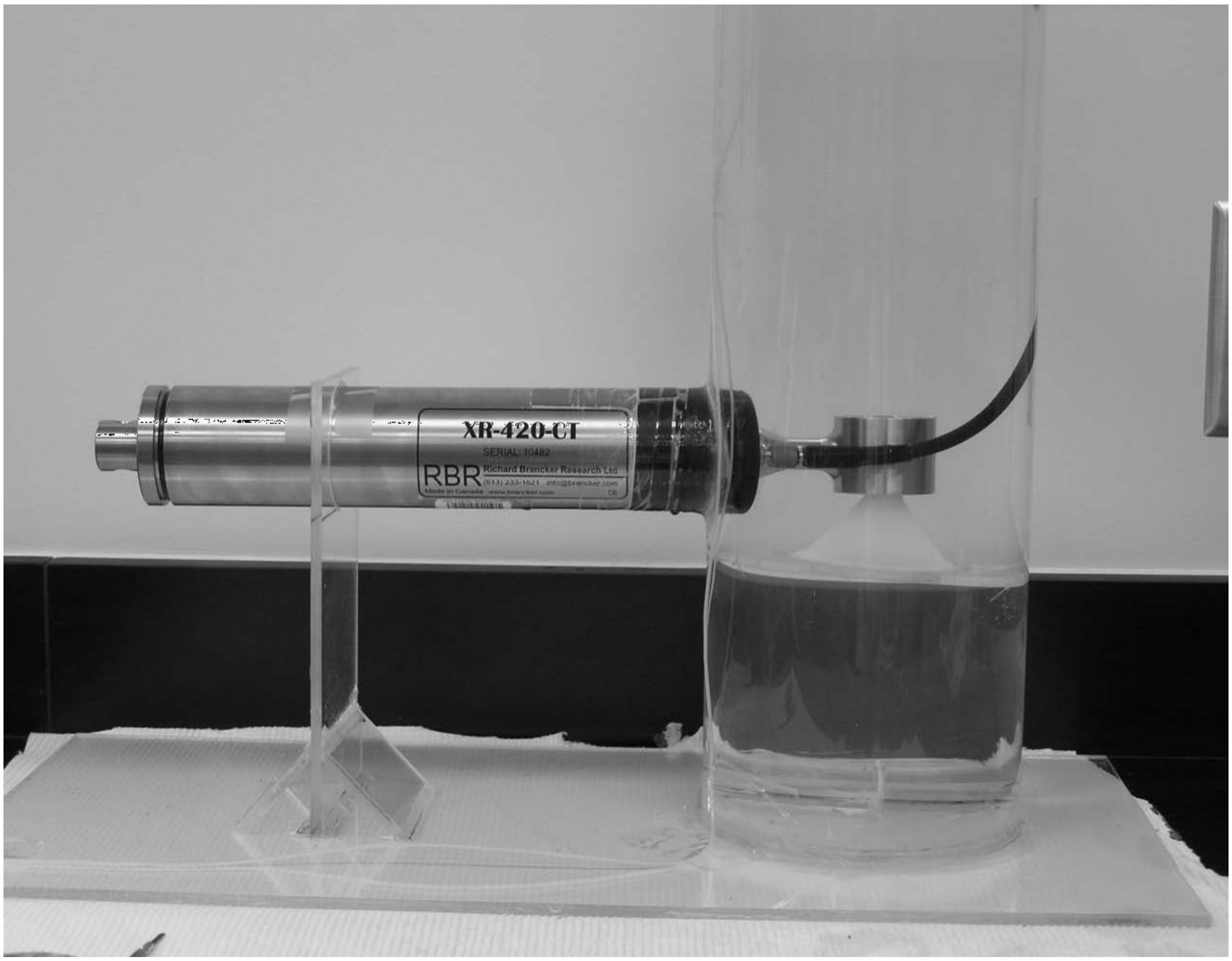

Figure 3. Laboratory test tank with Brancker conductivity sensor installed.

Bubble size verification was determined by a set of different techniques. The first technique that was used is volume displacement. A 10 ml graduated cylinder was placed on top of the conductivity cell to eliminate the need for a hydrostatic pressure correction. The number of bubbles required to displace a given volume of water (different volumes depending on bubble size) was counted. The volume of an individual bubble will then be calculated by:

$$Vbub = Vd/Bn$$

Where Vd is the volume displaced and Bn is the number of bubbles required to displace that volume. The second technique was by optical means. Pictures were taken of the bubbles using a digital camera. Behind the bubbles, a meter stick was placed allowing for direct determination of bubble diameter. Volume was calculated using the volume of a sphere equation (V_{bub}= 4/3Br^3).

Figure 4. System configured for *in situ* testing, including funnel and pressure case.

Once the sensor system was calibrated in the laboratory, it was taken to the field for an in situ evaluation. For these tests, the deployment setup incorporated a simple triangular pyramid made out of ¼" acrylic sheeting. The bottom opening was 45x45x45cm, tapering to a 14mm opening at the top, with sides sloping at 70 degrees. It was found that above 65 degree slope bubbles tend not cling to sides of funnels. The CT attached to the top and was supported by a saw horse type frame. The funnel and frame were placed on a sheet of plywood to avoid sinking into the bottom. A bottle was then placed at the top of the setup to collect gas to later truth the results calculated.

The Tattletale data logger and batteries were housed in an aluminum pressure housing built to withstand a 6,000m immersion so that it can be used for deployments at hydrate sites as well as for these shallow water tests.

Results and Discussion

Laboratory tests: Using the hardware described above, bubbles were introduced into the sensor, producing the data shown in figure 5. Conductivity (on the Y axis) decreases each time a bubble passes through the orifice. This result clearly shows that samples are being acquired at a sufficiently rapid rate to allow for more than adequate characterization of each bubble. The noise in the baseline signal is inherent in the sensor, requiring the construction of a simple low-pass filter (simple R-C circuit) to reduce the noise level without compromising sensitivity.

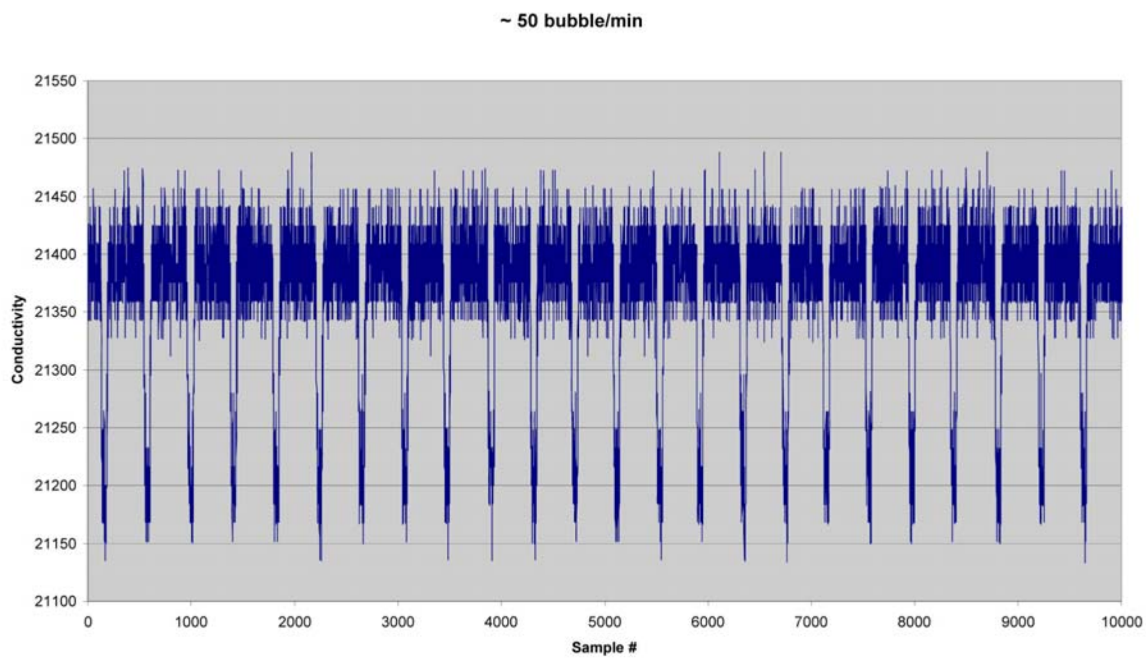

Figure 5 Bubbles passing through the sensor are detected as spikes of reduced conductivity lasting for a fraction of a second. In this experiment, samples were acquired at the logger's maximum rate of approximately 1kHz.

Thirteen different orifice sizes were utilized, with each orifice creating a different sized bubble. Volumes for these bubbles, ranging from 20ml to 957ml, were then calculated using volume displacement (figure 6). Each of these bubble volumes were streamed through the cell and were sampled at 500Hz and 1kHz. These runs were duplicated in waters of salinity 40-15 (changing by 5) to observe, if any, the effect of salinity on the results. Data files were also created with a known volume of gas but different sizes of bubbles, to help truth the mathematics that will be developed as part of Martin's thesis.

North Carolina Cape Lookout bight deployment:

To assure that the in situ setup was working properly, it was tested at the dock using divers and measured volumes of air. The system was suspended from the UNC Marine Institute pier and divers injected known volumes of air under the funnel which were then captured in the bottle. Volumes were then compared and the data shown in figure 7 were obtained. All decreases in the conductivity (y axis in arbitrary units) on the graph are bubble signals.

After setup was found to be working, it was deployed at Cape Lookout Bight, NC where methane bubbles from the seafloor naturally. Here the sensor was placed on the bottom, 30 feet deep, for 2-3 hours, during a low tide cycle, to observe how the CT responded to natural bubbling. The funnel worked well with 120 ml of gas being captured in the reservoir bottle at the top. The data obtained from that test are depicted in figure 8.

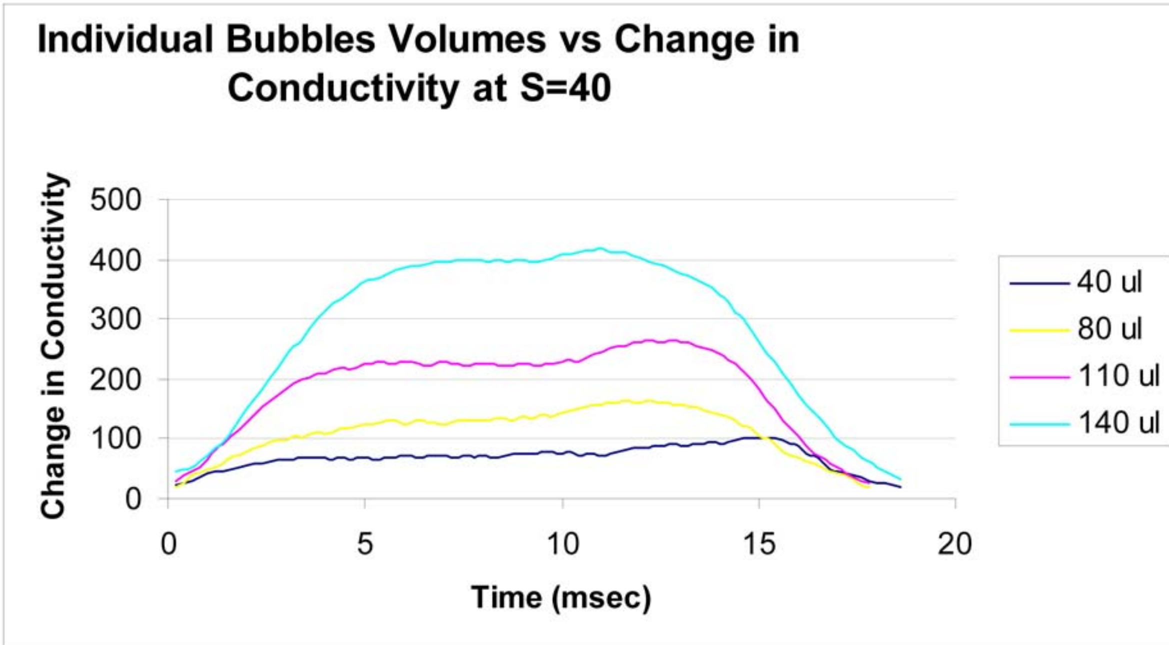

Figure 6 Response of the system to varying bubble sizes.

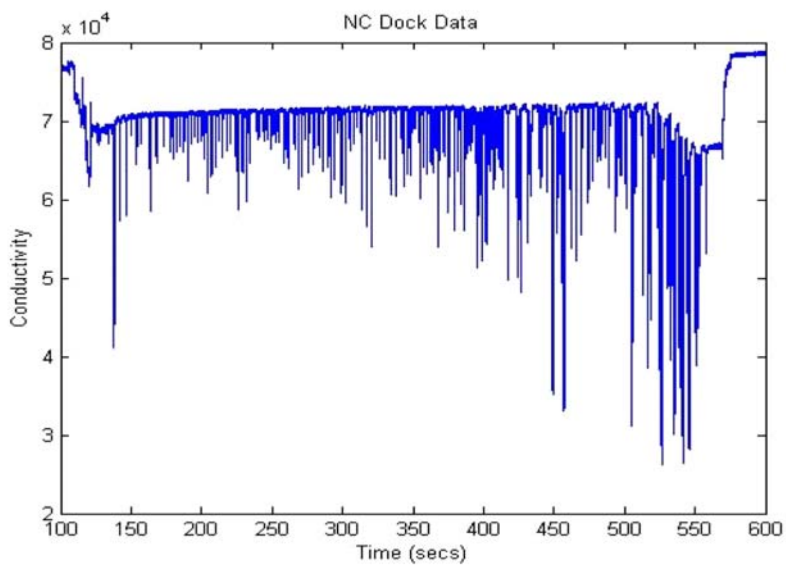

Figure 7. Record of air captured by the system suspended from the dock.

The graph in Figure 8 shows the fluctuation in conductivity as the tide changes, yet the bubble signals can still be seen as decreases from the conductivity trend. After the low tide was complete, the time when the most bubbling occurs, the system was relocated to shallow water where more known volumes of gas were bubbled through the sensor for more calibration testing.

Conclusions

These experiments have successfully demonstrated that the concept of using a conductivity sensor to measure bubble flux is valid. The laboratory tests proved that the volumes measured are accurate and repeatable and the field tests provided data that will be used to better understand the system and its response to such highly variable conditions. The project and data will continue to be developed by Martin as part of his Master's thesis and the system and its design details will be made available to other investigators as required.

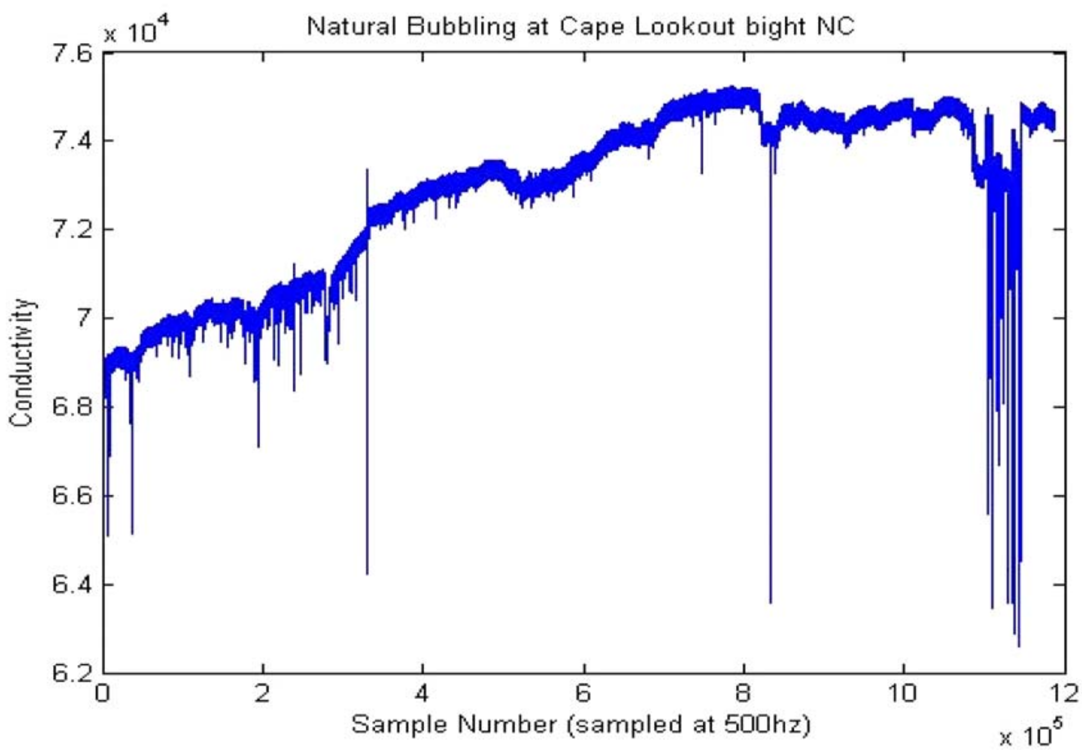

Figure 8. Conductivity as affected by tide.

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Project: DE-FC26-02NT41628
(DOE, Subcontract to University of Mississippi)

Mid-Infrared Sensor Systems for Continuous Methane Monitoring in Seawater

Methane detection using attenuated total reflection (ATR) spectroscopy.

Annual Technical Report

Research Activities December 01, 2003 – November 30, 2004

Boris Mizaikoff (PI) and Gary Dobbs

Atlanta, October 2, 2005

ABSTRACT/SUMMARY

This annual technical report summarizes progress towards development of methane detection and monitoring systems based on mid-infrared (MIR) attenuated total reflection (ATR) spectroscopy for deep-sea applications during the periods from December 01, 2003 – November 31, 2004. Representative figures are provided in the appendix; more details can be found in the progress report.

- A brief summary of the significant works performed in the first project period, December 01, 2003 through May 31, 2004, is provided.
- Modeling and design of an optics platform to complement the constructed electronics platform for successful incorporation into 'sphereIR' has continued.
    - AutoCAD design and manual construction of mounting pieces for 4 primary optical components were completed.
- Initial design concepts for IR-ATR sensor probe geometries have been established and evaluated.
    - First evaluations of a novel horizontal ATR (HATR) sensing probe with fiberoptic light guiding have been performed and validate the design concept as a potentially viable deep-sea sensing probe.
- Ray tracing simulations have been performed to evaluate light propagation through HATR elements to facilitate the optimal design of both the sensing probe and optical configuration of 'sphereIR'.
- Continuing investigations for ideal methane sensing membranes have been carried out evaluating the methane enrichment capabilities for polydimethylsiloxane (PDMS) extraction membranes commonly utilized as introduction membranes in underwater mass spectrometers.

Alternative measurement strategies based on direct evanescent field sensing will be developed in 2004/2005 for the passive monitoring of in-situ hydrate formation/dissociation in deep-sea environments. In addition, further investigations to optimize the design and configuration of the optics compartment for 'sphereIR' will be concluded. Based upon current results, we anticipate the final construction and first field tests of a miniaturized multi-component IR sensor system capable of in-situ, deep-sea methane detection and passive monitoring of gas hydrate formation/dissociation by natural processes in deep-sea environments during continuation of this project in 2005/2006.

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LIST OF GRAPHICAL MATERIALS

ANNUAL TECHNICAL REPORT

Summary of works from December 01, 2003 through May 31, 2004

Significant progress in the construction of a second generation submersible mid-IR sensing platform, 'sphereIR', was achieved during the first project period of this year. First, the electronics compartment design (Figure 1) and fabrication (Figure 2) were completed. Following this development, initial modeling of the optics compartment for 'sphereIR' commenced. Additionally, the development of second generation control system software for 'sphereIR' incorporating spectrometer control, automated data evaluation, power saving features, and programmable sampling capabilities suited for deep-sea deployment was completed using the Microsoft Visual Basic programming language. Finally, continuous investigations for optimal methane sensing membranes suited for deep-sea applications and pressure influences on IR-ATR spectroscopic measurements were performed. Complete details can be found in the semiannual progress report for this time period.

Modeling of optics platform for 'sphereIR' in AutoCAD

Following procedures used in the design and construction of the electronics compartment, the first step toward the design and construction of the optics compartment for 'sphereIR' began with accurately modeling the primary spectrometer optical components required for sensor operation using AutoCAD software. The model components have and will aid finalization of the design, development, and construction processes of the internal sensor platform. Currently, the relative positioning of the primary spectrometer optical components including the IR light source, aperture/optics block, and interferometer block have been modeled as shown in **Figure 3**. These three primary components require precise positioning and will require the majority of space in the optics compartment. This model is currently being used to help position the remaining primary (HeNe laser and Stirling cooled MCT detector) and secondary optical components (mirrors, lens, and prisms) in order to maximize the use of available space inside the instrument housing. In addition, the final selection, modeling, design, and construction of the remaining primary and secondary components including optimized sensor probes and the complimentary optics baseplate is underway.

Design and construction of mounting pieces for 'sphereIR' primary optical components

Continuing the progress of modeling the primary optical components for 'sphereIR', 6 robust mounting pieces for the aperture/optics block and interferometer block have been designed and constructed. Additionally, 8 mounting pieces for the HeNe laser have been designed and constructed as depicted in (Figure 4). Final designs and construction of mounting pieces will be completed upon successful investigations of signal generation and radiation propagation through HATR elements. Thus, the final layout of the optics platform will be completed and constructed leading into the initial testing phase for the submersible IR-ATR sensing platform anticipated in 2005/2006.

Initial design concepts of mid-IR sensor probes for 'sphereIR'

The mission critical aspect in developing viable submersible optical sensors is the engineering of optical chemical sensor probes for interfacing the encased spectrometer with the marine environment. Thus, it is of paramount importance to optimize the probe design for ensuring delivery of radiation to the transducer surface, maximizing signal transduction, and effectively guiding the generated signal to the detection module. In addition to an optimized probe design for interfacing the enclosed spectrometer to the adjacent environment, effective manipulation and coupling of the radiation into the active sensor head is required. For 'sphereIR', two probe designs are currently under investigation: (i) a compact silver halide fiber probe (**Figure 5**) and (ii) a horizontal attenuated total reflection (HATR) crystal probe with fiberoptic coupling (**Figure 6**).

For 'sphereIR', fiberoptic coupling of IR radiation from the light source after modulation by the interferometer to the active sensor head, and subsequently to the detection module, is essential due to compression of the instrument housing[1] with depth resulting in misalignment of the optical components. Guiding radiation via fiberoptics ensures that the optical alignment is maintained even at harsh environmental conditions, as previously shown with the 'TUBE-IR'.[2] The first generation of submersible IR systems ('TUBE-IR') utilizes silver halide fibers for light guiding and the active evanescent field sensor head.[2] This concept will be adapted to compliment the 'sphereIR' system by providing a more compact all-fiberoptic sensor head. While an all-fiberoptic sensor probe is expected to provide the desired analytical performance based on previous experience,[2-9] the lifetime of silver halide fibers is limited and restricts long-term sensing applications without frequent maintenance. Consequently, an alternative probe design based on a combination of a planar waveguide transducer with fiberoptic signal coupling is under investigation for extending sensor deployments with reduced maintenance requirements.

Ultimately, the sensitivity of submersible IR chemical sensor systems depends upon the amount of radiation delivered to the transducer, the effective measurement pathlength, and the percentage of radiation relayed to the detector element. Thus, it is required to provide effective coupling of radiation into the sensor probe, a maximized effective measurement pathlength, and minimized radiation losses from the multiple coupling interfaces of a fiber-crystal-fiber (f-c-f) probe. Therefore, initial investigations have been performed to evaluate the feasibility of this design as well as the behavior of radiation propagation through the sensing element to facilitate effective design concepts for the optical configuration of 'sphereIR'.

Evaluation of fiber-crystal-fiber sensor probe concept

Initial test measurements were performed to evaluate feasibility of developing a novel mid-IR sensing probe utilizing a horizontal ATR crystal as the sensing element with fiberoptic light guiding. The first evaluation measurements were carried out to map the radiation focused onto a MCT detector element while incrementally stepping (700 μm intervals) a silver-halide coupling fiber (700 μm dia.) across the beveled in-coupling facet of a typical commercially available 72x10x6 mm trapezoidal ATR element (Figure 7). Figure 7A shows a scheme of the fiberoptic light coupling into a vertically mounted HATR crystal. Results from these first measurements, depicted as a surface map in Figure 7B, show that the fiber-crystal coupling concept can be utilized for guiding light to the HATR sensing element. Additionally, Figure 7B displays the intensity of detected radiation is strongly dependent on the position of the coupling fiber at the HATR in-coupling facet and the importance of establishing robust optical mounts to ensure optimal operation in harsh aquatic environments.

Additional test measurements were performed to verify the capability of generating evanescent field spectra with fiberoptic light coupling into a HATR element. This was achieved by depositing a 10% w/v solution of poly(styrene-co-butadiene)/toluene (PSCB) prepared by dissolving approx. 1 g of PSCB (Aldrich Chemical Company, Milwaukee, WI) in 10 mL of toluene (Certified ACS grade, Fisher Scientific, Fair Lawn, NJ) at room temperature and briskly stirred for 1 h. on the measurement surface of a vertically mounted HATR crystal and evaluating the PSCB residue absorption after toluene evaporated with either fiberoptic light coupling or mirror light coupling. In addition, PSCB was deposited on the side facets that will be utilized for mounting the HATR element in the sensor probe casing. This was done to ensure no signal interferences would result from mounting the HATR element as envisioned. Exemplary results for these measurements are provided in Figure 8. From Figure 8, it is clearly displayed that fiber coupling has the same capability of generating evanescent field absorption spectra as typical mirror coupling. Furthermore, even with a 10-fold increase in deposition of PSCB/toluene solution on the side facets, there was no measured absorption of the polymer residue showing that use of the side facets for mounting the HATR element will not degrade the performance of this probe design. All IR-ATR absorption spectra for these measurements were 50 scan averages with 4 cm^{-1} resolution.

Further investigations are underway to thoroughly investigate light propagation through HATR elements and signal generation at the sensing interface via evanescent field interactions with discrete deposits of PSCB residues along the measurement surface. This work will aid in optimizing the sensitivity of deep-sea IR sensor heads by investigating parameters such as the optimal cone of radiation for coupling into the transducer, the HATR element geometry to efficiently deliver radiation to the transducer-sample interface, and the probe geometry to minimize signal loss when guiding the signal to the detector.

Ray tracing simulations of light propagation through HATR sensing elements

First investigations to model light propagation through HATR sensing elements were performed. Figure 9 displays the radiation profile along the sensing interface with increasing cone angles of radiation coupled into an HATR element. Additionally, Figure 10 displays the radiation profile exiting the HATR element for three different cone angles. These ray tracing simulations graphically reveal precise information on the behavior of light propagation through HATR elements for various optical parameters. Thus, the ray tracing results provide vital information for the rational development of optimal deep-sea IR sensor probes. Resulting, the ray tracing platform will play a crucial role in the optical design of 'sphereIR' by providing a platform for testing the selection of secondary optical components and placement of all optics components to maximize signal generation at the sensing interface and efficiency of light guiding from the source to the detector module.

Methane enrichment in polydimethylsiloxane (PDMS) membranes

Polydimethylsiloxane is the typical introduction membrane material for underwater mass spectrometers.[10-12] Therefore, this polymer material was of interest as a potential methane enrichment membrane for IR-ATR sensors. First, an appropriate ATR crystal coating strategy was developed using a 10:1 ratio (5g, 0.5g) of PDMS base to catalyst (EIS Industrial, El Paso, TX) diluted with 25 mL of chloroform (Fisher, Certified ACS). The solution was enclosed in a vial and mixed with a glass stirbar for 5 minutes forming a viscous solution. Using a spin-coating technique followed by 1 hour heat treatment at 110°C, a 4-7 μm coating was produced using 1400 μL of solution deposited on a 50x20x2mm germanium (Ge) crystal. An IR-ATR spectrum of the PDMS coating was collected to verify that no significant PDMS absorption bands were present around 3020 cm^{-1} and 1305 cm^{-1} which would interfere with methane sensing (Figure 11). From the ATR absorption spectrum of PDMS, it is concluded that polymer absorption does not represent a significant interference in the spectral regions of interest for IR-ATR methane sensing.

To assess the methane enrichment capability of the PDMS membrane, IR-ATR spectra were collected as 100 scan averages with 4 cm^{-1} resolution to monitor methane enrichment into the membrane as methane gas (CP 99%, AirGas) was purged through a custom horizontal ATR flow cell. A PDMS layer was coated on a 72x10x6 mm ZnSe crystal following procedures for the Ge crystal except that only 1000 μL of solution was used as a result of the decreased surface area. In Figure 12A, the integrated peak values for methane absorption regions (3020 cm^{-1} and 1305 cm^{-1}) are displayed versus time. In this figure, it is clear that methane will diffuse into the PDMS membrane and follows a diffusion type curve as displayed with the fit for the 3020 cm^{-1} methane absorption region. However, there is a sinusoidal drift with 45-90 minute cycles associated with this measurement series. This behavior is most likely the result of room temperature fluctuations as diffusion is dependent upon the gradient of methane concentration in air/polymer. The methane concentration in the sample chamber can be closely approximated using the ideal gas law, $PV=nRT$, such that temperature fluctuations of a few °C (commonly observed in our laboratory) could lead to this behavior as a result of the temperature dependence of methane gas concentration in the sample chamber. Figure 12B displays a portion of selected IR-ATR spectra with the methane absorption peaks highlighted. Further measurements to enrich dissolved methane from a saturated aqueous solution at room temperature were unsuccessful.

A number of improvements to a custom pressure cell have been devised and will be implemented in 2004/2005 to allow simulated real-world investigations of enrichment membranes at hydrate forming conditions. Additionally, a novel approach for detecting hydrate structures by direct IR-ATR measurements will be investigated in the laboratory with the improved pressure cell sampling chamber. This approach has the potential to significantly improve in-situ monitoring capabilities for natural hydrate formation and dissociation processes in deep-sea environments. Currently, Raman measurements can be made to ascertain this information, but this measurement procedure requires active focusing of the excitation laser to collect measurement data.[13-15] Thus, Raman measurements are not well-suited for passive sampling procedures required for stand-alone in-situ applications without human interaction.

FIGURES

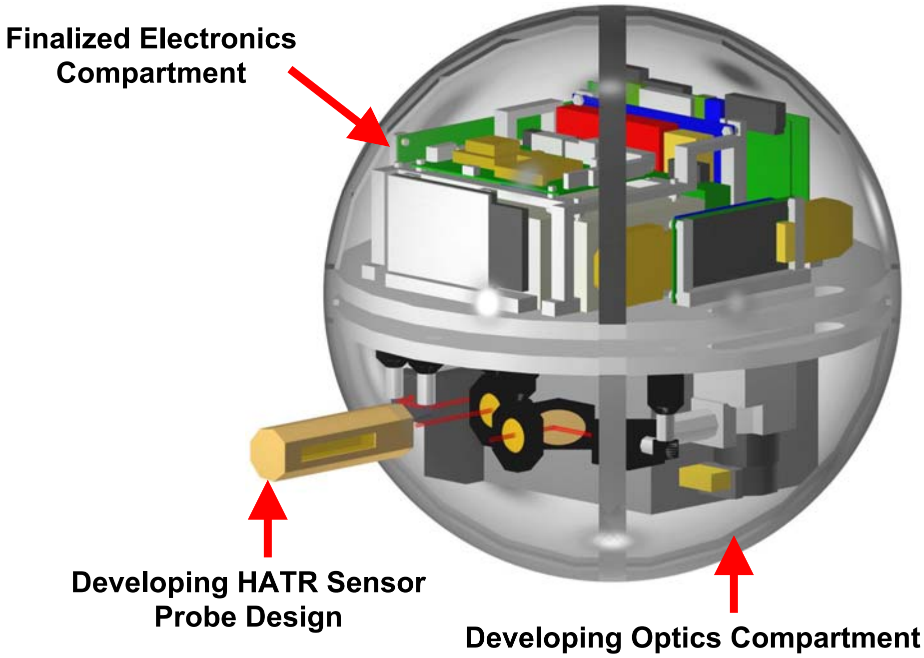

Figure 1: *Rendered model of 'sphereIR' displaying the finalized electronics compartment, ongoing development of the optics compartment, and initial concepts of a horizontal attenuated total reflection (HATR) mid-IR deep-sea sensing probe.*

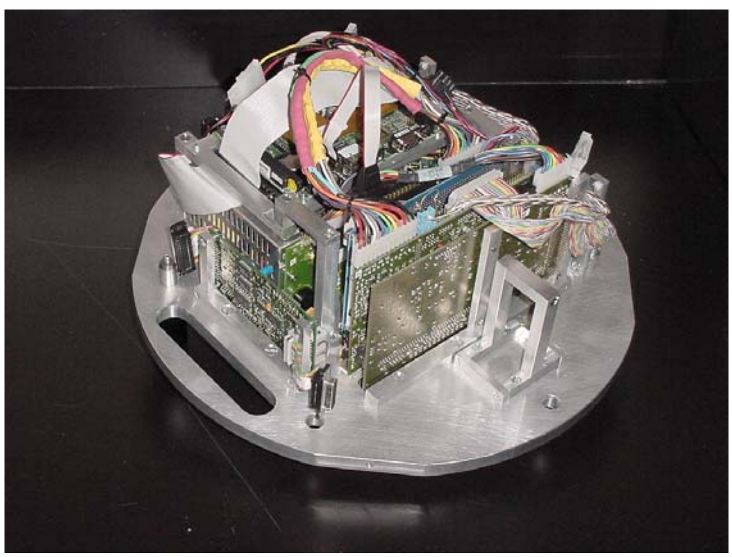

Figure 2: *Graphic display of the completed construction of the electronics compartment for 'sphereIR'.*

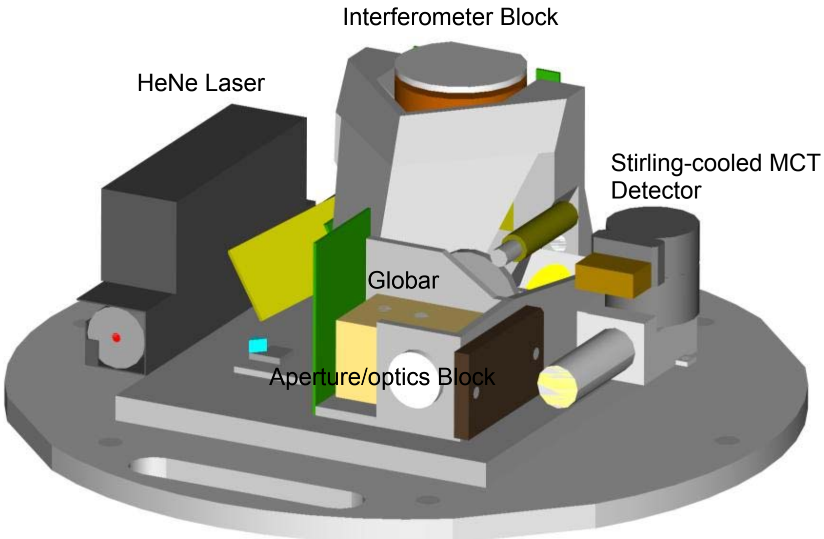

Figure 3: *Rendered scheme of primary spectrometer optical components for 'sphereIR'.*

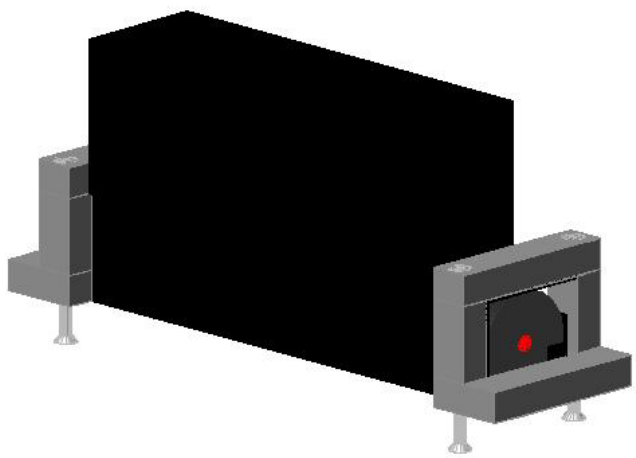

Figure 4: *Rendered graphic displaying the modeled HeNe laser, mounting pieces, and fasteners.*

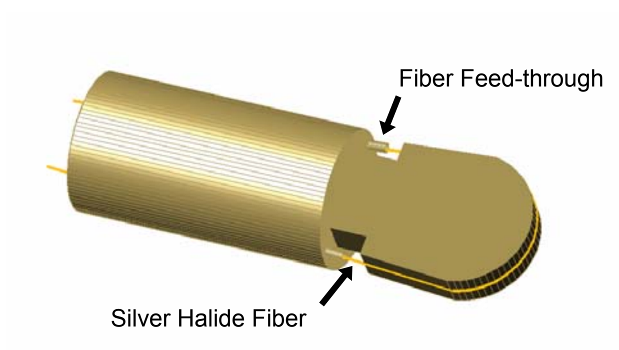

Figure 5: *CAD-schematic of working prototype design of an all-fiberoptic sensor probe for 'sphereIR'. Approx. probe length: 15.24 cm; approx. diameter: 5.08 cm. The exposed fiber will be coated with a methane recognition membrane.*

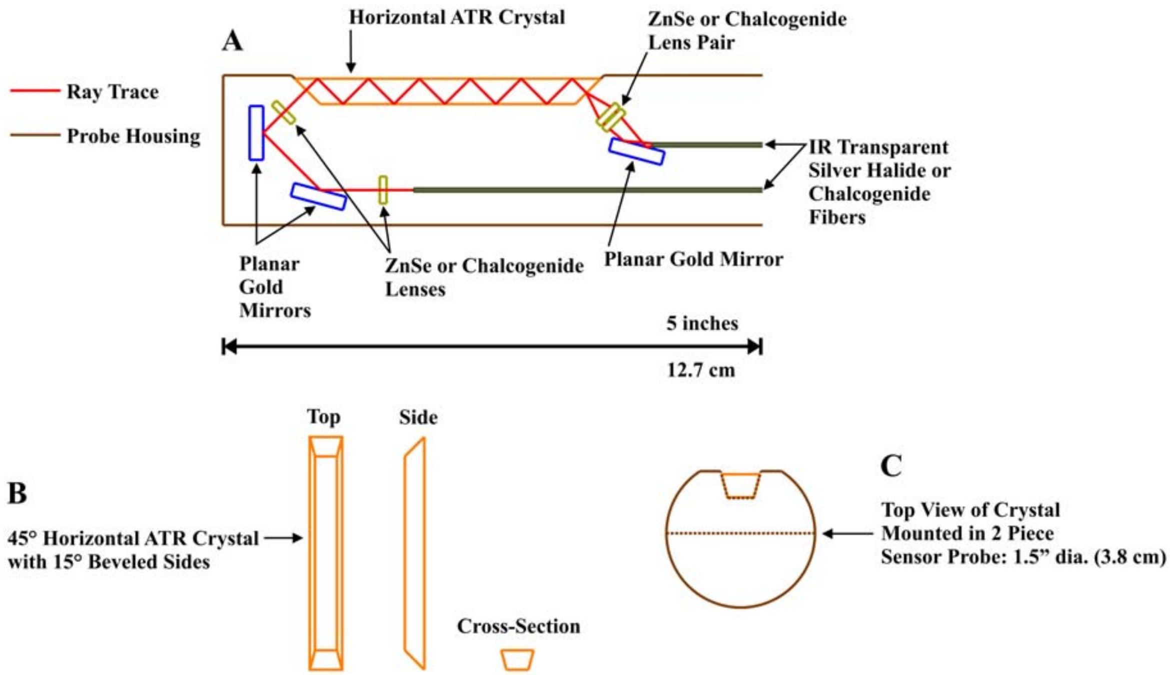

Figure 6: *(A) CAD-schematic of a fiber-crystal-fiber probe for 'sphereIR'. (B) CAD-schematic of a custom designed ATR crystal with 15^o beveled sides. (C) CAD-schematic of the top view of the f-c-f probe for 'sphereIR'.*

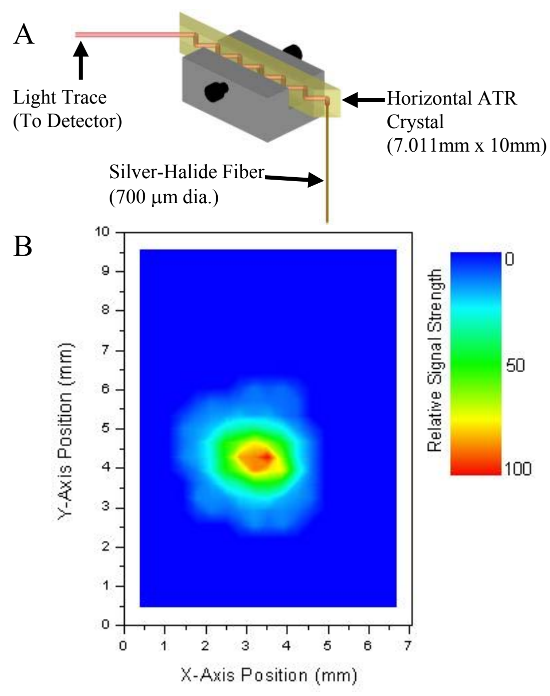

Figure 7: *Experimental setup for investigating samples at elevated pressures with integrated Stirling-cooled MCT detector.*

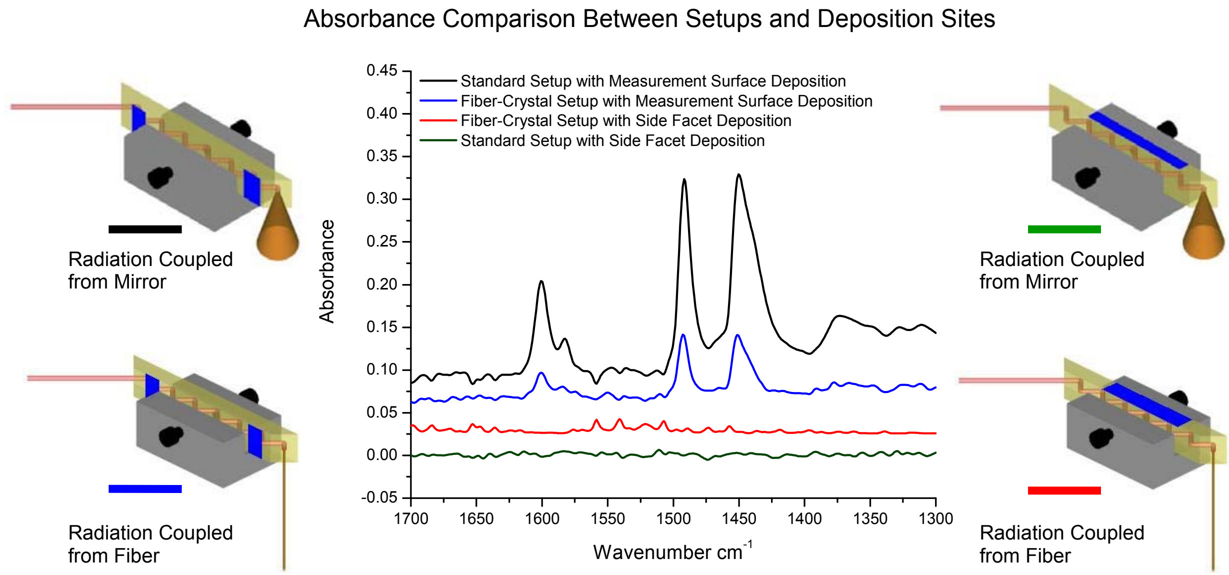

Figure 8: *IR-ATR absorption spectra of PSCB with respect to light coupling technique (cone represents mirror; cylinder represents fiber) into a vertically mounted HATR crystal and deposition location of PSCB/toluene solution.*

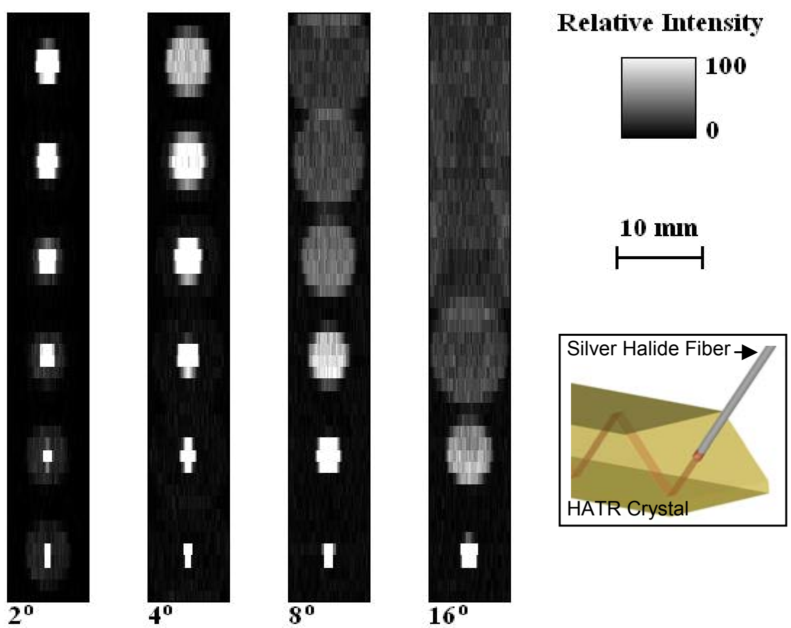

Figure 9: *Surface map displaying radiation intensity of the evanescent field probing the sensing interface of a HATR element with increasing cone angles.*

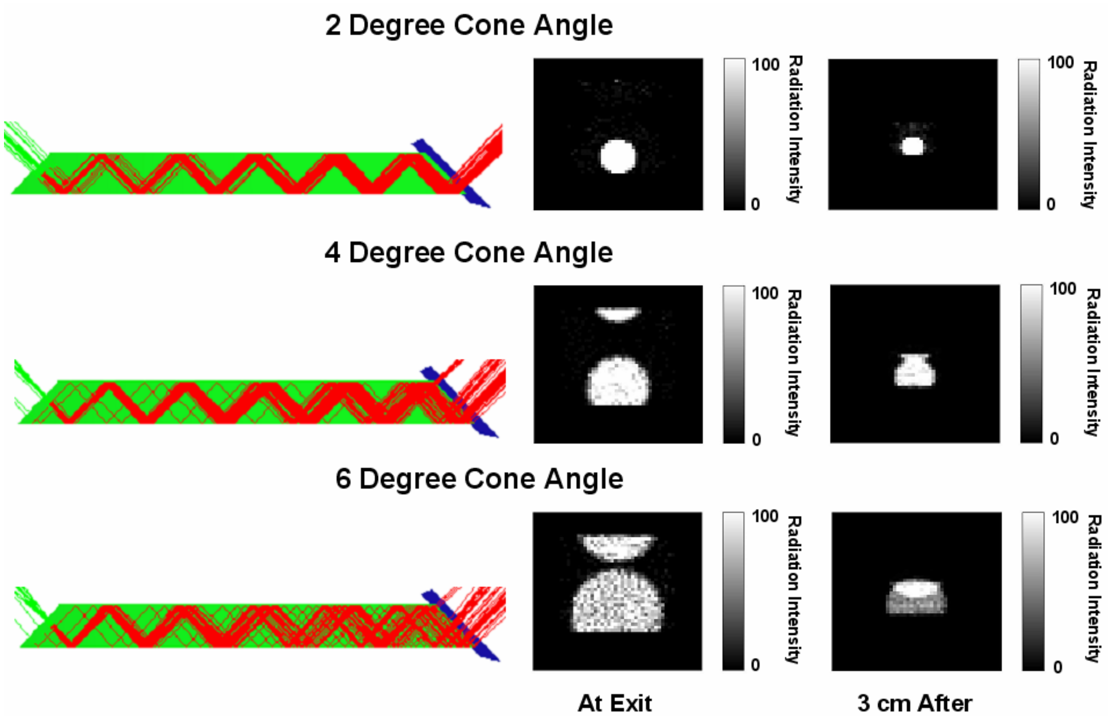

Figure 10: *Rendered drawings of optical ray traces through a modeled HATR element and the resultant radiation density for light exiting the crystal at the out-coupling facet and 3 cm after the out-coupling facet.*

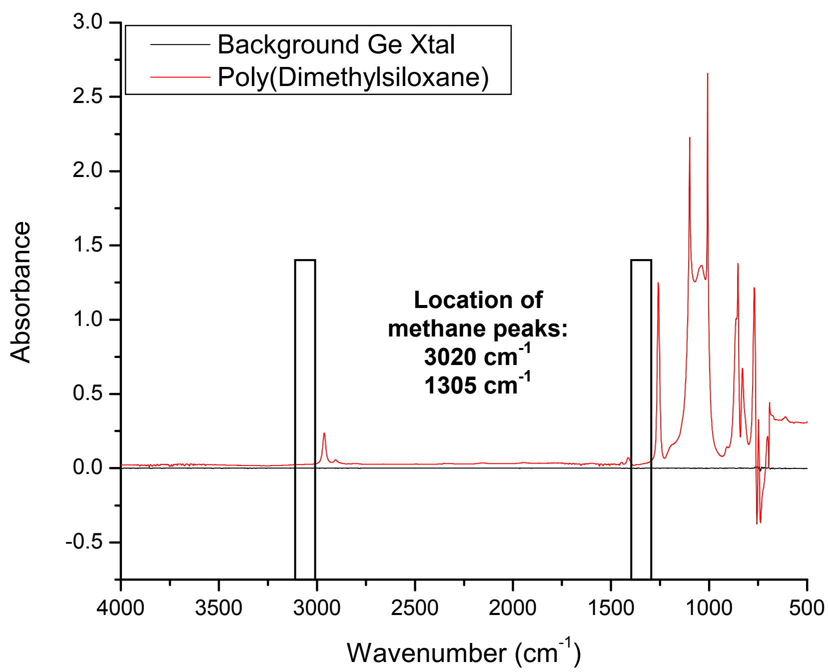

Figure 11: *IR-ATR absorption spectra of PDMS with the reference spectrum and highlighted regions of methane absorption.*

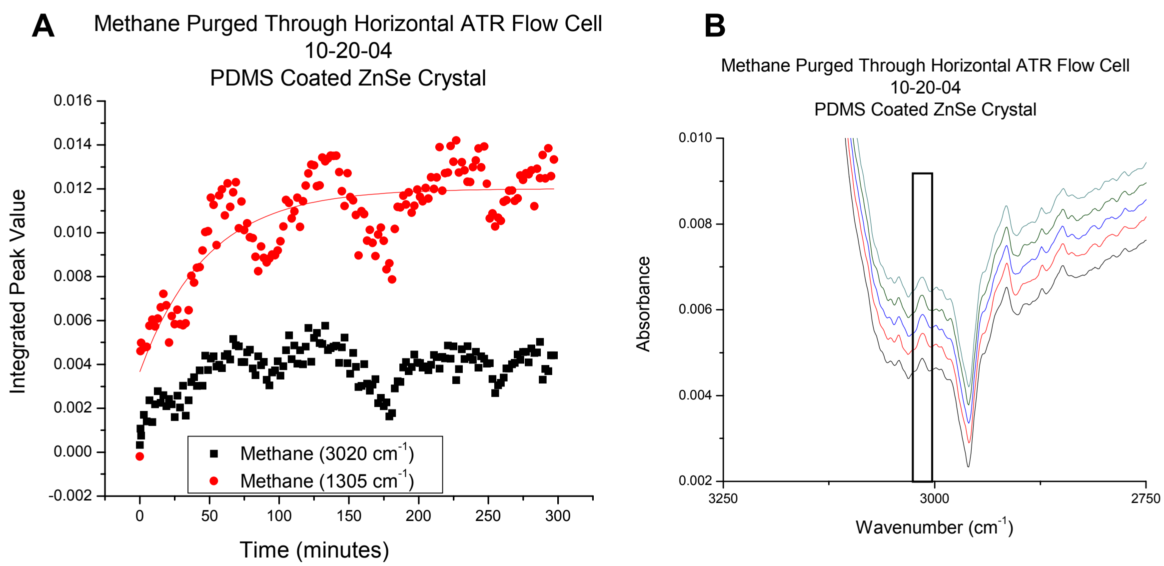

Figure 12: *(A) Integrated peak values of methane absorption bands plotted versus time for methane diffusion into a PDMS membrane. (B) IR-ATR spectra of the methane absorption at 3020 cm*$^{-1}$ *enriched into a PDMS membrane.*

ABBREVIATIONS

MIR	mid-infrared
ATR	attenuated total reflection
IR-ATR	infrared attenuated total reflection
HATR	horizontal attenuated total reflection
CAD	Computer Assisted Design
PDMS	polydimethylsiloxane
ASL	Applied Sensors Laboratory
Ge	Germanium
ZnSe	Zinc Selenide

SCIENTIFIC CONTRIBUTIONS

Oral Presentations:

2004 "Investigating Polymer Coatings for Infrared Methane Sensing Applications in the Deep Sea", **Ashley M. Baena**, Gary T. Dobbs, Boris Mizaikoff, SERMACS 2004, 11-04, Research Triangle Park, NC (oral presentation).

2004 "Progress Update for Construction of a Mid-Infrared Spectroscopic Sensor for Methane in Seawater", **Gary T. Dobbs**, Frank Vogt, Boris Mizaikoff, Semiannual Meeting of the Gulf of Mexico Hydrates Research Consortium, 10-04, Oxford, MS (oral presentation).

2004 "IR-ATR Spectroscopy for Underwater Sensing Applications", **Gary T. Dobbs**, Peter Boezerooij, Neil Pennington, Frank Vogt, Boris Mizaikoff, EUROPT(R)DE VII, 04-04, Madrid, Spain (oral presentation).

2004 "Progress in Construction of a Mid-Infrared Spectroscopic Sensor for Methane in Seawater", **Gary T. Dobbs**, Peter Boezerooij, Neil Pennington, Frank Vogt, Boris Mizaikoff, Semiannual Meeting of the Gulf of Mexico Hydrates Research Consortium, 03-04, Oxford, MS (oral presentation).

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

DOE Award Number: **DE-FC26-02NT41628**

Interim Report covering the period

June 2004 – November 2004

Submitted by

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Date: April 2005

ABSTRACT

Work has continued on the final development of the electronic part of an acoustic logging system designed for investigating fine-scale temporal changes in sea floor acoustic reflection responses. During this final phase, much of the time allocated to the project has been given over to testing and commissioning the complete system.

Subject to further funding, future work will be directed towards final design and build of a system ready for deep water deployment, with the emphasis on optimizing transducer specifications and packaging for operation at the Gulf of Mexico Gas Hydrate Monitoring Station.

CONTENTS

1. 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).

2. 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 did suffer some delays along the way (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 now complete.

3. EXPERIMENTAL DEVELOPMENTS

A detailed specification for the electronic instrument was included in the previous interim report (December 03 to May 04). During this final phase, all system components underwent further extensive testing prior to the final instrument commissioning.

4. RESULTS AND DISCUSSION

The challenges of the system development were described in the previous progress report.

At this stage, it is probably worth pointing out that aspects of the project proved far harder than originally expected and that the development team experienced some severe problems along the way meaning that overall bench development time was at least twice that originally estimated. There was no single major problem, the problems that absorbed the time were essentially three, the first of these perhaps a bit surprising:

(i). Because of the ability now to realize circuit elements in simulation, and the accuracy and ease with which simulated designs can now be brought from paper to PCB and then to the bench, virtually all of the circuit elements when tested separately early on, worked first time. This sounds like a major advance, but the effect was that these circuit elements were adopted far faster than would have been possible a few years ago. However, the simulations have limits to the number of parameters that can be varied: when these circuit elements were put under software control problems emerged that the simulation would never have seen.

(ii). The major problem was that the sheer number of usefully variable parameters made this into a far more complex device than its size might suggest. By far the biggest single use of time was in debugging the vast number of variations that the system allows. An element of this that is common to all modern electronics development at component level is that IC manufacturers' data sheets tell you what you must know, and what they want you to know. However, all complex ICs have parameters that the manufacturers may want to hide, or at least not publicize, and parameter variations that they do not know about. The debugging process has to discover all such non-declared parameters.

(iii). It proved remarkably difficult to emulate the real acoustic world in the lab, and thus tests in real water with real batteries are needed. Very minor assumptions that were made to build a lab test rig were found not to be compatible with real testing, and so real-world testing has proved very time absorbing simply because test parameters have to be selected, and sometimes hardware modification has been needed, to make things work.

However, despite the above and the associated time over-runs, the final device met every element of the original specification.

5. CONCLUSIONS

The chosen electronic instrument design integrated many state of the art technologies, and tests have shown the data recording and source quality to be excellent. The project objectives have been fully realized, with the instrument meeting the hopes set at the outset.

Subject to the successful outcome of a follow-up proposal, future efforts will be concentrated on optimizing transducer specifications and packaging for deep water operations.

CONCLUSIONS

This report covers the accomplishments of the fourth 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, 2005, 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 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

A-D	alternating-direct (current)
ALA	acoustic line array
ATR	attenuated total reflection
AV	Atwater Valley
BHA	borehole array
BBLA	benthic boundary layer array
CAD	Computer Assisted Design
CT	conductivity and temperature sensor
CTD	conductivity, temperature, depth (sensors)
CMRET	Center for Marine Resources and Environmental Technology
DATS	data acquisition system
DOC	Department of Commerce
DOE	Department of Energy
DOI	Department of the Interior
DRS	Data Recovery System
EU	European Union
FY	Fiscal Year
Ge	Germanium
GLA	geophysical line array
GOM	Gulf of Mexico
HATR	horizontal attenuated total reflection
HLA	horizontal line array
HRC	Hydrates Research Consortium
HSZ	Hydrate Stability Zone
IDP	Integrated Data Power Unit
IR	infrared (spectroscopy)
JIP	Joint Industries Program
MC	Mississippi Canyon
MFP	matched field processing
MIR	mid-infrared
MMRI	Mississippi Mineral Resources Institute
MMS	Minerals Management Service
MS	monitoring station
NETL	National Energy Technology Laboratory
NIUST	National Institute for Undersea Science and Technology
NOAA	National Oceanographic and Atmospheric Administration
NURP	National Undersea Research Program
OLA	Oceanographic Line Array
PCB	pressure compensated battery
PFA	pore-fluid array
PDMS	polydimethylsiloxane
PSCB	poly(styrene-co-butadiene)
PVC	polyvinylchloride

R-C	resistivity-conductivity circuit
ROV	remotely operated vehicle
SBC	Santa Barbara Channel
SFO	Sea Floor Observatory
SFP	Sea Floor Probe
SSD	Station Service Device
T-O	Time Zero
UNC	University of North Carolina at Chapel Hill
US	United States
USGS	United States Geological Survey
VLA	vertical line array
ZnSe	Zinc selenide

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 would have been 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 surfaced. 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

Modifications to the design of the monitoring station/sea floor observatory are described below and are illustrated in Figure 1.

CHANGE 1: ARRAY TYPE

One external factor affecting the establishment of the station is the 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 Program (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 located at a site appropriate to the other requirements of the monitoring station, 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. Although these arrays are temporary, they will provide much valuable data at a fraction of the cost of a borehole array.

The JIP has indicated that there may be a 2006 hydrate drilling program. If this materializes, the opportunity to emplace a borehole array in a JIP borehole can be revived. Otherwise, other opportunities will be pursued.

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.

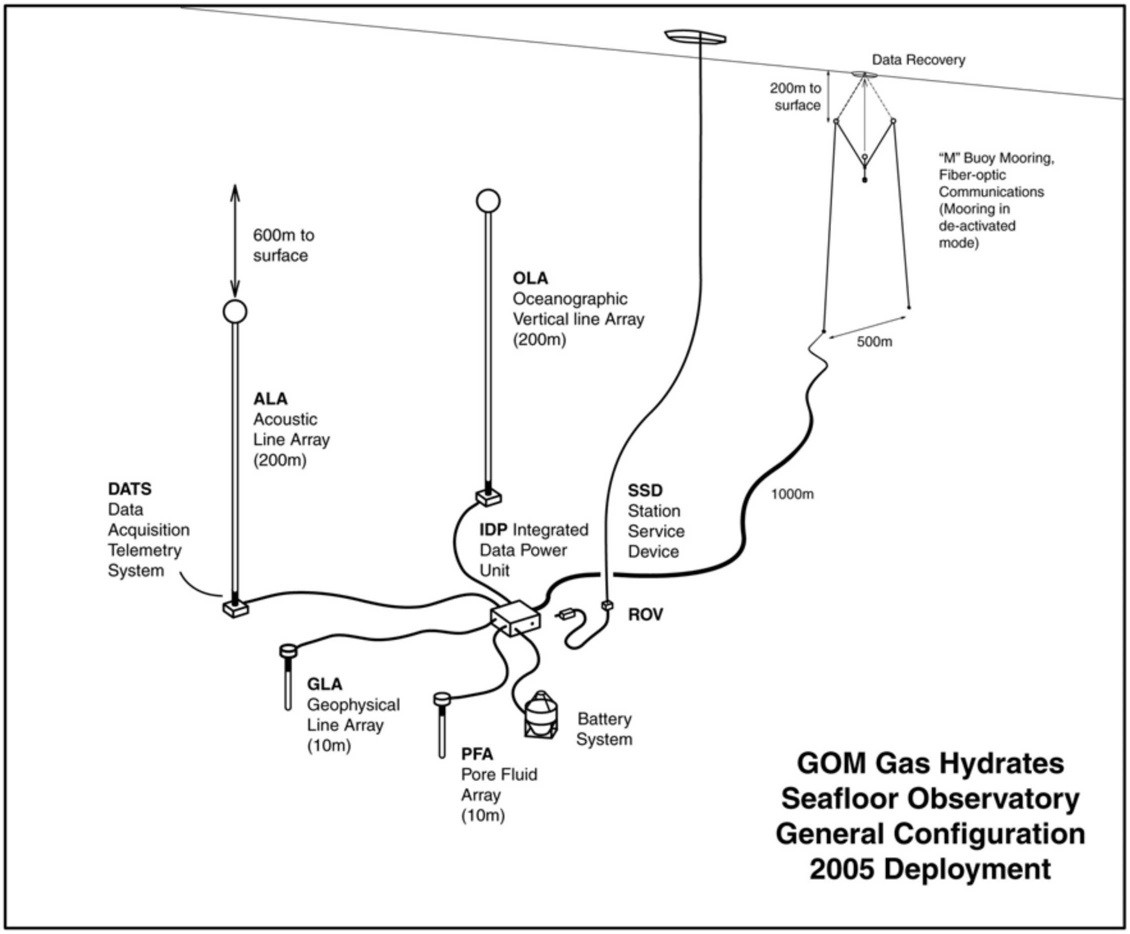

Figure 1. Diagram of the monitoring station/sea floor observatory.

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.