

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

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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 innovate research methods and construct necessary instrumentation.

A year into the life of this cooperative agreement, we note the following achievements :

- Progress on the vertical line array (VLA) of sensors:
  - Software and hardware upgrades to the data logger for the prototype vertical line array, including enhanced programmable gains, increased sampling rates, improved surface communications,
  - Cabling upgrade to allow installation of positioning sensors,
  - Adaptation of SDI's Angulate program to use acoustic slant ranges and DGPS data to compute and map the bottom location of the vertical array,
  - Progress in T<sup>0</sup> delay and timing issues for improved control in data recording,
  - Successful deployment and recovery of the VLA twice during an October, 2003 cruise, once in 830m water, once in 1305m water,
  - Data collection and recovery from the DATS data logger,
  - Sufficient energy supply and normal functioning of the pressure compensated battery even following recharge after the first deployment,
  - Survival of the acoustic modem following both deployments though it was found to have developed a slow leak through the transducer following the second deployment due, presumably, to deployment in excess of 300m beyond its rating.
  
- Progress on the Sea Floor Probe:
  - The Sea Floor Probe and its delivery system, the Multipurpose sled have been completed,
  - The probe has been modified to penetrate the <1m blanket of hemipelagic ooze at the water/sea floor interface to provide the necessary coupling of the accelerometer with the denser underlying sediments,

- The MPS has been adapted to serve as an energy source for both p- and s-wave studies at the station as well as to deploy the horizontal line arrays and the SFP.
- Progress on the Electromagnetic Bubble Detector and Counter:
  - Components for the prototype have been assembled, including a dedicated microcomputer to control power, readout and logging of the data, all at an acceptable speed,
  - The prototype has been constructed and preliminary data collected,
  - The construction of the field system is underway.
- Progress on the Acoustic Systems for Monitoring Gas Hydrates:
  - Video recordings of bubbles emitted from a seep in Mississippi Canyon have been made from a submersible dive and the bubbles analyzed with respect to their size, number, and rise rate. These measurements have been used to determine the parameters to build the system capable of measuring gas escaping at the site of the monitoring station,
  - Laboratory tests performed using the project prototype have produced a conductivity data set that is being used to refine parameters of the field model.
- Progress on the Mid-Infrared Sensor for Continuous Methane Monitoring:
  - Preliminary designs of mounting pieces for electrical components of 'sphereIR' have been completed using AutoCAD software,
  - The preliminary design of an electronics baseplate has been completed and aided in the optimization of positioning electrical components inside the instrument housing,
  - First spectroscopic investigations of the highly permeable polymer, poly(trimethylsilyl)propyne (PTMSP), as a potential sensing membrane for methane, have commenced,
  - High-pressure multireflection ATR measurements were continued during this project period to investigate the potential influences of hydrostatic pressure on sensing principles and data evaluation strategies.
- Progress on the Seismo-acoustic Characterization of Sea Floor Properties and Processes at the Hydrate Monitoring Station:
  - work has concentrated on the design and building of the hardware, bench testing and preliminary field trials,
  - development work to extend the capability of the electronics to allow remote operation on the seabed for up to 3 months at a time done.

As referenced in some of the subcontractors' reports, efforts of the Consortium to cooperate with and leverage off the activities of the Joint Industries Project have necessitated some changes in the monitoring station design and schedule. These changes are more fully described in the Appendix.

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

## **INTRODUCTION/PROJECT SUMMARY**

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

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

## **EXECUTIVE SUMMARY**

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

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

The centerpiece of the monitoring station, 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 will be comprised of hydrophones to record water-borne acoustic energy (and measure sound speed in the lower water column), thermistors to measure water temperature, tilt meters to sense deviations from the vertical induced by water currents, and compasses to indicate the directions in which the deviations occur. Although still being discussed, it now appears that the project may be better served if some vertical arrays are converted to horizontal line arrays (HLAs). The prospective horizontal water-bottom arrays, will consist of hydrophones and 3-component accelerometers and will be laid upon, and pressed into, the soft sediment of the sea floor. They will be arranged into a cross so that they simulate two perpendicular arrays. Their deployment will be accomplished by means of a sea-floor sled (see the section, this document, on the Sea Floor Probe) designed to lay cable and deploy probes into shallow, unconsolidated sediments. This sled will also be used as a seismic source of compressional and shear waves for calibrating the subsurface seismo-acoustic array commissioned by the Joint Industries Project (JIP).

The prototype VLA has been completed together with the associated data logging and processing systems. The system consists of 16 hydrophones spaced at 12.5 meter intervals with an overall length of 200 meters. The sensitivity and spacing of the hydrophones is critical to the data acquisition process with regard to the objective focus on near sea floor features such as hydrate bodies. This system was tested in Atwater 14 and Mississippi Canyon 798 in October, 2003. Vertical Array data were retrieved successfully from both sites. Novel processing techniques are being developed for these data by consortium participants who are currently funded by the Minerals Management Service.

The Sea Floor Probe (SFP) and its delivery system, the Multipurpose sled (MPS) have been completed. The probe has been modified to penetrate the <1m blanket of hemipelagic ooze at the water/sea floor interface to provide the necessary coupling of the accelerometer with the denser underlying sediments. This system has now been modified to include the capability of the MPS of laying the HLA cable and of serving as both the energy source and recording vehicle for p- and s-wave data collection.

Video recordings of bubbles emitted from a seep in Mississippi Canyon have been made from a submersible dive and the bubbles analyzed with respect to their size, number, and rise rate. These measurements have been used to determine the appropriate parameters and configuration for the acoustic system to monitor bubble activity of escaping gas at the site of the monitoring station.

Initial tests of the electromagnetic bubble detector and counter have been performed with standard conductivity sensors. The device detected nonconductive objects as small as .6mm, a very encouraging result. Components for the prototype have been assembled, including a dedicated microcomputer to control power, readout and logging of the data. Laboratory tests of the prototype have produced a data set that is being used to modify the design prior to construction of the field unit. The system will be tested on a submersible and deployed at a gas vent.



Progress has been made toward minimizing system maintenance for the Mid-Infrared Sensor for Continuous Methane Monitoring through increased capacity and operational longevity. Modeling of sensor components using AutoCAD software has been done in an effort to improve the design and development process of the "sphereIR". Trials of the system have been made with the highly permeable polymer, poly(trimethylsilyl)propyne (PTMSP). Studies of the possible effects of hydrostatic pressure on the system have been done. Deep sea tests are planned for the near future

Seismo-acoustic characterization of sea floor properties and processes is a priority for the hydrate monitoring station research effort. Adaptation of the MPS to coordinate with the development of this acoustic-logging device, aimed at monitoring temporal variations in seabed acoustic responses has commenced. Field trials have not produced significant data. Adjustments specific to the impediments are being made. Further field tests are scheduled to test the performance of the device throughout its period of development.

## **EXPERIMENTAL**

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

## **RESULTS AND DISCUSSION**

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

**CONTINUATION OF WORK ON THE VERTICAL LINE ARRAY**

**ANNUAL TECHNICAL REPORT**

**June 1, 2003 through November 30, 2003**

**Paul Higley, Specialty Devices, Inc.,**

**JUNE 25, 2004**

**AWARDED UNDER DOE COOPERATIVE AGREEMENT #DE-FC26-02NT41628**

# Gas Hydrate *In situ* Monitoring Station Vertical Array

## Abstract

A near sea floor, 200 meter vertical acoustic array is being developed as part of a long term sea floor monitoring station to study gas hydrate deposits. This report addresses progress in the development of a vertical seismic array system specifically designed for 3 dimensional mapping of shallow gas hydrate deposits. The time frame covered in this report includes the second year of development of this vertical array. The report discusses progress in the data logger, vertical array, sensors elements, deployment tests, software and plans for future efforts. The program included production of 2 additional arrays and refurbishment of the year one array. Progress in the development of and Seafloor Observatory (SFO) and incorporation of these vertical arrays in the plans for the SFO have modified the design goals of the Vertical Arrays. The modifications are discussed in this report.

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## 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 the sea floor. A data logger and a pressure compensated battery pack were mounted at the bottom of the hydrophone array. The array was suspended via glass flotation and anchored with an expendable concrete weight. 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, with shots fired and timed in sequence with

the data collection regime programmed into the near bottom mounted data logger. An acoustic modem based communication system allowed the surface ship computer to reprogram and direct this data collection regime. This communications link to the sea floor equipment also provided an ability to recover sample data sets to assess and alter the data collection parameters.

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

During October, 2003, additional deployments of Vertical Array #1 were performed. Deployment sites included an 830 meter water depth site and a 1,305 meter water depth site. This last site was 300+ meters beyond the design depth for the Vertical Array #1. These deployments served to test improvements to hardware and software and to identify design items that should be addressed in the deeper design depth Vertical Arrays #2 and #3.

### **Executive Summary**

Progress during FY 2003 included further development of the data logger, the vertical array sensors and systems software. A Vertical Array was deployed during October, 2003 to test these improvements. These deployments included a deployment in 1,305 meter water depth which is 305 meters deeper than the design depth of the array. Valuable information was gained for the design of deeper deployment capable vertical arrays.

Software and hardware upgrades to data logger for the prototype vertical array included enhanced programmable gains, faster sampling rates, and improved surface communications.

The vertical array cabling was also upgraded to allow installation of positioning sensors.

SDI's Angulate program was adapted to use acoustic slant ranges and DGPS data to compute and map the bottom location of the vertical array. Progress was also achieved in T<sup>0</sup> delay and timing issues for improved control of data recording.

### **Experimental**

#### *Positioning sensors*

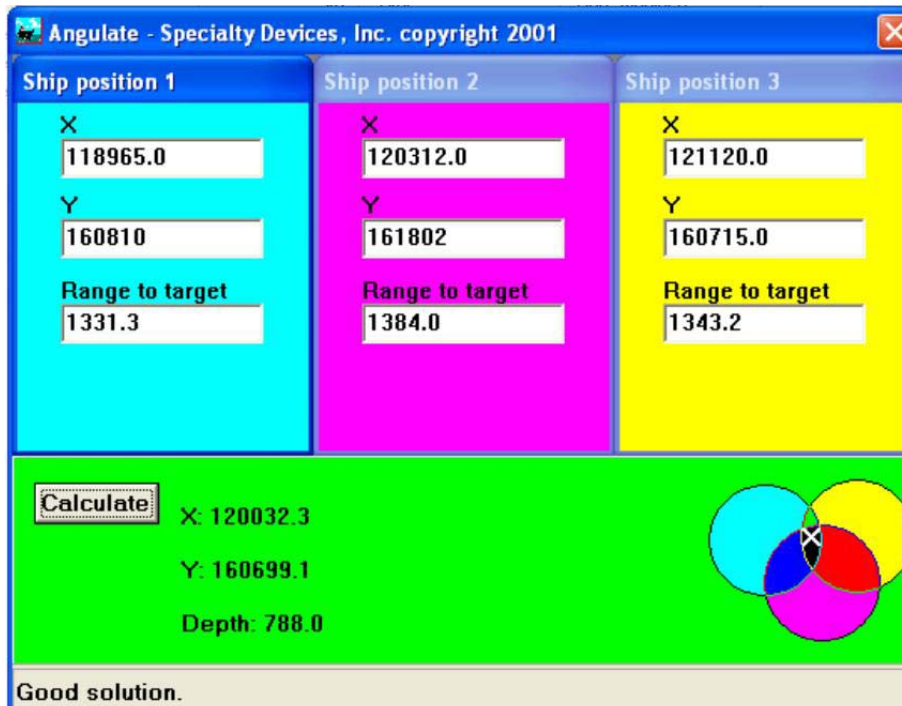
The positioning sensors include 2 axis inclinometers and a compass. The inclinometers and compass report using RS-485 protocol to a serial port on the data

logger computer. This protocol allows long distance serial communications and individually addressable serial devices on a single pair of data lines. The microprocessor in the DATS unit separately powers up one of the compass/tilt sensor packages and then addresses the package to retrieve and store the data. The inclinometers and compass are to be included in a single housing with two such systems mounted to the vertical array. The first year vertical array cable was equipped with connectors and wiring for these sensors. The sensors have been acquired and tested. The housings have been designed and the data logger software is being modified. The housings should be built and pressure tested and the software completed and tested during the spring of 2004.

### *Bottom Location Software*

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

Figure 1. An example of the Angulate program results



This software was tested and performed well during the October, 2003 deployment cruise.

### *Data Logger Software*

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

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

During the second half of 2003, this software was upgraded to include the ability to measure propagation delays for timing pulses and correct the surface and sub-surface clock synchronization utilizing the smart modem range finding function. This effort is limited in its ability to accurately coordinate times between the surface ship firing control clock and the sea floor mounted DATS data acquisition computer. This is a problem as clock drift accumulates over longer deployment times. The anticipated cure for this problem was to be provided by the availability of a real time high speed telemetry between the seafloor mounted data loggers and the surface firing computers.

The high speed telemetry was to be provided via a fiber optic cable connection from the seafloor mounted DATS to the shore and a radio telemetry capability from the shore to the surface ship. The fiber optic communications link is not to be available until well after the SFO is to be deployed and an alternative plan is being developed. The alternative plan includes the use of a pop-up buoy carrying a fiber optic communications link to the sea floor. The pop-up buoy will be brought up when a sound source is to be used and returned to the sleep mode at all other times. This plan will be developed and a funding source sought as a replacement for the fiber to shore system no longer available.

### **Results and Discussion**

A deployment cruise was performed during October 7<sup>th</sup> through the 14<sup>th</sup>, 2003. The cruise included a deployment in an 830 meter water depth site. During this deployment the Vertical Array was successfully deployed and recovered. Data were retrieved from the DATS data logger and the pressure compensated battery was recharged. A second deployment was then made in Atwater Valley at a 1,305 meter water depth. This deployment site is 305 meters deeper than the design operating depth for Vertical Array #1. The deployment was made in an attempt to both acquire much needed data from this site and to evaluate the performance of the Vertical Array design prior to building additional Vertical Arrays. The array was successfully deployed and communications were established. A series of lines were shot with an acoustic source. The communications with the array indicated the system was functioning well.



Figure 2. Vertical Array Prepared for Deployment

At the end of the planned data collection the array communications ceased. We also encountered difficulty with communications to the Benthos acoustic release. However, the release function was successful and the Vertical Array was recovered.

There were several developments of note resulting from this deeper deployment.

1. The DATS unit maintained normal function throughout the deployment and recovery and a full data set was retrieved from it's hard drives.
2. The Acoustic modem used to communicate with the DATS unit appeared to no longer function. The modem was found to have developed a slow leak through the transducer. This is a direct result of deployment well beyond the design depth. The modem appears to be repairable. The manufacturer has models of this modem that are rated for greater depths.
3. The problem with the communications to the acoustic release was later traced to a setting on the deck console that did not match with the releases.
4. The cable was initially tested and appeared to have survived.
5. The pressure compensated battery functioned normally and survived without detriment a temporary inversion during a deployment event. During both deployments the battery energy supply was more than sufficient.

## **Conclusions**

Although the second year effort was begun later than planned, progress has been significant. The majority of the planned changes to the data logger and surface system software were completed and tested during the fall 2003 deployment cruise. This cruise served to test and refine the vertical array hardware and software. The completion of the hardware and software design for the two additional deeper water capable vertical arrays has been extended due to the additional capability needed to fully integrate these arrays with the latest version of the SFO design. Refinements are progressing in parallel with the hardware construction.

## **Acronyms**

DGPS – Differential Global Positioning System

SDI – Specialty Devices, Incorporated

SFO – Sea Floor Observatory



CONSTRUCTION OF THE PROTOTYPE SEA FLOOR PROBE

ANNUAL TECHNICAL REPORT

June 1, 2003 through November 30, 2003

J. Robert Woolsey, University of Mississippi

JULY 9, 2004

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## ABSTRACT

The multi-sensor monitoring station will, in its final configuration, include a variety of sensors. These sensors will occupy locations on the sea floor, in the water column, and in the shallow subsurface of the sea floor. The purpose of the Sea Floor Probe (SFP) is to install sensors that will be located in the shallow subsurface and to test the SFP concept. As the concept of the monitoring station has evolved, the development of the seafloor probe has been expanded to include a multipurpose towed sled (MPS), the construction of which has been funded by Minerals Management Services (MMS), for deployment of the probes; the focus of the probe's utility has shifted toward the s- and p-wave sound generation, for use as an energy source for the Borehole Vertical Line Array (BVLA), commissioned by the JIP to be included as part of the Station. The SFP has been modified to penetrate the less-than-one meter blanket of aqueous, hemipelagic ooze, so as to provide the necessary coupling of accelerometers with the denser underlying sediments.

Recent modifications to the Monitoring Station design include the deployment of Horizontal Line Arrays (HLAs) on the sea-floor. As in the case of the BVLA, the HLA system will require the services of the SFP/MPS. The SFP/MPS has been modified to enable both the laying of the HLA cable, fitted with both hydrophones and accelerometers, for p- and s-wave recording, and the generation of a suitable, p- and s- wave synchronous, p- and s- wave energy signal.

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## INTRODUCTION

Early in the life of the Gulf of Mexico, Hydrates Research Consortium, the group addressed the critical need to understand the structural frame work of the hydrate stability zone (HSZ). In order to understand gas hydrates, - their characteristics and related phenomena, including physical, chemical and bio-chemical interactions - it is vital to develop an understanding of their habitat. In order to undertake an investigation of such complexity, better tools would have to be devised to enable the acquisition of seismic data

with the highest possible resolution, at affordable cost. Commercial, 4-Component Array (4-C), surveys could provide the quality data required, but at a cost beyond project means. In collaboration with Dr. Angela Davis, Bangor, Wales, (renowned for her expertise in shear wave seismic technology) a plan was devised to provide a viable, cost-effective solution.

To accomplish the stated goals, it appeared necessary to develop remotely operated systems for working on the seafloor. Two systems have been designed and constructed for this multipurpose task. The Sea Floor Probe (SFP) is designed to push a 3-C accelerometer into the sea floor. The design incorporates experience with an earlier, failed attempt, at using conventional, ocean bottom seismometers (OBS). The problem was, and remains, the seabed; in the area of interest, the sea floor is blanketed by aqueous hemipelagic ooze, 0.5 to 1.5m thick. In the conventional deployment, the OBS's tended to float on the ooze, presenting an obstacle to the necessary coupling with the more dense seabed substrate, and resulting in a degraded recording of the s-wave signal.

## EXPERIMENTAL

The SFP has been designed to rectify the problem of coupling of accelerometers with the sea floor. The new design (DOE/NETL funded), provides a means of implanting a 3-C (component) accelerometer into the dense substrate, enabling a satisfactory coupling for s-wave conveyance. Also, a hydrophone is attached for simultaneous p-wave recording, in effect, providing a 4-C system. The SFP utilizes high pressure air to actuate a remotely controlled pneumatic piston, on which the 3-C accelerometer, embedded in a disposable point, is loosely attached. The latter is designed to provide satisfactory coupling, but also, to enable retrieval of the SFP on command.

The second system, the Multipurpose Sled (MMS funded), portrayed in Figure 1, is designed for tow along a predetermined tract via a mechanical/communication conductor cable, by the support vessel. The sled performs several functions, one of which is to serve as a platform for mounting/deploying the SFP and its support components. The SFP pneumatic cylinder/drive piston is mounted at the rear of the sled, and is connected to the high pressure air supply tanks (stowed forward) via appropriate tubing, valves and electronics for actuation and control. At the rear of the sled, aft of the SFP drive apparatus, is mounted a detachable/recoverable, integrated data/power (IDP) unit. The IDP supplies power, provides data-logging of the p- and s-wave seismic data via the SFP, and a modem for communication (through the water column).

The SFP emplacement operation involves lowering of the sled to the seabed, sending the command signal via the tow/communication cable to push the SFP into the sea floor, retract the push rod, leaving the accelerometer embedded in the substrate (along with the hydrophone), both connected to the IDP via a short cable. The command to detach the IDP, (connected to the SFP) is sent via the cable. The IDP is activated and separated from the sled.

The sled is now free to transform into its function as a towed platform for conveyance of the seismic energy source, designed to provide both p- and s- wave energy. The latter system consists of a pair of 15 cubic inch, water guns, mounted in tubes, ported through the bottom of the sled, with center lines oriented at an angle of 90° to each other.

The guns are fired directly into the bottom, alternately, and in sync with the receiver on the IDP.

Expansion of the Monitoring Station/Sea Floor Observatory program to include the Bore Hole Vertical Line Array (BVLA), (the principal 4-C system for p- and s- wave recording), the SFP role is now viewed as less a monitoring station primary mode of operation and more an exploratory system and mission. The "gun platform" roll for the sled is now, however, expanded as the sole active means of energizing the BVLA.

More recent modifications to the Monitoring Station design include the deployment of Horizontal Line Arrays (HLAs) on the sea-floor in the form of a cross, the diameter of which is designed to approximate the water depth (or about 800m for the proposed MC 798 site). As in the case of the BVLA, the HLA system will require the services of the SFP/MPS. As in the case of the BVLA, the HLA system will require the services of the SFP/MPS. During this reporting period the SFP/MPS has been modified in its design to include the capability of

- a. laying of the HLA cable, fitted with both hydrophones and accelerometers, for p- and s-wave recording, and
- b. the generation of a suitable, p- and s- wave synchronous, p- and s- wave energy signal.

It is expected that the SFP/MPS system will perform these multiple functions thus serving in both deployment and data-collecting capacities.

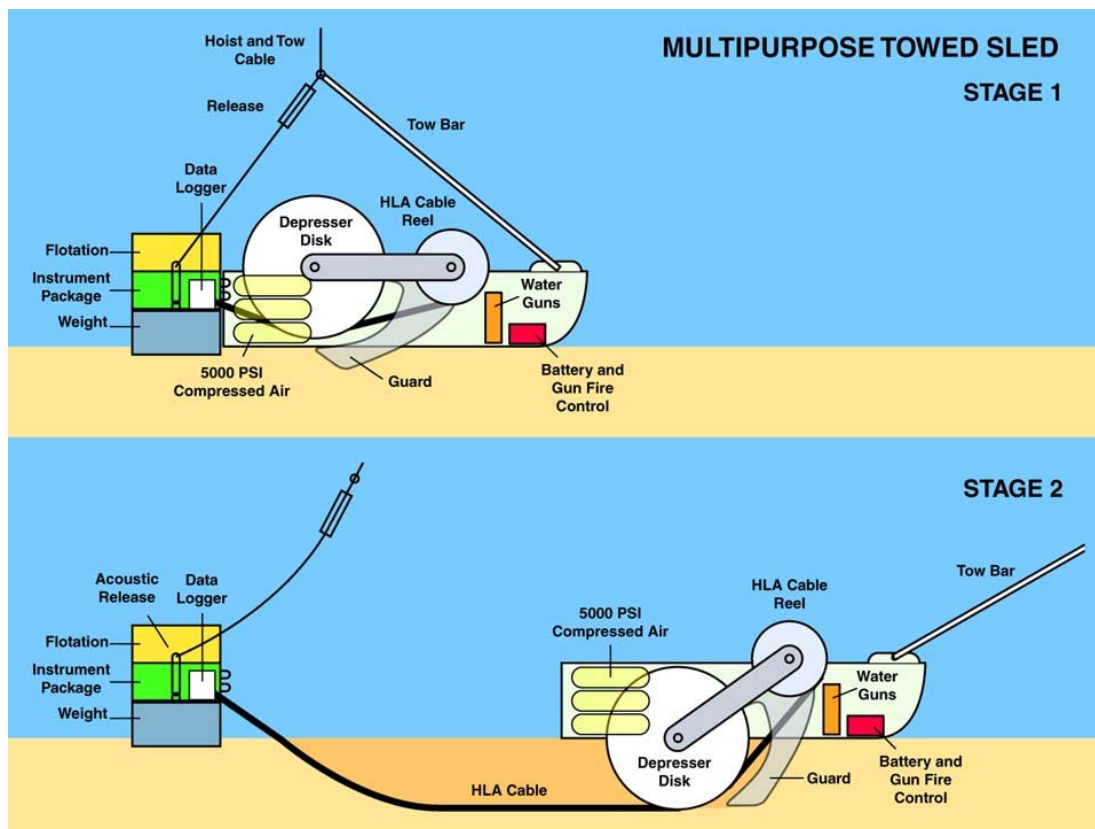


Figure 1. Multipurpose Towed Sled

## RESULTS AND DISCUSSION

Work completed to date includes successful designs for the basic SFP and MPS systems. Both systems have been tested, successfully, in shallow water, near shore. As the mission of the sea floor observatory has evolved to include design modifications in complementary systems, so too, these systems' designs have been improved. For example, in the case of the added BVLA application, it was necessary to modify the system to include a surface deployed telemetry buoy, for synchronization with the BHA, main station IDP via a surface connection with the Data Recovery System, during gun sled, shooting operations. These modifications have been funded recently, and the relevant work is scheduled for the near future. On completion of these new tasks, the systems will be tested, again, in shallow water and then in the deep.

During an early test of the SFP concept, it was discovered that a system would be required whereby the firing and receiving of the signals would be synchronized. To effect the needed communication between the ship and the signal being fired from the fore region of the MPS, a data modem and fire-control data logger have been added to the sled which will be towed on a "live" multipurpose cable capable of both towing the sled and of transmitting signals to and from the support vessel. Synchronization of the system will be accomplished by means of a telemetry buoy which will serve as a major component of the Data Retrieval System (DRS) for the monitoring station (see Figure 2). Prior to the deployment of the monitoring station, anticipated in the spring of 2005, there will be a shallow water test of the telemetry buoy and the firing sequence of the MPS.

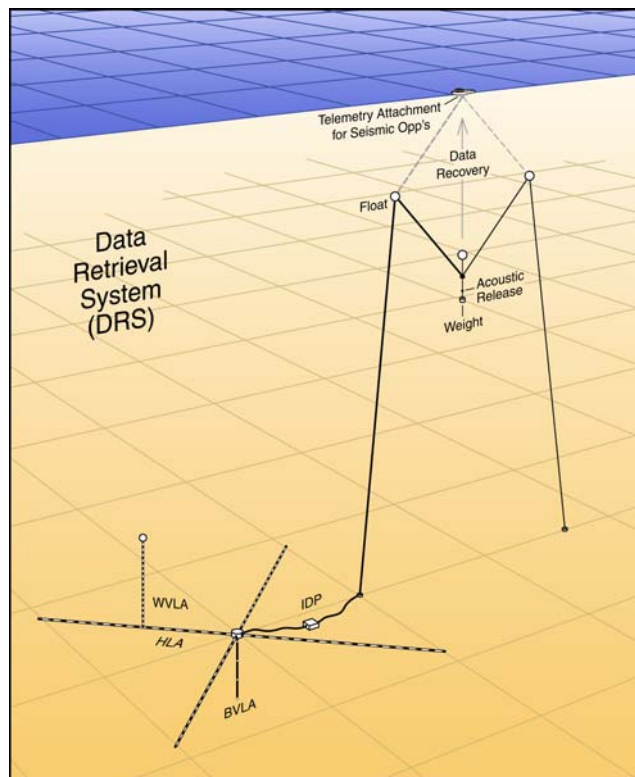


Figure 2. Monitoring Station Design

## CONCLUSIONS

Both the sea floor probe and the multipurpose sled have been modified to accommodate the HRC's desire to cooperate with the JIP's efforts to emplace a borehole array at the site they will drill in the initial drilling phase of their hydrates research cruise in the fall of 2004. The design modifications will be tested prior to deployments to test the borehole vertical line array and to lay the Horizontal Line Array cable.

## ACRONYMS

BVLA – Borehole Vertical Line Array  
DOE – Department of Energy  
DRS – Data Retrieval System  
GOM – Gulf of Mexico  
HLA – Horizontal Line Array  
HRC – Hydrates Research Consortium  
HSZ – Hydrate Stability Zone  
IDP – Integrated Data Power unit  
JIP – Joint Industries Project  
MC – Mississippi Canyon  
MMS – Mississippi Minerals Management Service  
MPS – MultiPurpose Sled  
NETL – National Energy Technology Laboratory  
OBS – Ocean Bottom Seismometers  
SFP – Sea Floor Probe

**ACOUSTIC SYSTEMS FOR MONITORING GAS HYDRATES**

**ANNUAL TECHNICAL REPORT**

**JUNE 1, 2003 THROUGH NOVEMBER 30, 2003**

**JERALD W. CARUTHERS AND RALPH R. GOODMAN**

**UNIVERSITY OF SOUTHERN MISSISSIPPI, DEPARTMENT OF MARINE SCIENCE**

**JULY 1, 2004**

**AWARDED UNDER DOE COOPERATIVE AGREEMENT #DE-FC26-02NT41628**

# ACOUSTIC SYSTEMS FOR MONITORING GAS HYDRATES

## ABSTRACT

Bubble clouds formed by the emission of gas hydrates into the sea can be directly observed by either optical or acoustical methods. The effects that bubble clouds have on the acoustic properties in seawater are well known [1] and depend on the nature of the bubble clouds (i.e., the size of the individual bubbles, their density, and the dimension of the cloud). The long-term objectives of this project are to: (1) examine acoustic concepts for the detection and monitoring bubble emission, (2) select the most promising method, (3) develop and test a measuring system, (4) deploy and retrieve the system, and (5) analyze the data and evaluate the results. The end product of this work is to provide a measure of the volume of gas that is produced at a selected site and selected characteristics of the plume. The result of this year's effort is the specification of an acoustic system that might best achieve this goal.

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Figure 2: A 30-element, 12-kHz planar array is planned based on three transducer modules, one of which is shown here. The array can be stacked vertically on their long sides to form a nearly box rectangular array 0.46 by 0.72 m or on their short sides to form a long array 0.24 by 1.4 m. The actual system will also have 150- and 300-kHz transducers mounted on it.....p.22

## INTRODUCTION

Bubbles, because of their drastic differences in mechanical properties from those of seawater, cause significant effects on acoustic signals passing through or scattering from



bubble clouds. These effects are dependent on the acoustic frequency, the sizes and number of bubbles, the geometry of the cloud, and the depth. The basic approaches for a monitoring system could be: (1) the measurement of a signal scattered from a collection of individual bubbles, (2) the measurement of the scattering caused by the bubble cloud itself, and (3) the measurements of attenuation or change in sound speed within the cloud. The physics of each of these concepts is well known, but their application to the study of the emission of gas hydrates has not been developed.

The first phase of this study was to examine the physical requirements of each of these concepts and to determine as best we could the practical requirements of the deployment for a gas hydrate scenario. A fundamental question is: What can be learned about the volume rate of emission of the gases? Each of these concepts was examined.

When a signal passes through a bubble cloud its speed is determined by the density of bubbles (commonly called the void fraction), the size distribution, and the frequency of the signal. The physical theory for this effect is well known. The sound speed ( $c$ ) in a cloud is given by

$$c = c_0 \left\{ 1 + 4\pi c_0^2 / \omega^2 \sum a_i D / D^2 + \delta^2 \right\}^{-1/2}$$

where the sum is over all the bubbles in the cloud,  $c_0$  is the sound speed without the presence of bubbles,  $a_i$  is the radius of a bubble and

$$D = (a_r/a_i)^2 - 1$$

$a_r$  being the radius for a bubble that resonates at the frequency  $\omega$  (radians per second) and  $\delta$  is a constant related to the losses due to resonance damping processes, usually on the order of 0.1. Note that if there is a large number of bubbles, the sum can be replaced by an integral with the number density  $n(a)da$ . This seemed to have some attractiveness, since a change in sound speed is measured in time and time can be accurately measured. For most frequencies the sound speed could not give any indication of the individual bubble radii and therefore isn't usually useful. However, an examination of the equation at low frequencies, removed from the resonances of the bubbles, shows that the sound speed is related to the total void fraction ( $\Phi$ ) by approximately

$$c = c_0 \left\{ 1 + (K_a/K_w) \Phi \right\}^{-1/2}$$

To measure this change would require the accurate placement of a source and a receiver on opposite sides of a bubble cloud. It also would require a low-frequency source that would have the inherent problem of a wide beam width. (For the bubble sizes we anticipate to be present, the frequency would have to be somewhere in the low kilohertz range.) Although it would give a direct measurement of the void fraction it was dismissed as being impractical because of the large size of acoustic arrays required to accommodate this technique.

The scattering caused by the bubble cloud itself is highly dependent on the size distribution, total bubble density, and acoustic frequency. A measurement of the acoustic scattering strength can be used to determine the average sound speed in the bubble column. Although, in principle, a system could be devised for this method of measurement,

it would be more complex than envisioned to be practical for deployment in deep water. The source and receiver would have to be placed a considerable distance from the cloud field in order for the measurement to have a tractable result. It could be worthy of further study in the longer term of research, but will not be considered further as part of this project.

## EXPERIMENTAL

Devising a system that uses the scattering from individual bubbles requires some knowledge of the cloud size, bubble sizes and number. This information was not available until last summer when a video was made from a submersible at what is known in the project as the shallow water site. Against a backdrop of a white board (marked in inches) it was possible to estimate the bubble sizes and number, and estimate their rise rate. Measurements of bubble sizes and rise rates were made from digital images taken from a short segment of the video (cf. Fig. 1). The bubbles in the field had an average apparent separation of about 2 cm (although this was difficult to estimate from a two dimensional perspective). Bubble radii ranged between 1 and 5 mm, although our confidence in the lower limit is tentative since it was difficult to resolve anything smaller than 1 mm. Estimates of the rise rates of the bubbles were determined to be about 25 centimeters per second, which agrees favorably with other observations for bubble with radii above about 0.3 mm.

For the approximately 500 m depth at a planned gas-hydrate site and the distribution of bubble sizes, the resonant frequencies (f) can be determined from the well known equation relating frequency to the radius (a) of a bubble

$$\omega = 2\pi f = \{3\gamma P/\rho a^2\}^{1/2}$$

The bubbles observed in the video images would have resonances from about 4.5 to 23 kHz. A difficulty will arise if there are smaller than our estimated 1 mm. The video images are not of sufficient resolution to determine if there are, in fact, smaller bubbles. The measurements seem to show a dominance of the larger bubbles with radii on the order of 5 mm. This problem is partially mitigated by the fact that the smaller bubbles will not contribute significantly to the total volume of gas emission from a site.

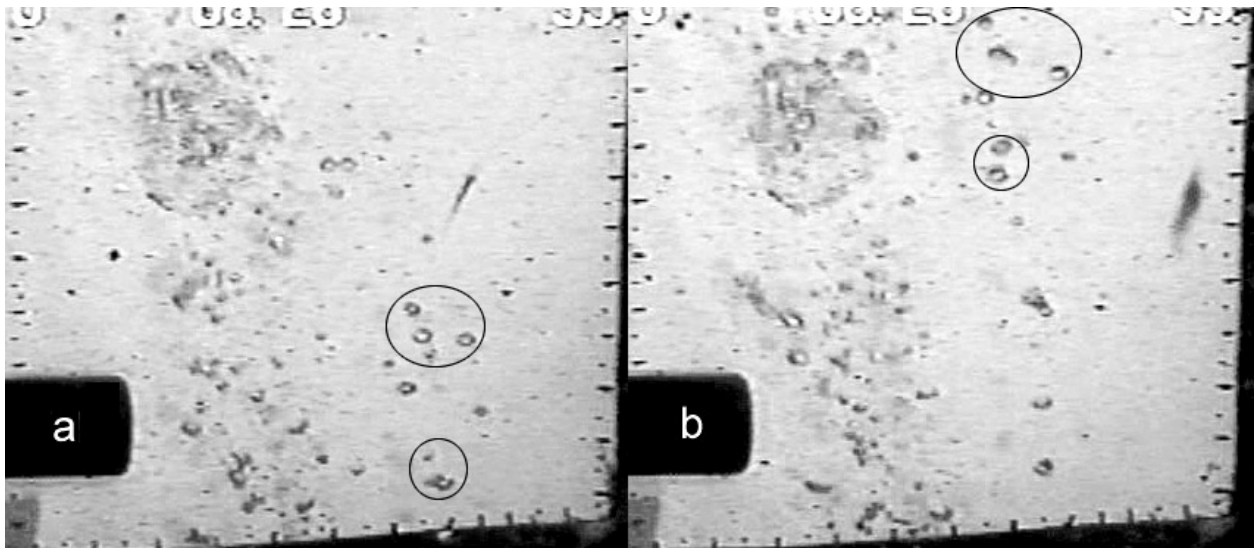


Figure 1: Two images of the bubble field taken 0.5 sec apart. Two groups of bubbles were followed during this interval (shown in circles). Both groups rose at about 25 cm/s.

## RESULTS AND DISCUSSION

From these measurements we were able to develop a concept for prospective design parameters for a measurement system. Our plan would be to develop a system that would produce a directional beam and sweep across the low-frequency range of bubble resonances. Additionally, it would have the capability to spatially resolve smaller regions with frequencies well above bubble resonance. (This high-frequency component of the system will also address some of the uncertainty concerning the smaller bubble sizes.) The first capability requires a large low-frequency source that covers a broad spectrum with relatively long CW pulses. This will necessarily have a low spatial resolution. We would envision a 12-kHz system that could be driven above and below transducer resonance to cover the frequency range of interest (Fig. 2). It would not need a great deal of acoustic power, allowing us to operate further off transducer resonance. We possess three transducer modules consisting of two rows of five elements each to make a planar array approximately 0.46 by 0.72 m (giving an approximately 13-deg. conical beampattern). It is planned, however, to retain configuration flexibility of the three modules. For example, they may be placed in line that is 0.24 by 1.38 m (giving an approximately 60- by 6-deg pattern). The thirty transducers will be individually phased to allow steering of the beam. The high-frequency capability will be based on two transducers operating at 150 and 300 kHz. The plan would call for construction of this system and testing it in shallow water before the deep-submergence components are constructed. Consideration for battery life and depth capability will be a major concern also. The plan would be to limit transmission to some reasonable schedule or to have a triggering mechanism based on bubble emission volume. The physical concept is that the high-frequency component will define the geometry of the bubble field by measuring the arrival times of the first and last back scattered signal. The low-frequency system will transmit a set of signals over a range of frequencies. The scattering will be from resonant bubbles at each frequency. Since the resonant frequency is associated with bubbles of fixed radii, the scattering strength of each bubble is known, so the total measured scattering strength for each frequency will give an estimate of the

number of resonant bubbles with the appropriate size. With the reasonable assumption that the distribution is continuous between samples, estimates can be obtained for the total volume that was ensonified.

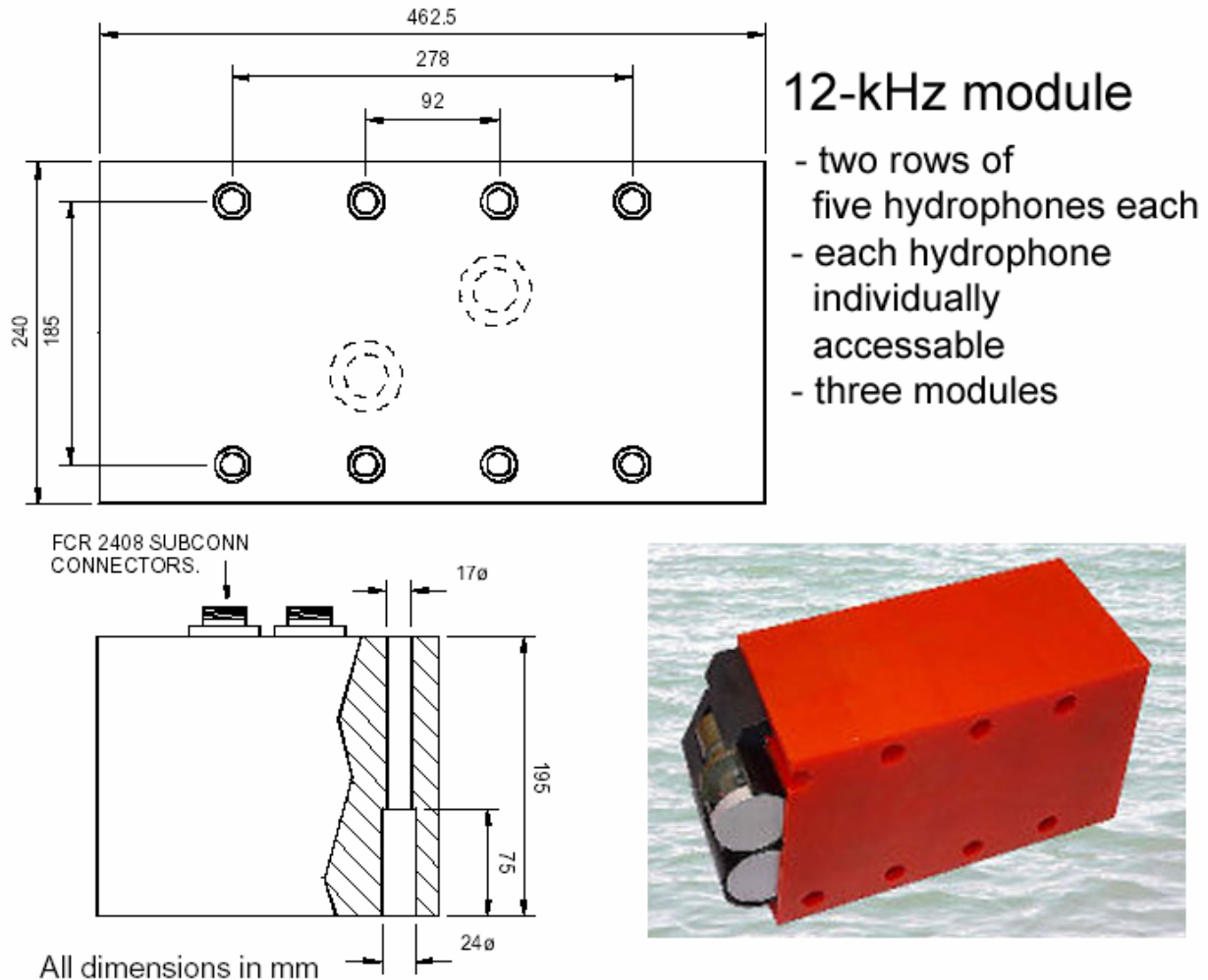


Figure 2: A 30-element, 12-kHz planar array is planned based on three transducer modules, one of which is shown here. The array can be stacked vertically on their long sides to form a nearly box rectangular array 0.46 by 0.72 m or on their short sides to form a long array 0.24 by 1.4 m. The actual system will also have 150- and 300-kHz transducers mounted on it.

## CONCLUSIONS

The flow procedure, as currently envisioned, is given below:

1. The high-frequency system transmits a short signal at each of 150 and 300 kHz. The time is measured between the onset of reverberation and its termination. From the time difference,  $\Delta T$ , the width of the bubble column is determined by

$$W = c/(\Delta T - \tau)$$

where  $c$  is the speed of sound and  $\tau$  is the signal pulse length. The area of the cross section of the cloud then can be approximated to be  $A = \pi W^2/4$ .

2. A set of low frequencies will be transmitted and the total backscattering strength for each will be determined from the reverberation level. This may require some modification if the loss of transmitted signal as it passes through the cloud. (Methods for doing this are already well known.)
3. The resonant scattering strength of a single bubble will be used to determine the number of bubbles of that radius needed to match the reverberation level.
4. Knowing the vertical beam width and  $A$ , the density of bubbles can be determined for each frequency.
5. By assuming a continuous distribution, the number density and total volume of bubbles can be determined.

## REFERENCES

- L. M. Brekhovskikh and Yu. P. Lysanov, 2002, "Fundamentals of Ocean Acoustics" Springer-Verlag, New York.

## ACRONYMS

CW	continuous wave
USM	University of Southern Mississippi

**CONSTRUCTION AND TESTING OF AN ELECTROMAGNETIC BUBBLE  
DETECTOR AND COUNTER**

**ANNUAL TECHNICAL REPORT**

**June 1, 2003 through November 30, 2003**

**Vernon Asper, University of Southern Mississippi**

**JUNE 16, 2004**

**AWARDED UNDER DOE COOPERATIVE AGREEMENT #DE-FC26-02NT41628**

# Construction and Testing of an Electromagnetic Bubble Detector and Counter

## ABSTRACT

A bubble detector has been built based on a technique used to measure the conductivity of water. The technique has been adapted to measure bubbles utilizing the fact that bubbles lower the conductivity of the water in which they are entrained. A current is induced in a pair of coiled wires, the magnitude of the induced current being dependent on the electrical conductivity of the water which the coil pair surrounds to measure the salinity and, therefore, the conductivity of the surrounded water column. Employment of the system enables researchers to determine the existence of, as well as the volume of, bubbles in the water column.

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## INTRODUCTION

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. The objective of this research is to build a bubble detector based on a technique which is used widely in the ocean to measure the conductivity of the water, but which can be adapted to measure bubbles as well because they lower the conductivity of the water in which they are entrained. This technique uses paired coils of wire, the dimensions of which can be tuned to suit the particular application. A current is induced in one coil of wire and a current is induced in the adjacent coil of wire, the magnitude of the induced current being dependent on the electrical conductivity of the water which the coil pair surrounds. This technique is used by many manufacturers of *in situ* sensors to measure water conductivity because conductivity is directly proportional to the salinity of the water due to what is known as the “law of constant proportions.” The widespread use of this technique indicates that it is well accepted and that its inherent sensitivity is appropriate for our application.

## EXPERIMENTAL

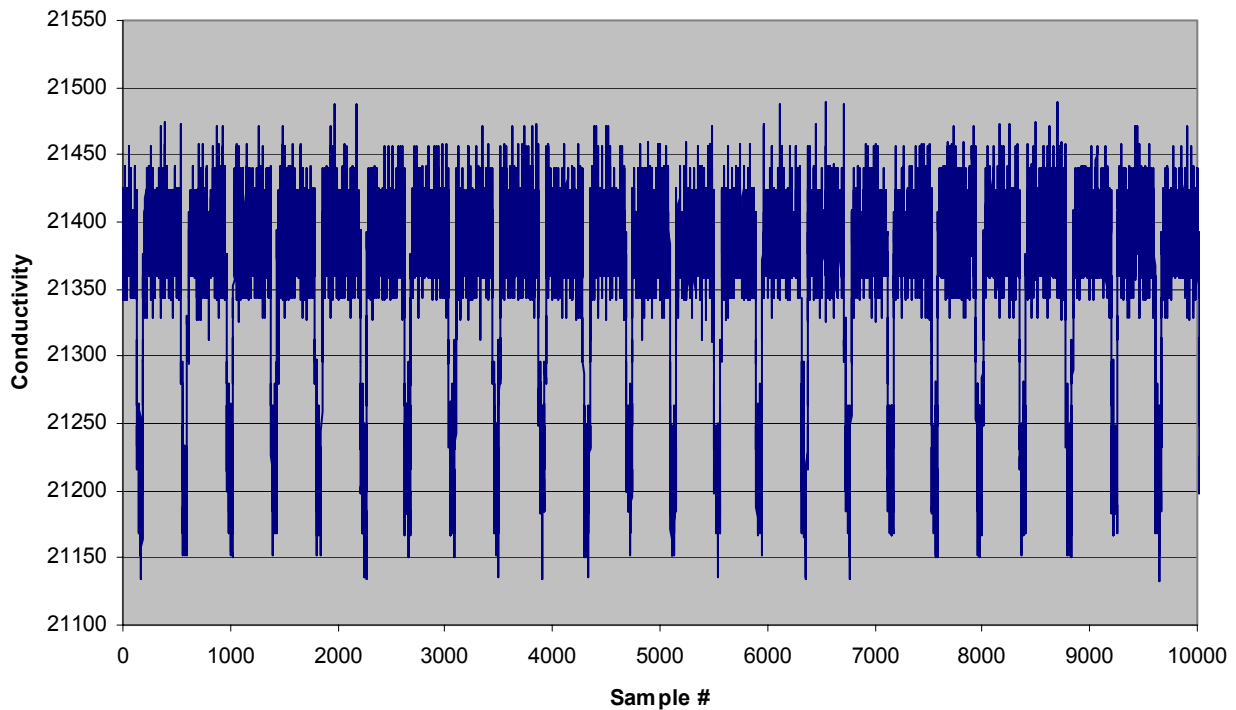
1. Design system: Before specifics of the design could be finalized, it was necessary to prove the concept. We acquired several standard conductivity sensors and performed initial tests and the results were quite promising. Using an Aanderaa conductivity sensor and water of salinity  $\sim 35$ , we were able to detect a non-conductive object as small as  $0.12 \text{ mm}^3$ . This equates to a bubble of 0.6mm diameter so it should be possible to detect, reliably, bubbles in the 1mm diameter target size range (volume of  $0.52 \text{ mm}^3$ ). Based on these results, we conducted an extensive survey of available sensors to select one that is sufficiently sensitive and that will provide a direct, analogue output for our data loggers.
2. Construct system: The only sensor available that is rated to  $>1,500\text{m}$  and which gives a pure analogue (0-5VDC) output is made by Richard Brancker Research, and we ordered one of these in January. The cost was over \$4,000, but we feel that the reliability and unique nature of this application warrant this expense. We have also been evaluating Onset Tattletale model 8 microcomputers and working with preliminary code to drive the sensor. The Tattletale will be required to control power, select between temperature and conductivity readouts (temperature is required for calibration of the conductivity sensor) and logging the data. Based on our results from borrowed Tattletaes, we purchased a dedicated Tattletale for the project, along with a third party (Persistor) data storage module. We also acquired and modified a pressure housing rated for 5,000m as well as the necessary cables to connect the data logger to the conductivity sensor.
3. Laboratory tests of the system: As construction of the field system progresses, we continue to perform detailed laboratory tests of the prototype system. Kevin Martin, the Master's student funded under this award, is developing a sensitivity map of the volume of water within and surrounding the loop and is measuring the system response to bubbles of varying sizes. Preliminary tests have shown that objects outside of the sample volume do have an effect and it is important to evaluate the degree of sensitivity to these effects. Mr. Martin positioned a calibrated non-conductive sphere at various locations and azimuths from the sample volume and recorded their effect on the measured conductivity. These tests will also be performed on the final system once it is completed in order to verify its function.

## RESULTS AND CONCLUSIONS

Using the hardware that we assembled for the detector system, we were able to generate the following data



~ 50 bubble/min



Conductivity (in arbitrary units on the Y axis) decreases each time a bubble passes through the orifice and clearly samples are being acquired at a sufficiently rapid rate to allow for more than adequate characterization of each bubble. However, there is more noise in the baseline signal than we would like to see and we are in the process of designing an aliasing filter (simple R-C circuit) that will reduce the noise level without compromising sensitivity.

## CONCLUSIONS

Our accomplishments have demonstrated that this concept is appropriate for the detection and quantification of bubbles exiting from a natural vent. We will continue now to refine the hardware and software to produce the final system that will be deployed in the vent field. We will also finalize the structural elements that will hold the sensor in position, but this is a rather elementary task and will be postponed until we have a more detailed understanding of the submersible deployment system and its limitations.

In the coming years, we would like to expand the capability provided by this system by acquiring more supporting information. This system will be able to accurately monitor the evolution of gas at a single vent and correlate this activity with changes in temperature.

However, there is no guarantee that these results will be applicable to a wider range of vents and it is therefore imperative to develop hardware that is capable of surveying larger areas. To this end, we will be proposing to add a high frequency sector scanning sonar and a digital camera to this package to monitor the overall evolution of gas across the vent

field and to acquire images of specific bubbles for verification. These results will be coordinated with those of other researchers working in the area to provide the overall project with an overall monitoring capability.

## **ACRONYMS**

VDC – voltage, direct current

R-C – resistor-capacitor

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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 June 01, 2003 – November 30, 2003*

**Boris Mizaikoff (PI), Neil Pennington, Lubos Hvozدارa, Frank Vogt, Markus Janotta,  
Gary Dobbs**

*Prepared June 15, 2004*

Atlanta, May 14, 2004

## ABSTRACT/SUMMARY

The annual technical report summarizes the progress towards development of methane sensing systems based on mid-infrared (MIR) attenuated total reflection (ATR) spectroscopy for operation in deep sea environments during the periods from December 01, 2002 – November 31, 2004. Representative figures are given in the appendix; more details can be found in the body of the report.

- A brief summary of the significant works performed in the first project period, December 01, 2002 through May 31, 2003, is provided.
- Modeling of sensor components using AutoCAD software was conducted to aid design and development of 'sphereIR'.
  - Preliminary designs of mounting pieces for electrical components of 'sphereIR' were completed using AutoCAD software.
  - The preliminary design of an electronics baseplate was also completed and aided in the optimization of positioning electrical components inside the instrument housing.
- First spectroscopic investigations of the highly permeable polymer, poly(trimethylsilyl)propyne (PTMSP), as a potential sensing membrane for methane have commenced and will continue in the following project periods.
- High-pressure multireflection ATR measurements were continued during this project period. The purpose of these measurements is to investigate the potential influences of hydrostatic pressure on sensing principles and data evaluation strategies.

Based upon current results, we anticipate the construction and first field tests of a miniaturized, multicomponent IR sensor system designed for in-situ, deep-sea methane detection during continuation of this project in 2003/2004.

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## **EXPERIMENTAL**

### **Summary of works from December 01, 2002 through May 31, 2003**

A number of significant advances toward the development of 'sphereIR' were achieved during the first project period of this year. First, a miniaturized control system implementing a chemometric data evaluation package was developed. The control system incorporates spectrometer control, automated data evaluation, power saving features, and programmable sampling capabilities suited for deep sea deployment of an autonomous sensor. The miniaturized control system is also capable of being linked to an optical internet connection for land based operational control when field deployed in the deep sea. A Stirling-cooled MCT detector was also successfully integrated with the commercially available Bruker IRcube FT-IR spectrometer. This accomplishment provides long-term, maintenance free detector operation that is essential for any deep-sea, autonomous infrared monitoring. Finally, initial design concepts for incorporating the required sensor components into a spherical glass instrument housing were determined. A modular, two-platform system to be constructed of ½ inch aluminum alloy 6061 was chosen, facilitating sufficient mounting space for all components while providing simplified design for construction and maintenance procedures.

### **Modeling of spectrometer components in AutoCAD**

The first step toward the design and construction of 'sphereIR' begins with accurately modeling the spectrometer components required for sensor operation using AutoCAD software. The reason for modeling the spectrometer components was to aid the design, development, and construction processes of the internal sensor platform. Modeling helped to position components in order to optimize available space inside the instrument housing. The modeling will also aid the design of robust mounting pieces and choose appropriate fasteners. The primary electrical components for the spectrometer that were modeled include; power supply, auxiliary detector interface board, custom designed detector control and monitoring board, detector pre-amp, two spectrometer-computer interface boards, computer hard disk drive, and embedded PC. The primary optical components for the spectrometer that were modeled include; interferometer block, HeNe laser, Stirling-cooled MCT detector, light source, lenses, mirrors, and prisms.

### **Design of mounting pieces for electronic components of 'sphereIR'**

Once modeling of the electronic components for 'sphereIR' was completed, the next stage was to design robust mounting pieces while minimizing space consumption. In order to minimize space consumption, vertical mounts were chosen for mounting the electronic components. The spectrometer power supply did not require any additional mounting pieces; it was ready for direct mounting onto an electronics baseplate. Exemplary models of electronic components with complementary mounting pieces and fasteners are provided (Figure 1). During the next project period, finalized construction schematics will be made and fabrication will begin.

## **Design of electronics baseplate for 'sphereIR'**

Once modeling and design of the electronic mounting pieces were completed, the next step was to design an electronics baseplate. A 15.37" diameter, 1/2" thick aluminum baseplate was determined to be an appropriate mounting platform during the previous project period. Models of the electronic components and their mounts were positioned around the electronics baseplate to optimize space while providing clearance from the instrument housing. Fastening points for the electronic component mounts were determined and incorporated into the design as well as wiring slots and anchoring points for a complementary optics baseplate to be finalized in the upcoming project period (Figure 2). Finalized construction schematics will be made and fabrication of an electronics baseplate will be completed early in the next project period.

## **First investigations with poly(trimethylsilyl)propyne (PTMSP)**

Spectroscopic investigations of the highly permeable polymer, poly(trimethylsilyl)propyne (PTMSP), have commenced (Masuda et al., 1983). First, an appropriate ATR crystal coating strategy was developed using a 1% PTMSP in toluene solution. A 1% PTMSP solution was prepared by dissolving 0.100 g of PTMSP (Gelest, Inc., Tullytown, PA) in 10mL of toluene (Aldrich, 99.5%). The solution was enclosed in a vial and stirred overnight until all PTMSP was dissolved forming a viscous solution. Using a drip coating with solvent evaporation technique, a 3-7 $\mu$ m coating was produced using 700 $\mu$ L of solution on a 50x20x2mm germanium (Ge) crystal. An ATR-IR spectrum was recorded using a bare Ge crystal as reference in order to confirm that the coating expresses no major absorption features around 3020  $\text{cm}^{-1}$  and 1305  $\text{cm}^{-1}$  which would interfere with successful methane sensing (Figure 3). From the absorption spectrum of PTMSP, it can be deduced that the polymer absorption does not represent a significant interference in the spectral regions of interest.

In order to assess the enrichment properties of the PTMSP coating, ATR measurements utilizing analytes that have been widely investigated in previous works with various polymer coatings were conducted (Vogt et al., 2003; Karlowatz et al., 2004; Mizaikoff, 1999). These experiments give an insight to performance of the novel coating with respect to polymers commonly used in research at the Applied Sensors Laboratory (ASL) (Vogt et al., 2003; Karlowatz et al., 2004; Mizaikoff, 1999). Initially, multicomponent measurements of model analytes tetrachloroethylene (TeCE) and 1,2 dichlorobenzene (1,2 DCB) were carried out using a vertical flow cell with a Bruker IFS66 FT-IR spectrometer to evaluate enrichment and regeneration behaviors of the new coating as well as display the multicomponent capability of the ATR-FTIR technique (Figure 4). A one liter solution with 5 $\mu$ L of TeCE and 5 $\mu$ L of 1,2 DCB diluted to volume with deionized water was prepared. An AliTea C8 MIDI peristaltic pump was used operating at 50rpm to pull solution through the vertical flow cell containing a PTMSP coated 50x20x2mm zincselenide (ZnSe) ATR crystal coated via the same technique described earlier. Measurements were taken with 4 $\text{cm}^{-1}$  spectral resolution and averaging 100 scans. The initial evaluation measurements were successful in displaying the potential use of PTMSP for a sensing layer. Analyte specific absorption bands were integrated and plotted over time to produce enrichment curves. The enrichment curves for TeCE and 1,2 DCB are provided (Figure 5) as well as the curves for sensor regeneration produced by rinsing the flow cell with deionized water and plotting integration values for the absorption bands versus time (Figure 6). Enrichment behavior of

the new coating appears very desirable for a sensing membrane; however, the regeneration behavior tends to be quite long for an ideal sensing membrane. Further studies will evaluate this behavior in the upcoming project period as well as performing a comparative analysis with a common polymer used in the ASL, Teflon AF.

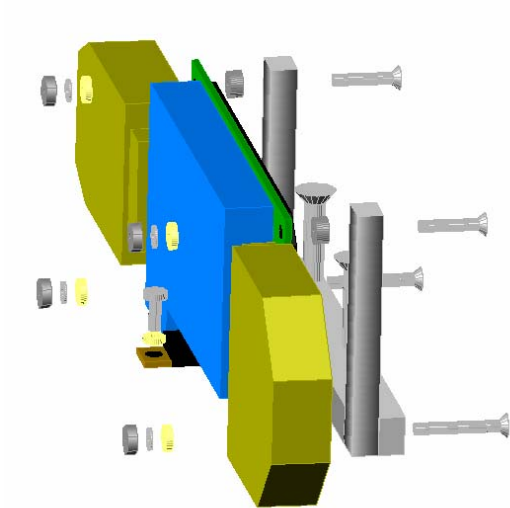
### **High-pressure multireflection ATR measurements**

High-pressure multireflection ATR measurements were continued during this reporting period to investigate the behavior of sensing principles in simulated deep sea conditions. A figure of the experimental setup is provided with the recently integrated Stirling-cooled MCT detector with a Bruker IRcube FT-IR spectrometer (Figure 7). Results reported previously indicated the potential influence of hydrostatic pressure on the dynamic equilibrium of water diffusion into a Teflon AF membrane. However, repetition of these measurements indicates that the reported results may be influenced by mechanical instabilities of the experimental setup such as leakage and gasket swelling. Future experiments are aimed to properly evaluate the influence of mechanical instability from the experimental setup. Two potential improvements to the pressure setup include replacing the viton seal with an indium seal and to fabricate a new faceplate that allows the use of silver halide fiber waveguides. Currently, the experimental setup does not allow us to fully investigate the range of pressures anticipated during the deployment of 'sphereIR'. To properly address the hypothesized influence of hydrostatic pressure on sensor principles and multivariate data evaluation, an improved experimental setup is required. The proposed improvements to reduce mechanical instabilities in the experimental setup are anticipated to broaden the range of experimental pressures in the laboratory and will be thoroughly evaluated when changes are integrated with the setup.

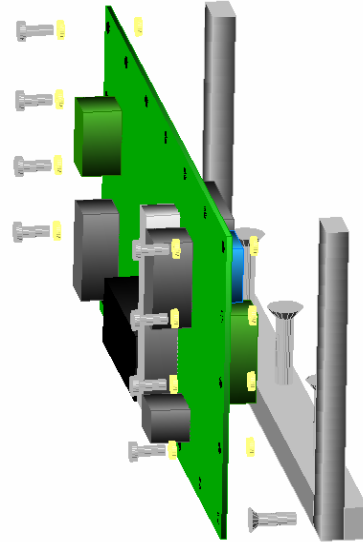


## FIGURES

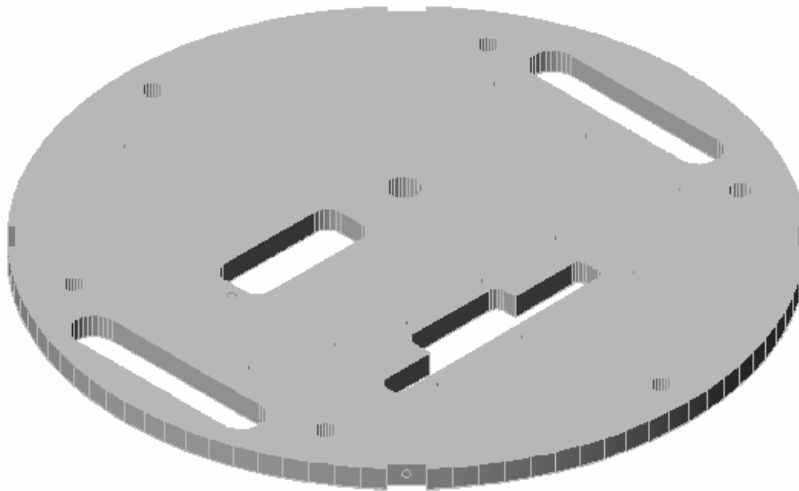
**Auxiliary Detector Interface Board**



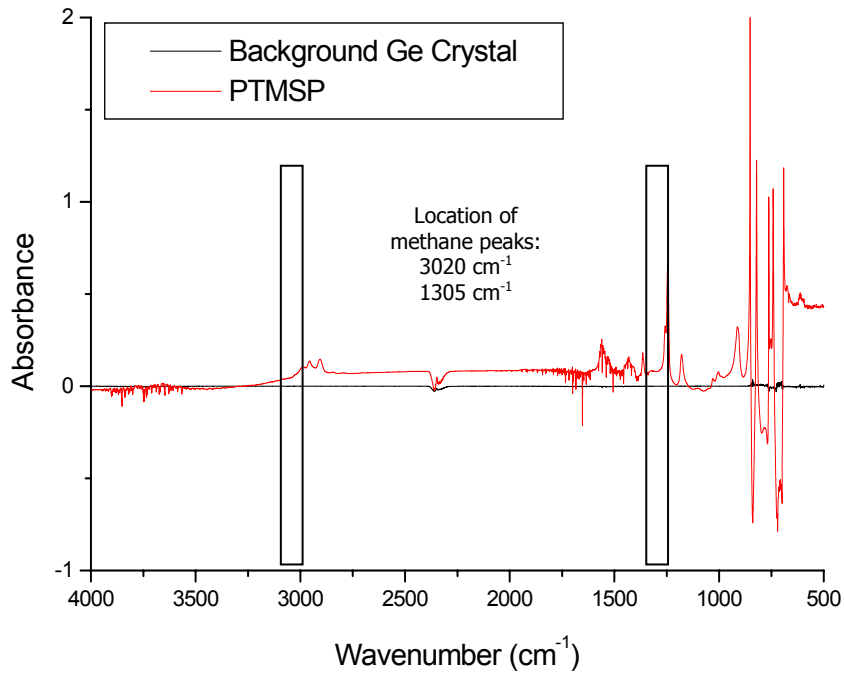
**Spectrometer-Computer Interface Board**



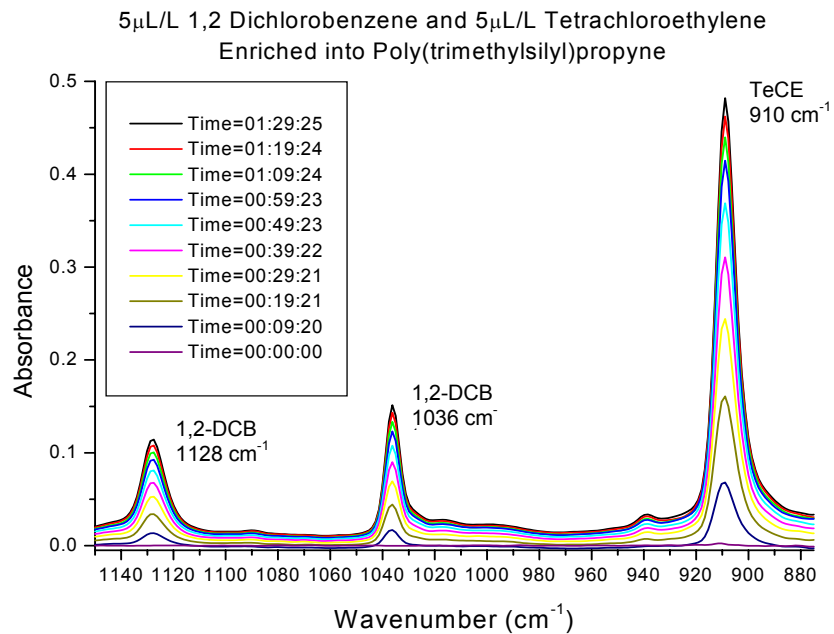
**Figure 1:** Modeling of two electrical components with corresponding mounts and fasteners for ‘sphereIR’



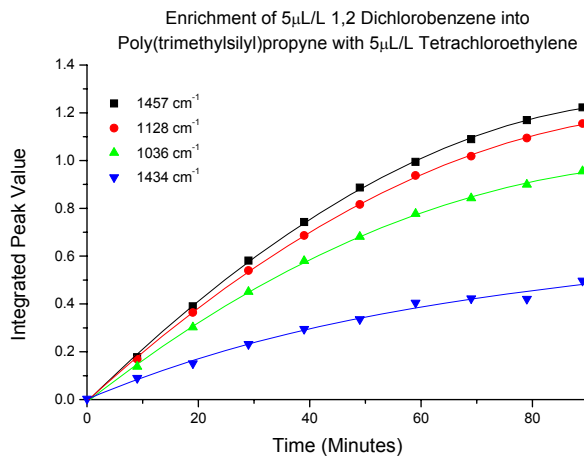
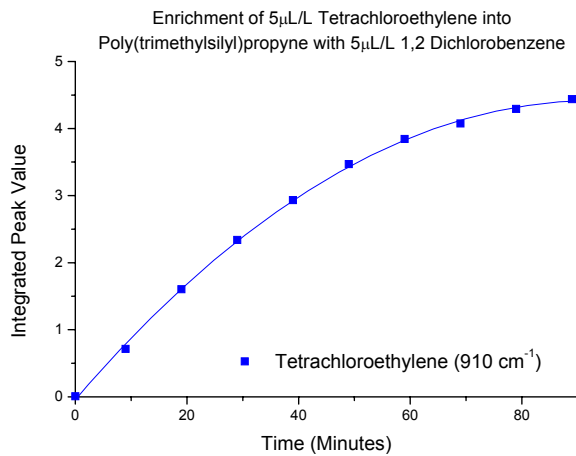
**Figure 2:** Modeling of electronics baseplate with fastening points, wiring slots, and attachment points for complementary optics baseplate.



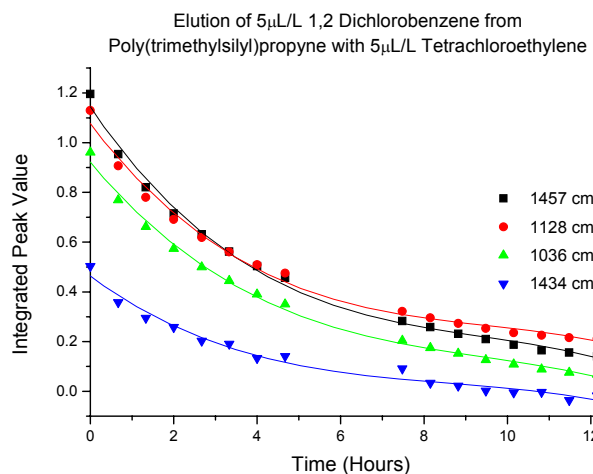
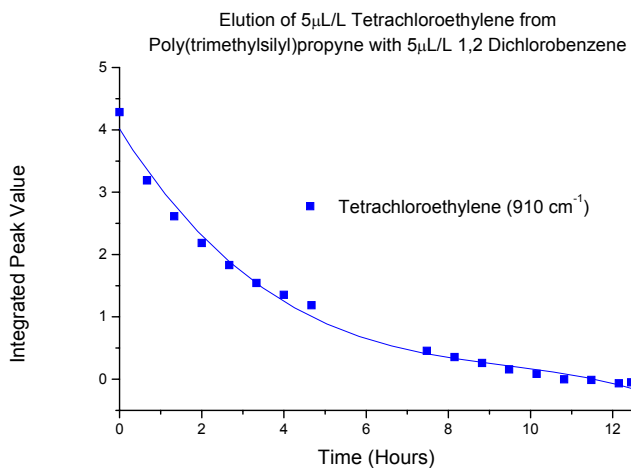
**Figure 3:** ATR-IR spectra of a poly(trimethylsilyl)propyne coated germanium ATR crystal.



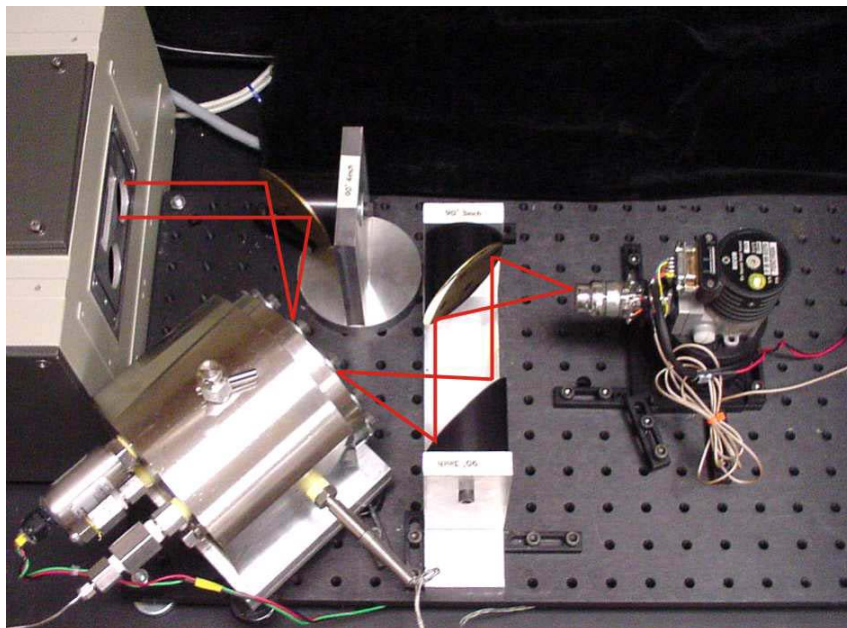
**Figure 4:** Multi-analyte ATR measurements of tetrachloroethylene and 1,2 dichlorobenzene enriching into a PTMSP coated ZnSe ATR crystal.



**Figure 5:** Enrichment curves for tetrachloroethylene and 1,2 dichlorobenzene into PTMSP.



**Figure 6:** Washing curves for tetrachloroethylene and 1,2 dichlorobenzene out of PTMSP.



**Figure7:** Experimental setup for investigating samples at elevated pressures with integrated Stirling-cooled MCT detector.

## ACRONYMS

IR	infrared (spectroscopy)
MIR	mid-infrared
ATR	attenuated total reflection
ASL	Applied Sensors Laboratory
AF	amorphous fluoropolymers
PTMSP	poly(trimethylsilyl)propyne
FT-IR	Fourier transforms infrared (spectroscopy)
ASL	Applied Sensors Laboratory
Ge	Germanium
ZnSe	Zincselinide
TeCE	tetrachloroethylene
1,2-DCB	1,2-dichlorobenzene
CAD	Computer Assisted Design
MCT	mercury-cadmium-telluride

## SCIENTIFIC CONTRIBUTIONS

### Oral Presentations:

“Investigating the Influence of Pressure on IR-ATR Spectroscopy for Underwater Spectroscopic Sensing Applications”, Gary T. Dobbs, Neil Pennington, Frank Vogt, Boris Mizaikoff, SERMACS 2003, 11-03, Atlanta, GA (oral presentation).

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Mizaikoff, B., 1999, *Meas. Sci. Tech.* *10(12)*, p.1185-1194.  
Vogt, F., Karlowatz, M., Jakusch, M. and Mizaikoff, B., 2003, *Analyst*, *128(4)*, p.397-403.

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

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

Annual Report covering the period

January 2003 – November 2003

Submitted by

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## ABSTRACT

Work on further developing a prototype acoustic logging device previously developed as part of a European Union-funded research project is well underway. The development work in the current phase of this DOE-funded project aims to extend the capability of the electronics to allow remote operation on the seabed for periods of up to 3 months at a time. Beyond the currently funded phase it is proposed to concentrate on transducer specification and development (to optimize pulse generation and reception) and packaging of the entire system for deep water deployment. To this end a continuation proposal (including a funding application) has been prepared and submitted. Once completed, it will be possible to investigate fine-scale temporal changes in sea floor acoustic reflection responses at the gas hydrate monitoring station, enabling inferences to be made on sea floor processes.

During the initial project period (to June 2003) a series of meetings were held to define operational requirements and draw up a design philosophy. Subsequently work has concentrated on design and build of the hardware, bench testing and preliminary field trials.

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## **INTRODUCTION**

As part of a European Union-funded research project (Sub-GATE), the Geophysics Group at the University of Wales Bangor designed and developed a prototype acoustic logging device for monitoring temporal variations in seabed acoustic responses. The aim of the EU project was to study freshwater and methane fluxes at the sediment water interface; the impetus for the work derived from earlier research related to gassy sediment structure and behavior conducted by the authors and others as part of the US ONR funded Coastal Benthic Boundary Layer Program (CBBL) and the German funded JOBEX Program (Richardson and Davis. 1998; Wever et al., 1998; Bussmann and Suess, 1998). The instrument developed within the Sub-GATE project was specifically for shallow water operations, and worked through an antenna and radio modem system providing a telemetric link to a remote laptop PC for data storage.

Within this DOE funded project, the intention is to further develop this acoustic logging instrument so that it is able to be pre-programmed for remote operation whilst under long-term deployment in the deeper water environment of the Gulf of Mexico. The development work is being carried out under a collaborative agreement between the University of Wales Bangor and Scimar Engineering Ltd. (as subcontractor to the University).

## **EXECUTIVE SUMMARY**

As part of a European Union-funded research project (Sub-GATE Project, 1998-2001), an acoustic device was developed and successfully deployed at a shallow vent site in the southern Baltic during a series of multi-disciplinary experiments aimed at studying submarine groundwater fluxes and transport-processes from methane rich coastal sedimentary environments. The rationale underpinning the research development and experimental trials was recognition of the value of the acoustic reflection signature for monitoring physical changes at the sediment water interface and within the subsurface structure.

Within this current DOE-funded research project the previously developed system is being further developed in readiness for deployment at the Gulf of Mexico Gas Hydrates Monitoring Station.

## **EXPERIMENTAL DEVELOPMENTS**

### *Design and development of the electronic component of the acoustic logger*

The current acoustic logger is being designed to satisfy the following operational requirements:



- Pre-programmable for remote operation
- Operational over deployment periods of several months
- Repeatable and controlled source signatures
- Rapid sampling rates (of the received signals)
- Appropriate recording lengths (two-way-times)
- Programmable for temperature and pressure sensors
- Easy downloading of data on instrument recovery
- Robust and reliable

The fundamental design philosophy has been to design a system that can be managed and maintained at sea. To this end, control functions within the instrument will be kept at the simplest level to give the greatest flexibility, with a PC used as a host environment to carry out the translation between internal machine settings and user-defined values.

The electronic system is currently being built on a six PCB set that splits out functions and allows easy swap out for maintenance and testing. The specific functions of the six boards are

- Low voltage power supply
- Processor
- A to D convertor
- Filter
- Transmit and high voltage power supply
- Auxiliary channel interface

## **RESULTS AND DISCUSSION**

The system development is at an advanced stage where the basic specification on hardware and instrument software is ready to be closed down for final testing. Some minor modifications to the design are being made based on discussions/ recommendation arising from the project workshop held in Oxford, MS (September 03). Some software features have also been identified that need to be added.

Preliminary bench trials (Figs. 1 and 2), tank trials (Fig. 3) and field trials have been undertaken and further trials are planned for the coming months. These will go hand-in-hand with the final stage hardware development program and progression with software work.

To date, field trials have not produced any significant data as the system is effectively still under development. The early trials have though been useful in providing a means to recognize that, whilst the electronic system is still undergoing modification, any sea trials should be carefully planned to minimize logistic problems.

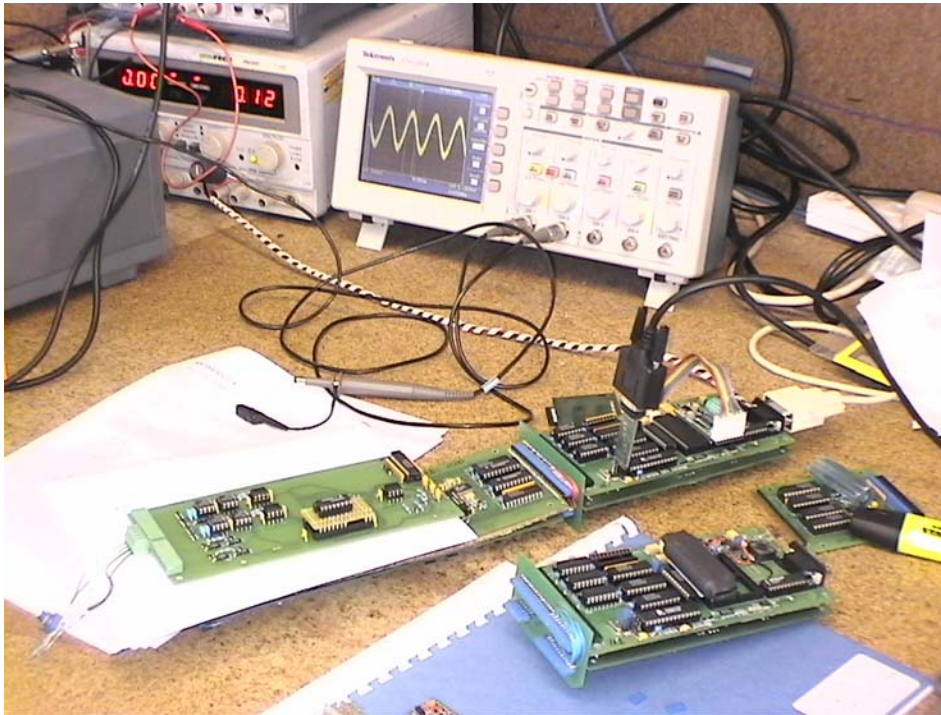


Fig. 1 Preliminary bench testing during instrument development.



Fig. 2 Photograph showing PCB sets.

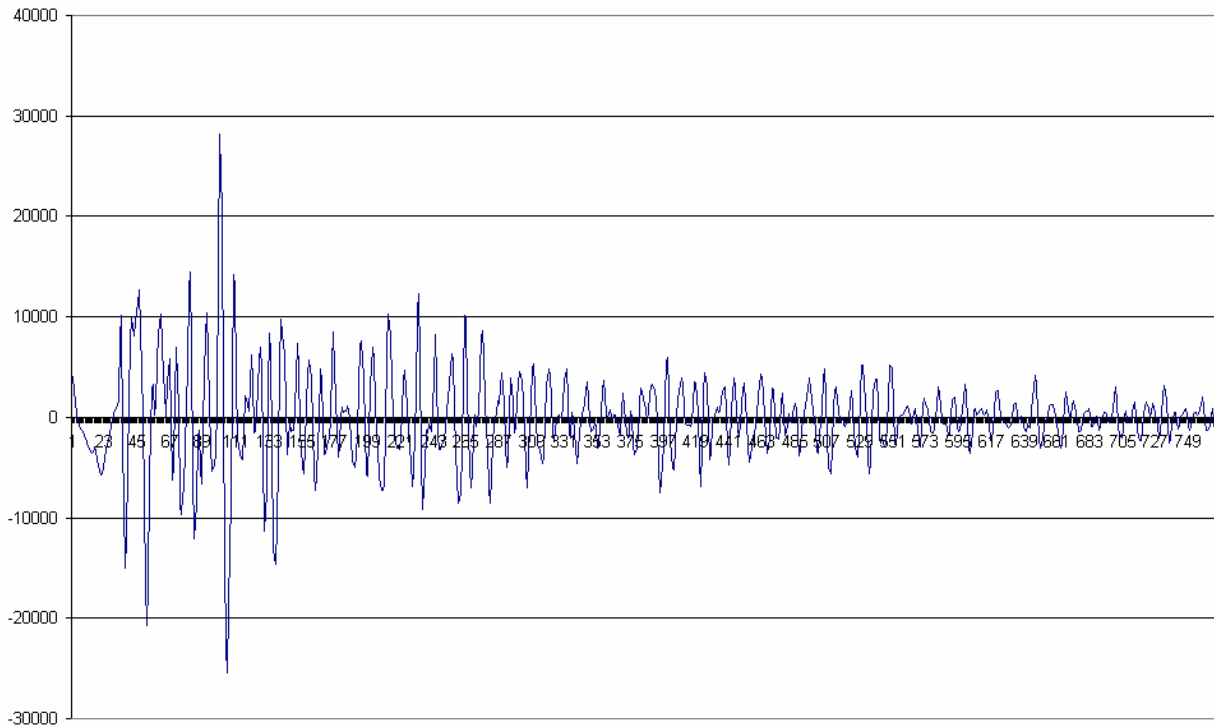


Fig. 3 Example record collected during tank trials.

## CONCLUSIONS

The electronic component of the acoustic logging system, as proposed, is on course for completion within the time-scale of the current project. A recently submitted proposal for continuation funding, if successful, will allow the complete acoustic logging system to be assembled and interfaced in readiness for deployment at the Gulf of Mexico Gas Hydrate Monitoring Station.

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- Richardson, M.D. and A.M. Davis (1998) Modeling methane-rich sediments of Eckernförde Bay. *Continental Shelf research* 18, Nos 14-15, 1671-1688.
- Wever, T.F., Abegg, F., Fiedler, H.M., Fechner, G. and I.H. Stender (1998) Shallow gas in the muddy sediments of Eckernförde Bay, Germany. *Continental Shelf research* 18, Nos 14-15, 1715-1739.

## **ACRONYMS**

CBBL	Coastal Benthic Boundary Layer Program
EU	European Union
ONR	Office of Naval Research
PC	personal computer
US	United States

## **CONCLUSIONS**

This report covers the accomplishments of the first year of Cooperative agreement Project #DE-FC26-02NT41628, between the Department of Energy and the Center for Marine Resources and Environmental Technology, University of Mississippi. The efforts of the Hydrates Research Consortium are reviewed and plans for the final phases of the project presented. This cooperative agreement has been extended to November 30, 2004, so that the subcontractors can complete their contracts while dovetailing their individual project goals with one another as well as with the overall goals of the monitoring station project. The evolution of the vision for the station has produced significant changes in its design and these changes are being addressed in continuous dialogue with the DOE as well as the JIP and the other station funding agencies, MMS and NOAA, in an effort to maximize the performance and utility of the final product. 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

1,2-DCB	1,2-dichlorobenzene
AF	amorphous fluoropolymers
ASL	Applied Sensors Laboratory
ASL	Applied Sensors Laboratory
ATR	attenuated total reflection
BHA	borehole array
BVLA	Borehole Vertical Line Array
CAD	Computer Assisted Design
CBBL	Coastal Benthic Boundary Layer Program
CMRET	Center for Marine Resources and Environmental Technology
CTD	conductivity-temperature-depth (sensor)
CW	continuous wave
DGPS	Differential Global Positioning System
DOC	Department of Commerce
DOE	Department of Energy
DOI	Department of the Interior
DRS	data recovery system
EU	European Union
FT-IR	Fourier transforms infrared (spectroscopy)
Ge	Germanium
GOM	Gulf of Mexico
HLA	Horizontal Line Array
HRC	Hydrates Research Consortium
HSZ	Hydrate Stability Zone
IDP	Integrated Data Power unit
IR	infrared (spectroscopy)
JIP	Joint Industries Project
MC	Mississippi Canyon
MCT	mercury-cadmium-telluride
MIR	mid-infrared
MMS	Mississippi Minerals Management Service
MPS	MultiPurpose Sled
NETL	National Energy Technology Laboratory
NIUST	National Institute for Undersea Science and Technology
NOAA	National Oceanographic and Atmospheric Administration
NURP	NOAA's Undersea Research Program
OBS	Ocean Bottom Seismometers
ONR	Office of Naval Research
PC	personal computer
PCB	pressure-compensated battery
PTMSP	poly(trimethylsilyl)propyne
ROV	remotely operated vehicle
SDI	Specialty Devices, Incorporated

SFO	Sea Floor Observatory
SFP	Sea Floor Probe
SSD	station service device
TeCE	tetrachloroethylene
US	United States
USM	University of Southern Mississippi
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 be anchored to the sea floor. Since water currents would cause the VLAs to deviate from vertical, each would also include inclinometers and compasses for determining the location of each hydrophone within the water column.

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

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

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

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



to explore a number of modifications but not to alter the original intention or basic mission of the SFO. This update documents that exploration and other developments.

## CHANGE 1: ARRAY TYPE

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

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

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

A second VLA is scheduled to be constructed. It will be equipped with off-the-shelf thermistors, CTDs, fluorimeters and transmissometers so that it 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.

## CHANGE 2: DATA RECOVERY

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

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

## CHANGE 3: POSITIVE SYNCHRONIZATION OF TEST SIGNALS

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

## CHANGE 4: ELECTRICAL POWER FOR THE SFO

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

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

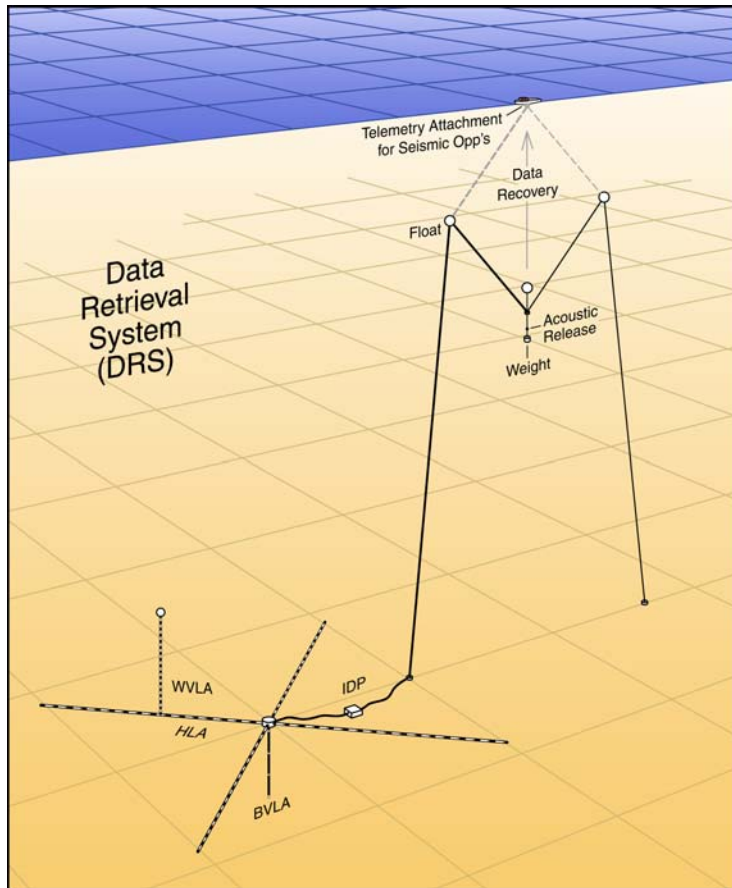


Figure 1. Diagram of the component parts of the sea floor observatory

## CONCLUSION

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

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