Deployment of an *In-situ* pH Calibrator on MARS Cabled Ocean Observatory

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***Abstract*—A recently developed in situ pH measurement and calibration system (pH Calibrator) has been deployed on MARS (Monterey Accelerated Research System) cabled ocean observatory located at Monterey Bay, California. The deployment took place at the depth 880 m, and lasted for more than two months. A key aspect of the instrument is user-defined auto-calibration, enhancing the accuracy of pH measurements in harsh, high-pressure environments, over long intervals, as reported here. Thus, the instrument takes full advantage of cable power and internet connectivity permitting real-time monitoring of pH, with calibration scheme optimized to achieve specific scientific objectives in response to local environmental factors. Here we report recent modifications to the instrument, which enhanced its effectiveness during the MARS cabled ocean observatory deployment.**

Keywords— Calibration; pH; Observatory

I. INTRODUCTION

Anthropogenic CO_2 is now recognized as a serious concern for science and society. In particular, high atmospheric CO_2 concentrations affect global temperatures, but as importantly, can reduce the pH of seawater throughout the world's ocean. Ocean acidification significantly affects the calcifying ecosystems, such as corals and some species of plankton[1][2]. Detection of the change in ocean pH on long time scale is important for scientists to investigate global climate change processes and understand the corresponding response of chemical and biological systems. pH also plays a significant role at highly productive biological communities distributed around mid-ocean ridge hydrothermal vents, which can change dramatically in space and time[3][4]. In situ measurement has been shown to be the most effective method to constrain the fluid chemistry at source conditions around the vent organisms. Thus, reliable in situ instrumentation that is capable of long term measurement and monitoring of fluid pH is highly required by the marine science community.

In recent years, numerous in situ electrochemical pH probes have been developed for deep sea applications[5][6]. However, there are two major limitations of these devices as a means to perform long term monitoring. First, reliable, long-term determination of ocean pH is still challenging, due to the signal drifts caused by temperature changes and uncertainty of junction potentials, which cannot be well characterized by conventional "on-deck" calibration method[7]. Even 1 mV potential drift can cause more than a 0.01 shift in pH, which obfuscates unambiguous assignment of the pH data to natural or sensor-related causes. Secondly, the lack of continuous power supply and direct data access methods usually requires scientists to make use of multiple device modules to reduce the power consumption and improve accuracy by redundancy. Most importantly, however, the scientist cannot interact with the pH sensor system, and address calibration issues in real time that might be caused by abrupt change in environmental factors.

To address these limitations, we developed a novel in situ pH measurement system (Fig. 1) that takes explicit account of the need for user defined and computer controlled calibration protocols. Accordingly, the pH value and operational status of pH and reference electrodes can be evaluated and performance simultaneously verified. The so-called pH Calibrator was initially tested as a stand alone instrument deployed either by submersible (HOV Alvin and ROV Jason II), or by wire-line in the course of hydrographic profiling[8]. More recently, the pH calibrator was modified and optimized for connection to subseafloor fiber-optic power cables in anticipation of the need for long-term monitoring. This paper presents the design of the calibration system, while also briefly describing results of the first deployment as a component of the MARS cabled ocean observatory network.

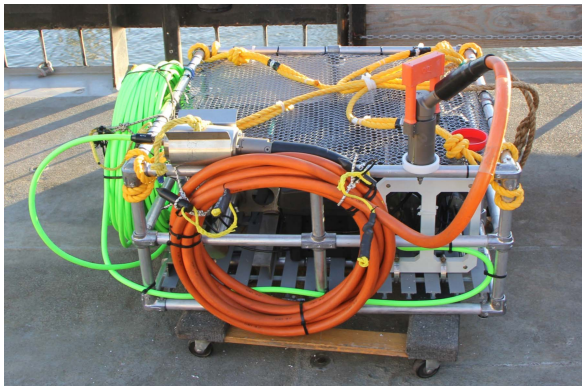

Fig. 1. Assembled pH Calibrator on the R/V Rachel Carson. The system with a dimension of 1.0 m×1.0 m× 0.5 m weighs about 172 Kg in air.

II. CALIBRATION METHOD AND SYSTEM INTEGRATION

The enhanced solid state iridium oxide pH electrode (IrO_x) represents the most fundamental component of the pH calibration system. This electrode is not only robust, facilitating deployment and recovery, but is also a highly precise instrument for acquisition pH data for acidic and basic fluids at temperatures from 100 to 175 °C and high pressure (25 MPa)[9]. The transformation of a lab-based instrument, however, into a device for pH measurement on the seafloor

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was challenging. Although the Ir/IrO_x sensor is a rugged pH measurement device, both lab and field based applications have confirmed the need for calibration on schedules dictated by time and environmental factors. Thus, considerable effort was invested in recent years on establishing sampling (pH measurement) and calibration protocols that offer that enhance performance and long-term application in challenging chemical and physical environments. Indeed, the scheme needed to include sampling, rinsing and calibration modes, all of which required dedicated computer control of pump and valve systems. Meeting this requirement, we developed a fluid flow system composed of a piston displacement pump (STH1CKCLF, FMI Inc) and solenoid valves (LVM10, SMC Inc). The main components of the pH Calibrator, fluid flow, communication and power distribution are depicted in Fig. 2[10].

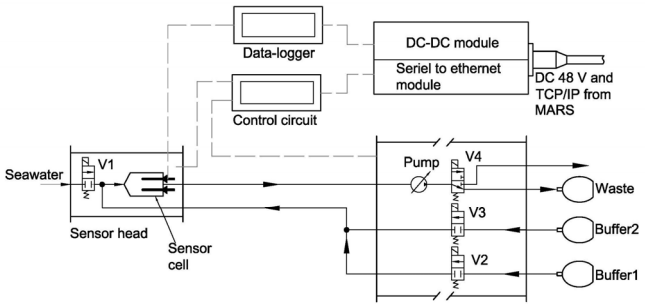

Fig. 2. Schematic diagram of the calibrator pH system. Lines with arrow and dash lines represent flow pathways and communication /power cabling respectively. The fluid flow system is contained in the oil filled chamber for pressure equilibrium.

A. Fluid flow system

The system is built as a continuous flow reactor based on the concept of flow chemistry as far as the synthetic efficiency is concerned. The fluid sample (seawater) and pH buffers are selected by the valves and pumped in a continuous sequence into the sensor cell (Fig. 3) to react with the electrodes, thus the pH measurement and sensor calibration are achieved in this process. The pump and valves can be operated automatically by a pre-assigned sequence, but also can be powered separately for the advanced needs of process control. The TCP/IP connection provided by the MARS observatory allows the real time control of the continuous fluid flow system over reaction conditions including flow rate, time and operation scheme. The sensor cell is designed with a volume of 1.03 ml, to reduce the residence time of the reagents. Four solid-state electrodes (IrOx pH electrode, Pt redox electrode, Ag|Ag_2S dissolved H_2S electrode, and Ag|AgCl reference electrode), a thermistor and a 1/8″ OD outlet tube are pressure sealed by a modified Conax™ compression seal fitting (Conax Inc). Viton sealant is selected because of its excellent resistance to decomposition at elevated temperature. The sensing tip of electrodes and thermistor are set on the same axial plane to minimize the temperature and chemical gradients on the measurements.

B. Data logging circuit

Sensor signals are acquired and processed by a custom designed high resolution datalogger circuit (Fig. 4) with the following specifications:

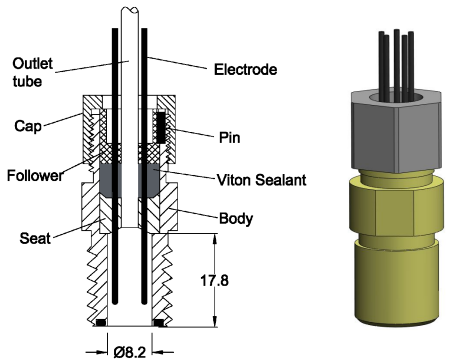

Fig. 3. Schematic diagram of the sensor cell depicting the seal mechanism used for electrodes and thermistor. Units are in mm.

- The dimension is 114 mm *31 mm*25 mm.
- Eight input channels are available: two high impedance sensor input channels, two low impedance sensor input channel, two thermocouple input channels and two thermistor input channels. These eight channels provide adequate measurement flexibility to enhance applications in deep sea environments.
- The two high impedance channels of the datalogger are especially designed with the input impedance of 10^{16} Ω, capable of use with YSZ (yittria-stabilized zirconia) ceramic and glass pH electrodes, which are characterized by extremely low input bias current and high resistance.
- The datalogger has a 14 bit 8-channel ADC and 64MB flash memory and uses RS232 or ICL (Inductively Coupled Link) interface for communication.
- The input of the four sensor channels ranges from -2V to +2V with the resolution of 0.25 mV. The thermocouple input ranges from 0-400 ºC and the resolution is 1 ºC.

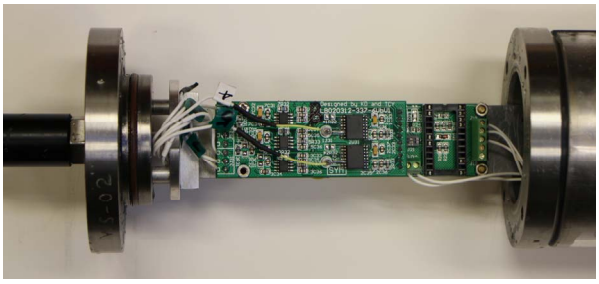

Fig. 4. The data logging circuit contained in the 7000 m depth rated pressure vessel.

III. DEPLOYMENT AND RESULT

The pH Calibrator was deployed on MARS cabled observatory at the depth 880 m on the seafloor of Monterey bay, CA on Nov. 12, 2012 (R/V Rachel Carson, ROV Ventana, dive# 3675, Fig. 5). The system successfully completed a two-

month field application and was recovered on Jan. 14, 2013 (dive # 3689).

After connected to MARS "science node", the pH Calibrator was remotely operated from University of Minnesota hydrothermal lab to conduct calibration cycles (Fig. 7). Each Calibration cycle is defined by three steps: step 1 is to draw the fluid sample (ambient seawater) into the sensor cell to perform pH measurement, and during step 2 and step 3 the pH buffer1 and pH buffer 2 are flowing through the electrodes respectively to perform two-point calibration. After the cycle operation, the flow cell will be filled with the last buffer to store the electrodes. It should be noted that the timing and step sequence of each cycle can be conveniently rearranged via internet communication for a certain science purpose.

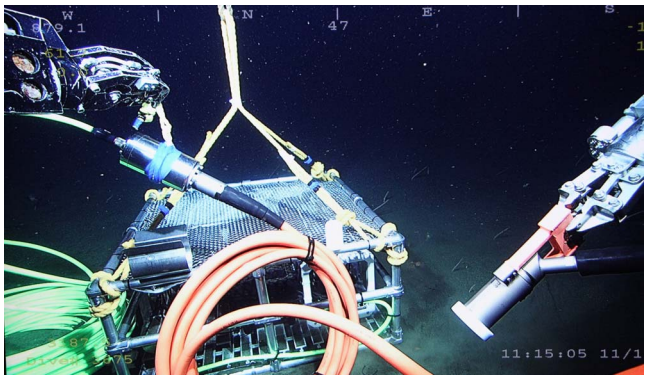

Fig. 5. Deployment of the Calibrator by the ROV Ventana on the seafloor at the depth of 880 m on Monterey bay seafloor (36°42'N, 122°11.2'W). In the picture, the manipulator of ROV Ventana is holding the ODI connector.

During this particular experiment, the flow rate was 10 ml/min, and measured potentials were collected from 24 readings averaged in the last two minute of each step. pH buffer 1 (pH=3.70) and buffer 2 (pH=10.41) prepared from reagent grade solid buffer chemicals (Fisher Scientific, PA) are used in this experiment. Each solution contained 0.57 mol/kg NaCl in keeping with the dissolved Cl^- concentration of seawater. During two-month deployment, eight full calibration cycles were performed (Table I). From Table I, signal drift can be clearly observed from potential readings of the pH buffers, as well as from the slope of the pH electrode with time, which underscore the necessary need of in situ calibration. Here we present data from two standard calibration cycles performed on Nov. 13, 2012 (Fig. 6 (a), corresponding to cycle 1 in Table I) and Dec. 13, 2012 UTC 2012 (Fig. 6 (b), corresponding to cycle 7 in Table I). In Fig. 6, the rapid change of the potential curve represents the mixing between fluids with different pH inside the sensor cell. The stable phase of an asymptotic curve shows full displacement of one of the fluids by another. The measured slope of the electrode can be deprived from the readings of the known pH buffers, thus the relationship between the cell potential reading [E(mV)] and seawater pH value can be expressed as follows:

$$E(mV)_{cycle1}=-56.845\ pH+602.04 \quad (1)$$

$$E(mV)_{cycle7}=-56.927\ pH+375.71 \quad (2)$$

In Fig. 6 (a), the electrodes were stored in alkaline buffer 2 before and after each cycle. After running this sequence of processes for several weeks (see Table I from cycle 1 to cycle 5), the offset between the actual and theoretical Nernst slope of the electrodes shifted about 2 mV/pH, which may be caused by structural distortion or from biofouling of the electrode in the alkaline environment. From cycle 7 shown in Fig. 6(b), the electrodes were stored in acidic buffer 1, and the actual slope of the electrode shows good agreement with its initial characteristics. In the normal deep sea operation, the drift of the signal or the unstable pH° (zero pH) and slope will cause great uncertainty of the in situ pH value. However, the in situ calibration function of the pH Calibrator provides an excellent method for long-term sensor deployment with the power and communication supplied by the MARS ocean observatory.

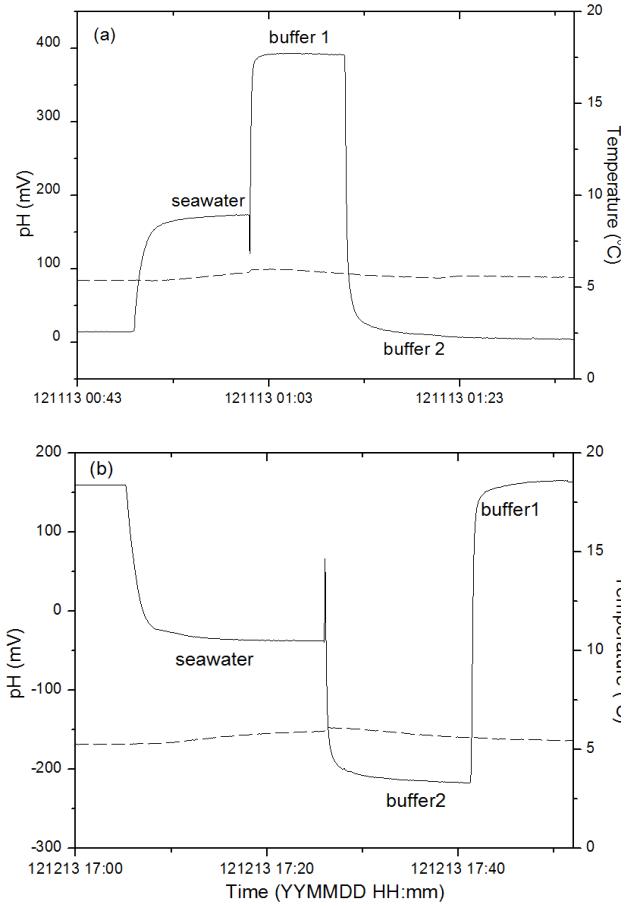

Fig. 6. Measured pH electrode potential (solid line) and temperature (dash line) of calibration cycles triggered on Nov. 13, 2012 UTC (cycle 1 in Table I) and Dec. 13, 2012 UTC (Cycle 7 in Table I).

IV. CONCLUSION

We have presented a method of using a novel fluid flow system to conduct in situ calibration needed to minimize signal drift associated with long term sensor deployment. The pH Calibrator instrument can be used with chemical sensors and sensor technologies for verification of data under the same conditions at which the data are obtained. Two month deployment on MBARI MARS ocean observatory has proven the functionality and reliability of the device. With the

flexibility of the system design, further development is expected for the deployment on US Regional Scale Nodes and NEPTUNE Canada ocean network.

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TABLE I pH DATA OF EACH CALIBRATION CYCLE.

Cycle # YYMMDD HH:mm	Sample	Potential (mV)	Temp (°C)	Theoret-ical slope	Actual slope (mV/pH)	Calculat-ed pH
1 121113 01:00	Seawater	173.29±0.39	5.8	-55.4	-56.8	7.54±0.01
	Buffer 1	391.71±0.32	5.8			
	Buffer 2	10.28±0.58	5.5			
2 121113 15:50	Seawater	176.43±0.57	5.6	-55.3	-57.4	7.58±0.01
	Buffer 1	399.41±0.27	5.6			
	Buffer 2	14.04±0.50	5.3			
3 121119 22:40	Seawater	54.15±1.77	6.1	-55.4	-57.3	7.51±0.03
	Buffer 1	272.61±0.42	5.6			
	Buffer 2	-111.57±0.32	5.4			
4 121211 15:20	Seawater	71.48±0.27	6.1	-55.4	-53.6	7.68±0.01
	Buffer 1	285.23±0.71	5.9			
	Buffer 2	-74.73±0.80	5.4			
5 121211 22:20	Seawater	56.16±0.3	6.1	-55.4	-54.2	7.69±0.01
	Buffer 2	-91.1±0.57	5.4			
	Buffer 1	272.45±0.2	5.9			
6 121213 00:05	Seawater	-97.49±0.3	5.9	-55.3	-54.9	7.44±0.01
	Buffer2	-260.36±0.3	5.6			
	Buffer1	108.2±0.3	5.4			
7 121213 17:05	Seawater	-37.35±0.25	5.9	-55.3	-56.9	7.26±0.004
	Buffer2	-216.9±0.29	5.6			
	Buffer1	165.08±0.32	5.4			
8 130110	Seawater	-3.588±0.20	5.94	-55.4	-57.3	7.26±0.00
	Buffer1	200.275±0.2	5.5			
	Buffer2	84.225±0.26	5.4			

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