An in-situ chemical sensor system for cabled ocean observatory applications at hydrothermal vents

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***Abstract*—An in-situ chemical sensor system was developed for long term monitoring of hydrothermal vent fluids as part of the US NSF Ocean Observatory Initiative (OOI) Regional Scale Nodes (RSN) in the Northeast Pacific Ocean. The sensor wand design is based on Yittria-stabilized zirconia (YSZ) ceramic membrane electrode in conjunction with Ag|AgCl reference electrode, Au or Pt redox electrode and Ag|Ag_2S (H_2S) electrode. The YSZ ceramic electrode was constructed with a titanium tube for the long term deployment application. To achieve high measurement accuracy, the high impedance signal of the YSZ ceramic electrode was converted to the low impedance signal by a pre-amplifier. The instrument utilizes the power supply and bandwidth of the fiber optic ocean cable to conduct continuous monitoring of the hot vent fluids. The instrument was deployed on Regional Scale Nodes (RSN) Axial Seamount site via MJ03C mid-power junction box. A modified version of the instrument was also deployed multi times by DSV Alvin during AT26-17 cruise on Axial Seamount and Main Endeavour Field (MEF) vent field, Juan De Fuca Ridge. This integrated electrochemical system has successfully measured pH, dissolved H_2 and H_2S of hydrothermal vent fluids at 300 °C and 220 bars.**

Keywords—YSZ; pH; electrode; hydrothermal; observatory

I. INTRODUCTION

The University of Minnesota (UMN) hydrothermal lab has long been involved in the development and application of integrated in-situ chemical sensor systems to constrain the temperature, pH, dissolved H_2 and H_2S parameters of deep sea hydrothermal vent fluids [1-4]. Many years of field deployments at hydrothermal vents along the mid-ocean ridges using DSRV ALVIN have proven essential to the scientific and engineering reliability of the chemical sensor system [5].

The chemical sensor system was initially designed as a self-contained system to permit real-time operation form the submersible. Sensor response was processed by a battery-powered high impedance input Datalogger and transmitted via the inductively coupled link (ICL) into the submersible [2]. The in situ sensor was a very efficient device in that it was possible to obtain pH and redox data for hydrothermal vent fluids from multiple structures on the seafloor during a single dive. The initial design of the instrument, however, precluded long-term deployment, which is required by the scientific community to better understand the cause and effect of the highly dynamic phenomena. To achieve this capability, the hydrothermal lab at UMN designed a new high temperature sensor system, while utilizing the continuous power and communication capability inherent to the OOI RSN cabled ocean observatory infrastructure in the N.E. Pacific [6]. With relatively minor modification, the redesigned sensor can function as a hybrid instrument, using either cable or battery power. The instrument configuration and field results are presented in the following section.

II. INSTRUMENT DESIGN

The electrochemical response of the sensor system is based on Yittria-stabilized zirconia (YSZ) ceramic membrane electrode with an internal reference pair (Hg/HgO). This is a primary pH electrode when combined with Ag|AgCl reference electrode, as was done here [3]. Moreover, by coupling the YSZ electrode with Au or Pt electrode, and an Ag|Ag_2S electrode, the sensor system can also simultaneously determine dissolved H_2 and H_2S concentrations of hydrothermal fluids [1][4]. The YSZ electrode is characterized by high internal resistance and ultra-low bias current, particularly at low temperatures (for example, 10^{11} Ω at 125 °C) [7]. Thus, the signal measurement is very challenging, and requires proper insulation and high input impedance voltmeter for the most accurate measurements. Although the prior design yielded numerous valuable data for the scientists, it lacked the long-term deployment capability on a vent orifice. First, it is very hard for a long slim profile of the prior design providing the insulation of the high impedance signal of the YSZ ceramic electrode to remain on location around a gibbous vent structure when attached with a heavy underwater cable during deployment. Also, the electronics cannot provide wired communication method and does not have the on board memory in case a stand-alone deployment is needed. To

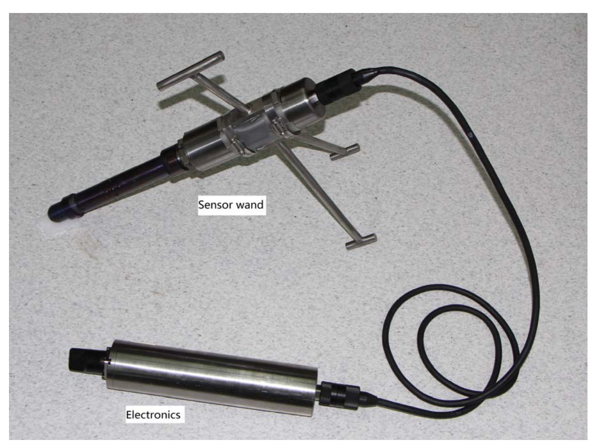

Fig. 1. Assembled sensor instrument with the sensor wand and electronics housing. The instrument weighs about 6 Kg in water.

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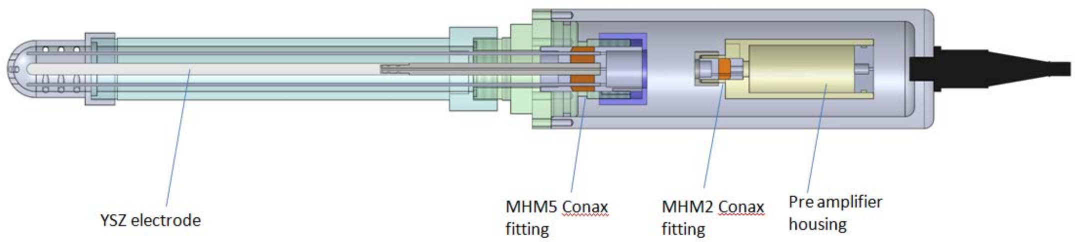

Fig. 2. Schematic diagram of the sensor wand. The electrodes and thermocouples are pressure sealed by a Conax MHM5 fitting. The wires of the pre-amplifier are sealed in a plastic housing by a MHM2 Conax fitting.

address these issues, the sensor instrument described in this article includes two separate units: a sensor wand and an electronics housing, connected by a 2 m underwater cable (Fig. 1). The sensor wand is equipped with a stand to position the tip of the electrode in the vent fluid. The electronics package is tethered to a 70 m underwater cable, which in turn is linked to a junction box. This design facilitates the deployment of the sensor wand by the manipulator of the submersible without disturbing the cable or electronics housing.

A. Sensor Wand Design

The sensor wand has a dimension of 480 mm length, 63 mm OD (Fig. 2) and weighs 4.8 kg in water. Other than the electrodes mentioned above, the sensor array also has two 1/16 OD titanium thermocouples to measure the hot vent fluids and ambient seawater respectively. The electrodes and thermocouple are pressure sealed by a modified MHM5 Conax fitting with a Viton sealant, contained in a 33 mm OD titanium sheath. The proper seal of Conax fitting needs to apply more than 110 pound • ft torque according to the specification, but normally would crush ceramic electrode. Thus, less torque than that specified is used, although lab tests are usually helpful in determining the optimal torque for each application. Furthermore, the Viton sealant of the Conax fitting tends to leak when the temperature exceeds 50 °C, which is typical for diffuse flow vent fluids. During the real time deployment, the position of the sensor wand will be monitored by the pilot to prevent such situation, which is impossible during the long term deployment in the turbulent diffuse fluids. Thus, for long term deployment, the Conax fitting lacks the reliability when tightened under the insufficient torque. To address these issues, the YSZ ceramic electrode was modified to permit the requisite high torque of the Conax fitting. As shown in Fig. 3, the YSZ ceramic sensor is constructed in two parts: a 6.35 mm OD, 0.76 mm wall thickness, 203 mm length hemispherically ceramic tube (Coorstek ceramic, CO), which is connected to a 6.35 mm OD, 1.0 mm ID, 101 mm length titanium tube. The 1mm ID through hole is EDM (Electrical discharge machining) drilled in a solid rod, allowing the signal wire to go through the center of the tube, meanwhile providing enough space for the O-ring grove. The titanium tube contains two high temperature Kalrez O-rings to accomplish the pressure seal with the ceramic tube. Thus, the titanium tube serves as a transition unit allowing the high torque applied to the Conax MHM5 fitting, which can provide a reliable pressure seal on the seafloor.

The high impedance voltage signal of YSZ ceramic electrode cannot transmit through the non-insulated underwater cable which is a main error source of the high accuracy measurement, thus a preamplifier circuit is used to convert the high impedance signal to low impedance signal (Fig. 2). The amplifier (INA 116) on the circuit has the input impedance of 10^{15} Ω and is powered by DC 5V from the electronics housing. The YSZ ceramic electrode and Ag|AgCl reference electrode are directly wired to the pre-amplifier circuit. The preamplifier circuit is sealed in a plastic housing with a piston for pressure compensation. The wires of the electrodes and DC 5V power are sealed by a Conax fitting (MHM2-040-V). The sensor wand will still function even if there is small amount of water leakage from the main MHM5 Conax fitting. These units are contained in a Titanium housing filled with silicone oil. The housing is designed to stand the pressure of ambient seawater rather than maintain pressure equilibrium, thus the ambient pressure will apply on the ceramic tube to maintenance its connection with the titanium rod.

B. Electronics and Signal Processing

The sensor signals are processed by a 14-bit 8-channel data logger with a RS 232 serial port [8]. A RS232 to RS422 converter is used to transmit the communication signal through the 70 m underwater cable to the junction box of ocean observatory. The data logger also has a 64 Mb Flash

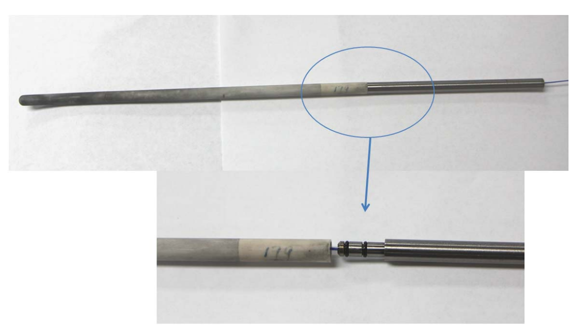

Fig. 3. Construction of YSZ ceramic electrode with a 203 mm length ceramic tube and a 101 mm length titanium tube. Two Kalrez O rings were used for water tight seal between the two parts.

memory for the data storage at the stand-along deployment application.

The eight input channels of the data logger are designated as follows:

CH1: High input impedance electrode/YSZ

CH2: High input impedance electrode/AgCl (high T)

CH3: H2 electrode

CH4: H_2S electrode

CH5: Type E thermocouple 1-high T

CH6: Type E thermocouple 2-low T

CH7: Thermistor input

CH8: On board thermistor

Four chemical sensor channels CH1 to CH4 were measured against the reference AgCl (low T) (Vref), which is wired with the ground. With the potential measured in each channel, the potential used to calculate each chemical parameter can be defined as follows:

$$E_{pH}= E_{ch2}-E_{ch1} \quad (1)$$

$$E_{H2}=E_{ch1}-E_{ch3} \quad (2)$$

$$E_{H2S}=E_{ch1}-E_{ch4} \quad (3)$$

Where the E_{pH}, E_{h2}, E_{H2S} is the potential used to calculate the pH, concentration of H_2 and H_2S. E_{ch1} to E_{ch4} is the potential measured in channel CH1 to CH4 respectively.

III. FIELD DEPLOYMENT

In Sep 2014, the in-situ sensor system was connected to medium power J-Boxes MJ03C (primary node PN3B) of RSN cabled ocean observatory by ROV ROPOS. The MJ03C site locates at Axial Seamount on the Juan de Fuca spreading center at depth of 1530 m [9]. The sensor wand was positioned at the top of a vent chimney (Fig. 4). As shown in Fig. 5, initial in situ data demonstrated a rapid response as the sensor wand reached the vent orifice. The readings of the chemical sensors responded instantly to the temperature of the vent fluid. The measured potential allowed determination of in-situ chemical data at the temperature 285 °C is shown in table I.

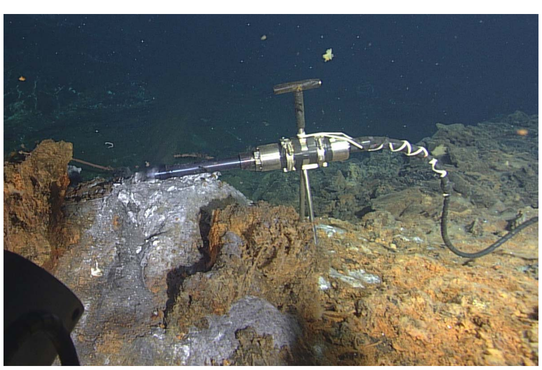

Fig. 4. The sensor instrument was deployed on Axial vent field via MJ03C junction box on RSN cabled ocean observatory.

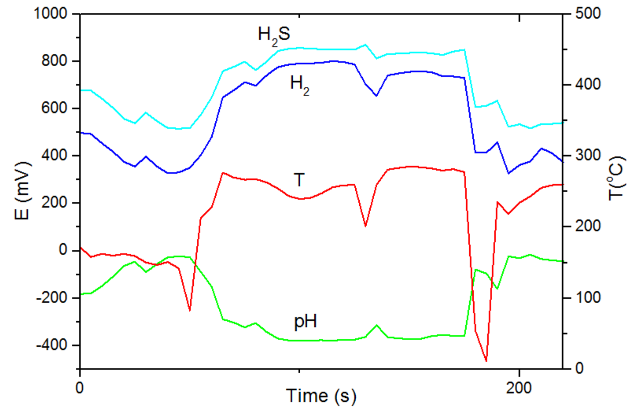

Fig. 5. PH and temperature data obtained from the intial deployment on the RSN cabled ocean observatory.

TABLE I. MEASURED POTENTIAL USED TO CALCULATE PH AND REDOX AT 285 °C

Sensor	Potential (mV)	In-situ value
pH	-373.75	4.64
H_2	755.75	3.5×10^{-2} mmol/kg
H_2S	835.75	2.1 mmol/kg

On cruise of AT26-17 with submersible Alvin and RV/Atlantis, the electrochemical sensor system was deployed during dive #4741 at ASHES vent field on Axial Seamount, Juan de Fuca Ridge. It was also deployed during dives #4743 and #4744 at MEF vent field at depth 2200 meters on the on the Juan de Fuca. The circuit of was reconstructed to be battery powered and equipped with a flash memory and ICL communication to facilitate the submersible deployment as a stand-alone unit. Fig. 6 shows the deployment at Bastille vent during dive #4743.The initial data recorded from this deployment is shown in Fig. 7.

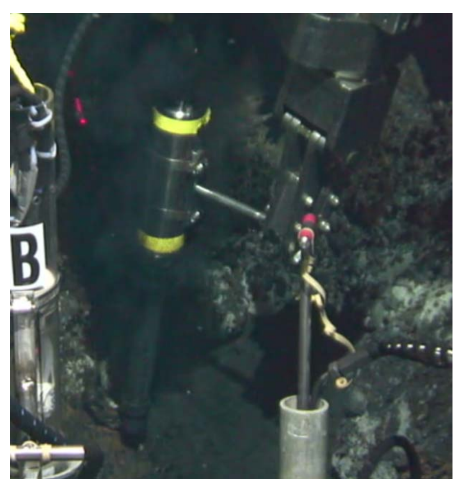

Fig. 6. The modified sensor system was measuring the high temperature fluids at Bastille vent during dive #4743 at MEF vent field with submersible Alvin at depth 2192 m.

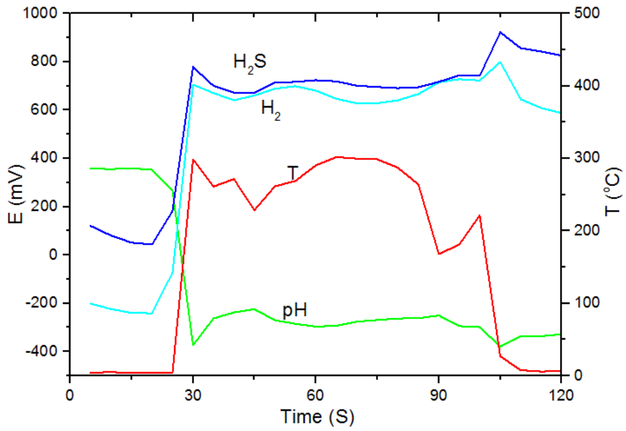

Fig. 7. PH and temperature data obtained from the intial deployment on the Bastille vent during dive #4743 at MEF vent field at depth 2192 m.

IV. Conclusion

To understand the chemical evolution of seafloor hydrothermal fluids continuous records of chemical and physical parameters are required. The recently designed in-situ sensor system provides just such information, both in real time and time series configurations. Thus, in addition to temperature, the electrochemical data can be used to constrain pH, dissolved H_2 and H_2S concentrations in the high-temperature hydrothermal fluids. The YSZ ceramic electrode and sensor wand were reconstructed to meet the long term deployment requirements. Field test at RSN cabled ocean observatory demonstrated that the sensor system was a useful tool to obtain the temporal variations of geochemical processes associated with hydrothermal venting on the mid-ocean ridge (MOR) crest.

Acknowledgement

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