Design and Development of the CO_2 Enriched Seawater Distribution System

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***Abstract*— The kinetics of the reaction that occurs when CO_2 and seawater are in contact is a complex function of temperature, alkalinity, final pH and TCO_2 which taken together determine the time required for complete equilibrium. This reaction is extremely important to the study of Ocean Acidification (OA) and is the critical technical driver in the Monterey Bay Aquarium Research Institute's (MBARI) Free Ocean CO_2 Enrichment (FOCE) experiments. The deep water FOCE science experiments are conducted at depths beyond scuba diver reach and demand that a valid perturbation experiment operate at a stable yet naturally fluctuating lower pH condition and avoid large or rapid pH variation as well as incomplete reactions, when we expose an experimental region or sample. Therefore, the technical requirement is to create a CO_2 source in situ that is stable and well controlled. After extensive research and experimentation MBARI has developed the ability to create an in situ source of CO_2 enriched seawater (ESW) for distribution and subsequent use in an ocean acidification experiment. The system mates with FOCE, but can be used in conjunction with other CO_2 experimental applications in deep water. The ESW system is completely standalone from FOCE.**

While the chemical changes induced by the addition of fossil fuel CO_2 on the ocean are well known and easily predicted, the biological consequences are less clear and the subject of considerable debate. Experiments have been successfully carried out on land to investigate the effects of elevated atmospheric CO_2 levels in various areas around the globe but only limited work on CO_2 impacts to ocean environmental systems have been carried out to date. With rising concern over the long-term reduction in ocean pH, there is a need for viable in situ techniques to carry out experiments on marine biological systems. Previous investigations have used aquaria that compromise these studies because of reduced ecological complexity and buffering capacity. Additionally, aquaria use tightly controlled experimental conditions such as temperature, artificial light, and water quality that do not represent the natural ocean variability. In order to study the future effects of ocean acidification, scientists and engineers at MBARI have developed a technique and apparatus for an in situ perturbation experiment, the FOCE experimental platform. At the time of this writing the FOCE system and associated ESW are attached to the Monterey Accelerated Research System (MARS) cabled observatory. Engineering validation and tuning experiments using remote control and real time experimental feedback are underway. Additionally, an extensive instrumentation suite provides all of the necessary data for pH calculation and experimental control.

The ESW is a separately deployed system that stores and distributes CO_2 enriched seawater. It receives power and communications via an underwater mateable electrical tether. The CO_2 enriched seawater is pumped into the FOCE sections from the ESW. This paper describes the design, development, and testing of the underwater ESW Distribution System as well as the software control algorithms as applied to FOCE. The paper covers the initial prototype, lessons learned, and the final operational version.

Keywords-ocean; acidification; pH; CO_2; underwater; perturbation; chemistry; MARS; MBARI;

I. Introduction

Scientists and engineers at the Monterey Bay Aquarium Research Institute (MBARI) have been carrying out a series of experiments over several years to better understand the long term effects of ocean acidification (OA). Currently, the ocean is absorbing on average 1 million tons of fossil fuel CO_2 per hour. Over the past 100 years, this has caused a decrease in the ocean's pH level by approximately 0.1 units. Based on the International Panel on Climate Change (IPCC)[1] Report AR4, the trend is predicted to continue with a further decrease by a minimum of 0.2 pH units the next century[2].

MBARI recognized early on that in situ results frequently give contrasting data to laboratory based experiments. This fundamental driver was the idea that brought about the creation of the Free Ocean CO_2 Enrichment (FOCE) experiments. The FOCE concept was created to provide scientists with an underwater platform for performing long duration in situ perturbation experiments[3]. Experimental site selection was dictated by the location of the Monterey Accelerated Research System (MARS)[4] cabled node. The depth of the node is close to 890 meters with an average temperature of 4.5ºC, which presented us with a series of technical questions. How do we deliver a source of CO_2 without a shore-based source? How do we conduct laboratory based experiments in the natural environment at reduced temperature and increased pressure[5]? How do we study organisms that may have a slow response to a reduced pH?

The MARS observatory supplies power and Ethernet communication to the FOCE system through one of 8 available ports. Graphical User Interface (GUI) software developed at MBARI gives the users real-time control over the instrumentation, allowing for adjustments during experiments. The software interface to FOCE allows the direct manipulation of pH and CTD sensors, internal water velocity control, multiple camera views and control of the enriched seawater distribution rate. Real-time feedback of sensor data and live video allow the user to monitor the direct effects of their experiments.

To accomplish the controlled release of CO_2 for OA experiments a method of storing and distributing the CO_2 enriched seawater was necessary. Some of the design requirements for the system included: a need to deploy the ESW separately from FOCE, ability to refill with CO_2 as needed, control of the ice-like hydrate layer formed, complete containment of the CO_2 enriched seawater, and the ability to accurately meter out the pH altering seawater.

II. BACKGROUND

A. FOCE

The deep water FOCE is comprised of three main sections: a center experimental chamber, and two 3 meter long wings that provide the time delay needed to complete the CO_2 reaction with ambient seawater. The dimensions of deep FOCE are 10 meters long, 1 meter wide and 0.5 meters in height (Figure 1). It should be noted the dimensions of any FOCE system are site and experiment specific. The center chamber has a hinged lid which allows scientists to add or remove animals of interest to the FOCE system.

A full instrumentation suite provides the user with a comprehensive data set. Internal to the deep FOCE are four pH sensors (two forward and two aft), a CTD, a velocimeter, forward and aft thrusters to manipulate internal current speeds, forward and aft cameras and lights, and a center video camera with external lights. External reference instruments include two pH sensors, an ADCP, and a CTD. The deep FOCE attaches to MARS via a 30 meter underwater mateable tether which provides 375Vdc and Ethernet communication.

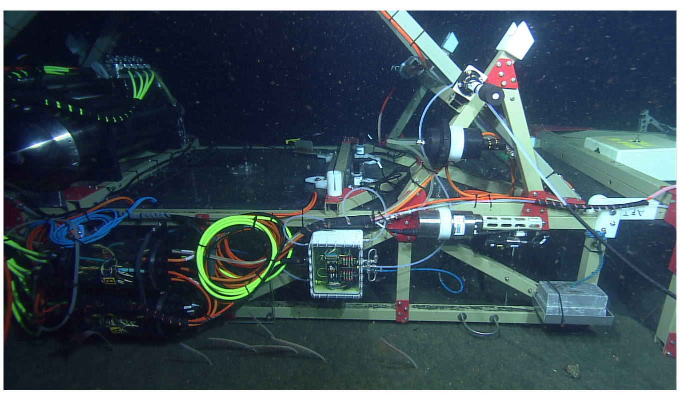

Figure 1: Center chamber of FOCE

B. MARS

The MARS cabled observatory resides in the Monterey Bay approximately 22 miles from Moss Landing at a depth of 890 meters on the Smooth Ridge of Monterey Canyon (Figure 2). It contains eight ports, each capable of delivering 1kW of power at either 375Vdc or 48Vdc with real time communication via 100 Mbps Ethernet communications for each port.

Figure 2: MARS Cabled Observatory

III. EVOLUTION OF THE ENRICHED SEAWATER SYSTEM

The final deployed Enriched Seawater Distribution System was the result of a stepwise approach to deep ocean CO_2 research. A number of experiments were performed and various apparatus developed in order to better understand the dynamics of CO_2/seawater mixing at depth. Each of these technologies and system tests led to the final ESW design. Key to this effort was fully understanding the initial functional requirements and taking those into consideration for each design during the prototype and experimental phases.

A. Initial Science Experiments

The first step in designing a deep-water pH laboratory was to understand the dynamics and kinetics of the chemistry associated with CO_2 equilibrating in seawater at all of our potential operational depths. The effect of pressure on the equilibrium state of chemical species in seawater can be readily calculated given the partial molar volumes of the reactants. However, there was no way to compute a priori the effects of pressure and temperature on the reaction rates. To address this we outlined an experiment to measure in situ the reaction rates and compare them with the laboratory established reaction rates to provide a baseline for future in situ engineering designs.

The experiment consisted of a valve injection system carried to various depths by the ROV *Ventana* (Figure 3). The system injected seawater enriched with liquid CO_2 into a test chamber and measured the pH shift over time. In this manner the equilibrium rate at each depth was found. These rates were found to be in excellent agreement with the Zeebe & Wolf-Gladrow model[6] over other published CO_2 reaction rate papers. From these measurements we calculated a series of curves for τ, or the relaxation time for a CO_2 reaction at a given depth (pressure) and temperature. Using these curves, a 3τ time will yield 96% equilibrium of CO_2 in seawater.

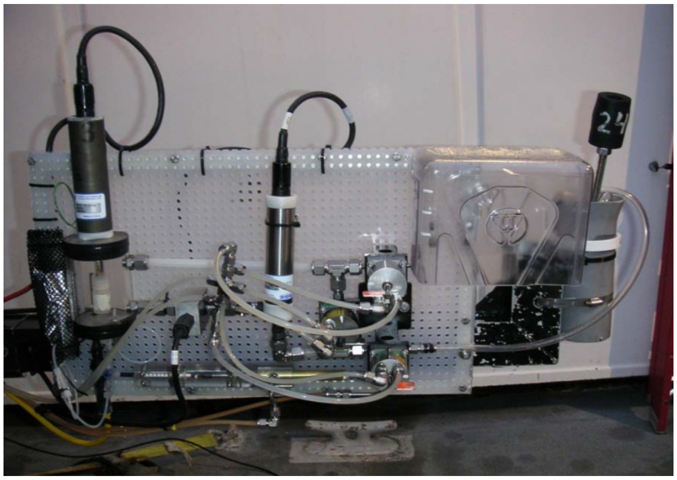

Figure 3: Peg board experiment used to calculate τ at various depths

Due to the cold temperatures of our FOCE deployment location at MARS, the next step was to verify the anticipated pH shift with the calculated path length and measured water current velocities at the specified depth. A four meter section of eight inch internal diameter plastic duct hose was fitted with a motor driven thruster at one end. The other end had a small simulation chamber of a basic FOCE chamber (Figure 4). A container with 56 liters of CO_2 enriched seawater equilibrated at sea level was prepared and attached to the apparatus through a pump. The experiment was housed in a tool sled on the ROV *Ventana* (Figure 4). At a depth of 1000 meters, the CO_2 enriched seawater was injected into a flow of surrounding seawater and pumped through the hose at various velocity rates. The results demonstrated the expected pH shift[3] as determined by our calculations.

Figure 4: Path length verification experiment on ROV *Ventana*

B. Engineering Tests

Once the team was satisfied with the path length requirements, the design moved forward with the actual FOCE flume and ESW systems.

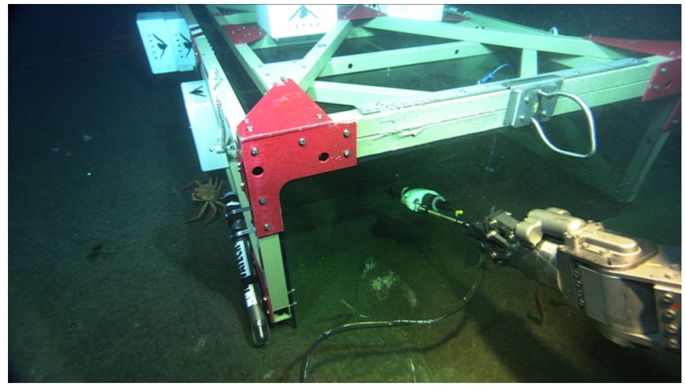

Figure 5: Wand injection of CO_2 enriched seawater into FOCE

The next test was focused on the path time delay incorporated into the FOCE system that was deployed at the MARS site. The ROV *Ventana* was once again sent down to perform a series of pH shift experiments using a sea level saturated mix of enriched sea water. As before, several carboys were filled with CO_2 enriched seawater and mounted to the ROV. This set of experiments verified that FOCE system could accurately measure modified pH reactions over a number of controlled rates via the fan thrusters. A wand was attached to the arm of the ROV enabling the enriched seawater to be pumped out in a specific direction (Figure 5). Once the ROV was onsite, the wand was positioned near a seawater entrance at one end of FOCE and the internal thruster fans activated. The FOCE GUI (Figure 6) clearly shows the pH probes measuring the plume transiting through the experimental chamber to the second set of pH probes and the separation of low pH water at timed intervals based on velocity control. The transit time was also shown to be adjustable by changing the velocity of the fan thrusters.

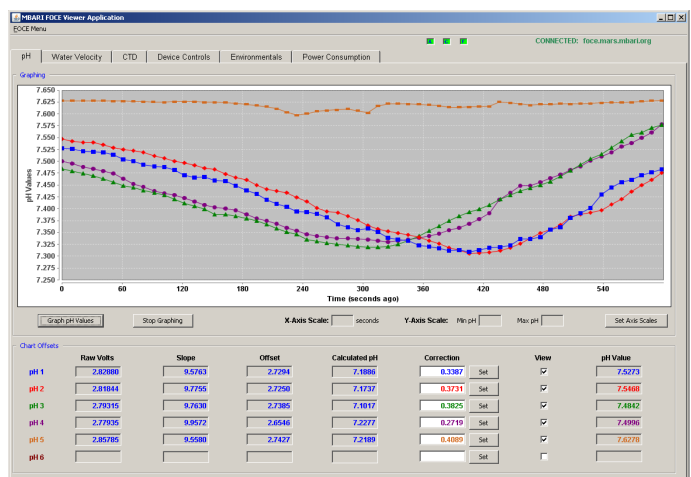

Figure 6: GUI displaying pH readings during wand injection test

The next step in the design process was to create a useful volume of CO_2 enriched seawater in situ and to be able to contain and distribute the fluid to the deep FOCE. However, due to buoyancy and hydrate skin formation on the liquid CO_2 at the depths and temperatures for deep FOCE we had another experiment to perform first. The potential problem was the interaction of seawater at the boundary layer between the liquid CO_2 and the ambient seawater. Prior CO_2 experiments had demonstrated that under certain conditions the hydrate-forming reaction can occur and CO_2 hydrate grows uncontrollably. Before committing to a deployable system fully outfitted with an instrumentation suite, we needed to test something simple which imitated the final concept well enough that we could trust our ESW system would work. This test required using a suitable amount of liquid CO_2 necessary to perform a multi-week experiment, and accounting for the natural phenomena that liquid CO_2 at our MARS site is buoyant. Fifty liters of liquid CO_2 would yield a two week duration experiment. The design for this experiment took advantage of the CO_2 buoyancy condition. A simple box-like structure was built with a partial opening below allowing the seawater to flow across the CO_2 hydrate interface. The open box measured 0.5 meters x 0.5 meters x 0.5 meters tall and was deployed adjacent to one end of the FOCE flume, fully covering that entrance. Internally, a horizontal sheet divided the internal volume into an upper and lower section. Two openings in this sheet allow ambient seawater to flow into and out of the upper volume. Vertical openings at each end allowed ambient water to pass through, become acidified, and then be drawn into the FOCE flume. A filling port allowed the addition of liquid CO_2. This design would not only allow CO_2 to be stored locally, but also allow us to monitor the boundary layer if the reaction went uncontrolled. We could calculate the actual use of CO_2 by looking at the pH changes in the FOCE system.

Once the upper portion was full of liquid CO_2, activation of the FOCE fan thruster drew seawater into the FOCE flume from the direction of the open-box that showed the ESW test was working. While not meant to be a long-term solution due to the open frame construction, this experiment did demonstrate that a hydrate layer between the CO_2 and the seawater was not an inhibitor to the concept and we had a very good chance of forming enriched seawater in situ. Now the problems became clear, how do we deliver liquid CO_2 safely to a remote site at 890 meters and implement metering of the resultant acidified fluid. It must also be noted here that CO_2 is not compatible with many materials, particularly Buna-N rubber and many plastics used in tubing, and aluminum. Some in depth engineering investigation was needed before we proceeded with a final design.

C. The First Generation Enriched Seawater System

As stated prior, due to the remote location of the FOCE frame, CO_2 must be delivered and stored locally. The prior testing of the box had gone well and the technical teams first thought was not to stray too far from this success. The ESW prototype was therefore designed with that thinking and to store as well deliver CO_2 enriched seawater in a manner that provided a selectable low pH condition in the experimental chamber of the FOCE frame. This next design of the ESW consisted of a rectangular enclosure, a one-atmosphere electronics housing, a brushless DC motor, a sight glass and a louver mechanism with position feedback. The louver system actuated two blades that closed and opened as requested to allow controlled seawater flow across the bottom of the liquid CO_2. The concept was to open and close the louvers much like a carburetor and enable the ratio of the two fluids to be altered quickly (Figure 7).

Power and communication to the ESW prototype were supplied from FOCE via an underwater mateable tether. The power was 375Vdc and the communication was 10BaseT Ethernet. The ESW prototype electronics can consisted of inrush limiting circuitry, a 24Vdc converter, an Ethernet-to-serial converter, and basic environmental monitoring. The serial connection was run out to the ELMO motor controller, which also used 24Vdc.

The main body of the ESW was a large rectangular stainless steel enclosure divided into an upper and lower section similar to the previous simple box experiment. The upper section stored the CO_2 and a mix of enriched seawater. Dividing the two sections was a plate with two mechanically actuated louvers. The lower section had a vertical opening on one side that matched the dimensions of the opening to the FOCE wing sections. By positioning the ESW prototype next to the FOCE flume and incrementally opening the louvers while the FOCE fan thrusters were activated, a variable amount of enriched seawater flowed into the FOCE frame.

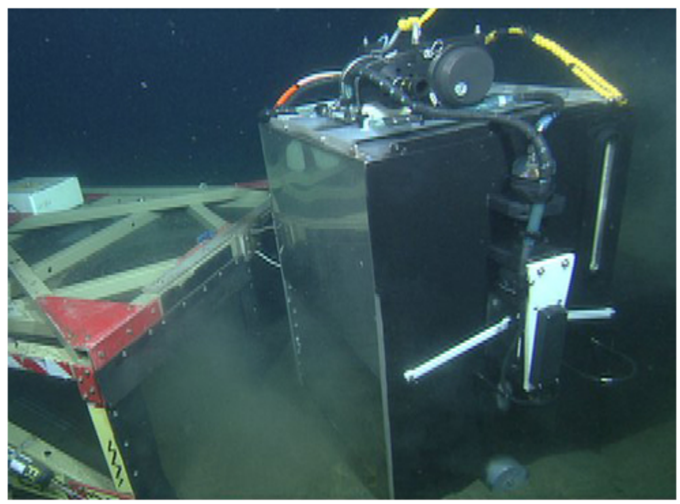

Figure 7: Prototype version of ESW

The louvers were positioned by command of a brushless DC motor and motor controller. Positional feedback of the louvers was determined via a magnetically sensitive feedback board. The louver feedback board was a potted circuit board with sixteen Hall effect sensors. A magnet mounted to the mechanical arm attached to the louvers slid past the board to indicate one of sixteen discrete positions.

The ESW prototype was filled with CO_2 through a port located just above the horizontal louvers. The liquid CO_2 was delivered by the ROV *Ventana* on a specially prepared toolsled equipped with carbon fiber piston accumulators capable of carrying the liquid CO_2 from the surface to the seafloor. The internal volume of this first ESW was 198 liters and was nominally filled with 40 liters of liquid CO_2. This quantity resulted in an enriched seawater mix with a pH under 4.0 but would drop to 3.4 pH or lower if given greater time to equilibrate.

Two experimental fillings were performed with mixed results. A pre-determined amount of enriched seawater could be sent through the FOCE flume and the expected pH was read via multiple pH sensors. However, it was soon discovered that once the process started, it could not be easily controlled or stopped. Because the density of the CO_2 enriched seawater is greater than that of the ambient seawater, any gaps or incomplete sealing around the louver mechanism would allow the enriched seawater to leak out. The only way to control pH within our desired conditions inside the FOCE was to keep the experiment running continuously until the CO_2 was exhausted. This issue was confirmed by monitoring the two external pH probes on the FOCE frame and observation of the background pH being inarguably outside the range of deep-sea water pH.

IV. The Enriched Seawater System

The second generation ESW (Figure 8) was designed to overcome the issues associated with the earlier version. The new design needed to control and contain the enriched fluid better and allow for experiments to be stopped and started as desired. Other issues that were not critical but we wanted to address were the hydrate frothing of the CO_2 during filling and increasing the internal volume to allow for longer experiments. The ESW would also need a pump - this was an added complexity that we had tried to avoid with the previous louver design. We required a positive displacement pump made from materials that could survive a highly enriched CO_2 acidified fluid (pH ~3) and the occasional presence of unreacted liquid CO_2. This presented a series of new technical challenges, however we had already investigated some potential solutions during the earlier concept design phase, so the material compatibility issue was the most immediate concern.

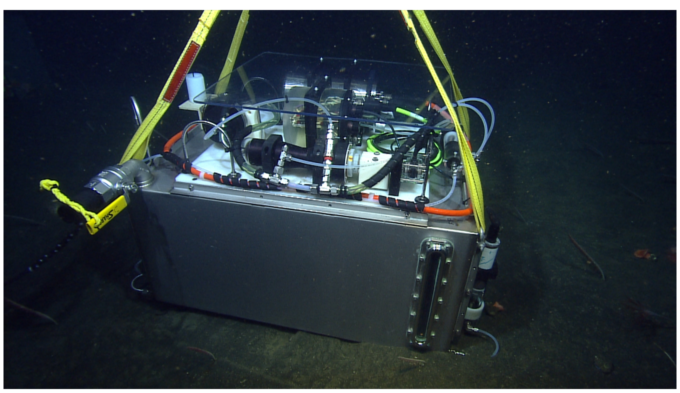

Figure 8: Enriched Seawater System

A. Mechanical

The ESW final design provides CO_2 enriched seawater to the FOCE frame from either end through the use of a valve control box (discussed in a subsequent section), to create the desired long-term low pH environment.

The delivery system was again comprised of a 316 stainless steel sheet metal tank. The tank was configured in a lengthened rectangular fashion to optimize surface area between the seawater and CO_2 thereby maximizing chemical interaction. The stainless steel containment tank capacity was increased to contain 240 liters. It also incorporates a slightly trapezoidal cross-section (36 in. long, 16 in. tall at one end, 18 in. tall at the other end, and 24 in. wide) resulting in a slanted bottom (Figure 9). This was intended to allow full use of enriched seawater by once again using the density difference with the most enriched seawater being slightly denser than un-enriched seawater. As seawater is pulled into the box by pumping out the enriched seawater it floats up and contacts the buoyant liquid CO_2. As the "fresh" seawater becomes saturated with CO_2, it becomes denser and sinks inside the box. This natural dynamic cycle serves to stir the seawater inside the CO_2 box and ensures we have a constant supply of low pH water available. The enriched seawater sinks to the deeper end of the tank where the outlet to the peristaltic pump is located. The tank also incorporates an inlet/fill valve at the top of one corner and an identical drain valve at the lowest point of the tank. The inlet/fill valve contains a receptacle that the MBARI ROVs can use for filling and re-filling the tank with liquid CO_2. The capability to refill was a key feature for the ESW. Having the ability to return and fill the ESW tank again and again enables experiments of almost entirely unrestricted duration. The location of the fill at the top of the tank corrected the frothing hydrate issue seen in the previous design and also minimizes potential hydrate blockage during filling. Once the tank is filled, the valve is shut and the filling wand removed.

The valves on the box also have the important job of permitting flooding of the box during deployment to the seafloor and venting/draining on recovery. A safety vent has also been incorporated into the tank preventing over-pressuration upon recovery. One end of the vent is placed at the bottom of the tank and the other end is above the top of the tank in a “goose neck” arrangement. The vent allows displaced seawater to flow out during CO_2 filling, and seawater to flow in as the enriched seawater is pumped into FOCE. This technique eliminates the use of a check valve with moving parts, springs and inherent material corrosion issues with seawater and CO_2 enriched fluids.

Stainless steel angles are welded to the external faces of the tank to provide rigidity and permit components to be mounted as well as providing lifting points. Every effort was made to minimize holes in the tank that could turn into leak paths.

A sight glass has been incorporated as a visual indicator of the level of the liquid CO_2 inside the box. Keeping in mind that the experiments will be deployed nominally for over a year, seals on the sight glass used PTFE to minimize gas absorption. All external components mounted to a UHMW plastic plate on the top of the tank. A recess was designed into the bottom of the UHMW plate allowing flow of seawater between the plate and tank to eliminate developing a large anoxic and corrosive area against the stainless steel.

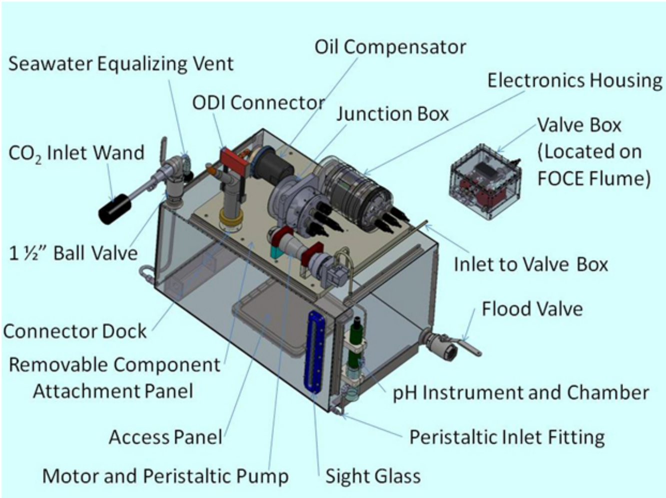

Figure 9: Mechanical schematic of the ESW

B. *Electronics*

The electronics of the ESW provide greater operational flexibility and more precise enriched seawater distribution than in the earlier version. There are four major components to the electrical system: the main electronics housing, peristaltic pump control, pH monitoring, and a dual valve directional system.

The main ESW electronics housing is mounted on the top of the ESW box and distributes all power and communication to the subsystems via three electrical penetrators. It provides inrush limiting to the 375Vdc input voltage, which is down converted by a 24Vdc Vicor module. 12Vdc and 5Vdc are also generated from the 24Vdc bus for use on lower level subsystems. Power and environmental monitoring are handled through custom made circuit boards. Ethernet-to-serial conversion is handled via a Digi serial server. There is no computer in the ESW; all control is handled through the main FOCE computer.

The peristaltic pump is used to precisely meter out the enriched seawater to the FOCE flume. It is driven by a brushless DC motor and an ELMO motor controller. The motor and controller are housed in an oil compensated housing, therefore all of the components must be pressure tolerant. The ELMO uses 24Vdc and serial communication; onboard flash memory allows for remote programming and tuning of parameters. The motor has a built in 15:1 gear reduction box which allows for a maximum of 720 RPM at the pump. Based on the necessary flow rates of the enriched seawater, the pump is never driven higher than 300 RPM.

The pH probe is inline with the exit tubing and it monitors the enriched seawater as it leaves the ESW. The digital pH probe is custom made with a full measurement range of 0 to 14 pH units. It uses 12Vdc and serial communication.

The dual valve directional system resides on the FOCE frame but is controlled via the ESW software. It allows the enriched seawater to be delivered to either end of the FOCE flume. The electrically actuated valves are housed in an oil filled housing. They operate from 24Vdc and use serial communication.

Ethernet communications and 375Vdc are supplied from a ten meter underwater mateable cable which connects to FOCE. The enriched seawater is delivered via 1/4 in. O.D. tubing between FOCE and the ESW.

The power consumption of the ESW is expected to be no more than 75 Watts when pumping and approximately 15 Watts when in monitoring mode. This power usage is combined with the main FOCE frame and is still well under the allotted usage of a typical MARS port.

C. *Control Software*

The deep ocean FOCE pH control system uses the ESW to inject carbon dioxide enriched seawater into the control chamber to lower the pH inside the chamber to a value representing an offset from the external environment.

The ESW does not include software systems itself apart from firmware to monitor conditions inside the electronics housing. It does present serial communication interfaces to control the ESW pump motor controller and environmental monitoring system. Since the serial communications ports are implemented using Ethernet to serial converters, the ESW system interface is simple and flexible, and suited to remote operation and distributed control. This generic interface makes it easier to integrate with different FOCE implementations.

The pH control system used for deep ocean FOCE combines SIAM (Software Infrastructure and Applications for MOOS), a distributed observing system middleware implementation developed by MBARI, with Open Source Data Turbine (OSDT), an open-source distributed data streaming package, used to enable communication between instrument services and control software (Figure 10).

MBARI developed SIAM to manage its deployed ocean sensor networks, e.g. the Monterey Ocean Observing System (MOOS). SIAM instrument services "wrap" and encapsulate manufacturer-specific instrument protocols with a generic SIAM network interface.

This uniform IP network interface (based on Java RMI) enables client software to access the many different interfaces presented by the instruments in a consistent way. It also enables architectural flexibility, allowing SIAM to be run anywhere on the network. FOCE uses SIAM for data collection, and the FOCE GUI (described below) is a SIAM client. SIAM operates within the deployed FOCE electronics so that experiments will continue even if the network connection is interrupted.

The deep ocean FOCE uses SIAM to collect data from all of its instruments and to implement the pH control system. The ESW pump and valves each have dedicated SIAM instrument services. These services are directed by the pH control service, or may optionally be directed by other clients, for example the FOCE GUI, or manually using SIAM clients.

Another SIAM service monitors the status of the ESW subsystem electronics, recording bus voltages, electronics housing temperature, humidity and water alarm status.

Data from FOCE is archived using MBARI's shore side data system (SSDS)[7]. In addition to the FOCE GUI, OSDT clients like Real Time Data Viewer (RDV) may be used to visualize FOCE data streams.

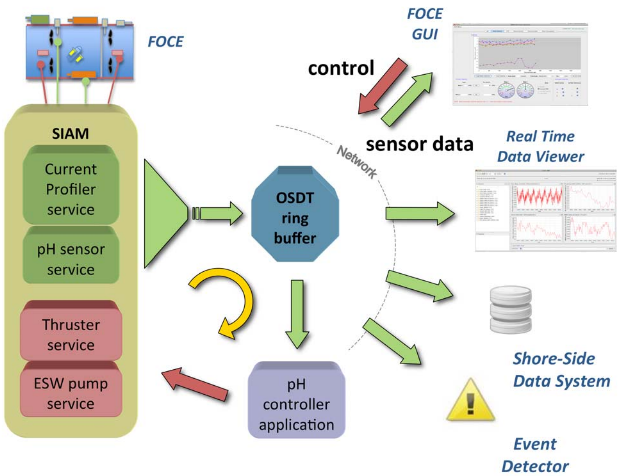

Figure 10: FOCE/ESW control system architecture

D. GUI Software

Communication with the ESW is handled by the FOCE GUI via JAVA Remote Method Invocation (RMI). The GUI (Figure 11) controls the closed loop system operation as well as manual control over the ESW subsystems. The GUI also displays all experimental data and environmental and power monitoring feedback.

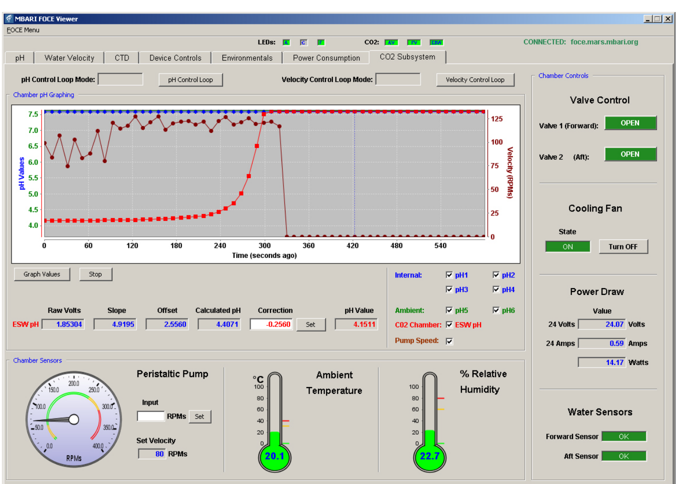

Figure 11: CO_2 tab of the FOCE GUI

V. DEPLOYMENT

The ESW was deployed in May of 2011 from the R/V *Pt. Lobos* and positioned on the seafloor using the ROV *Ventana.* The ESW is physically located approximately three meters away from the FOCE frame which allows the ROV to easily access and fill the ESW with liquid CO_2 without interfering with FOCE. The electrical tether and seawater tubing were connected to the FOCE frame. It successfully powered up, and although there was no CO_2 delivered during that deployment, the peristaltic pump was monitored visually and water movement to the FOCE frame was verified.

For the next month, testing of the subsystems proceeded without incident. In June of 2011, CO_2 was delivered to the ESW via the ROV *Ventana*. Similar to past experiments, we used the 56 liter carbon fiber piston accumulators to deliver liquid CO_2 to the ESW. Our initial fill of the ESW amounted to approximately 100 liters of liquid CO_2. The sight glass on the ESW clearly showed the CO_2/seawater boundary. The measured pH of the fluid exiting the ESW enclosure was 3.60.

VI. ESW RESULTS IN TESTING WITH FOCE

An initial set of pH tests with the ESW attached to the FOCE frame were performed to verify proper system operation. The two primary controls available during these tests were the velocities of the internal FOCE fan thrusters and the ESW pump. Adjusting the FOCE fan thruster velocity affects both the dynamics and kinetics of the pH chemistry. Dynamically, the velocity of the fan thrusters controls the transit rate of the CO_2 enriched seawater through the FOCE flume. The transit rate, in turn, affects the ratio of the ambient and enriched seawater. The ratio of the two fluids then determines the final reaction time. The slower the fan thruster, the longer the lag time between when the enriched seawater first enters the FOCE flume and when it reaches the center experimental section. The longer the lag time, the more reaction time is available, and therefore the closer the measured pH will be to equilibrium. Adjusting the velocity of the ESW pump affects the fluid mixing ratio (between the background seawater and the CO2 enriched seawater), this changes the end-point pH which in turn affects the kinetics of the pH chemistry. The more ESW added, the lower the end-point pH and the faster the kinetics of the reaction.

One such test was to confirm the system could reach the expected pH level as a function of ESW pump speed. To ensure proper reaction time in the FOCE flume, the internal fan thrusters on FOCE were set to a fixed velocity. The peristaltic pump on the ESW was then activated and held steady for 30 minutes in 50RPM increments (Figure 12). The expected pH drop at each pump speed was measured by the four internal FOCE pH probes. The two external FOCE pH probes also measured some variation in pH level. This was the result of bottom water currents driving the pH altered seawater exiting FOCE back towards our external pH probes.

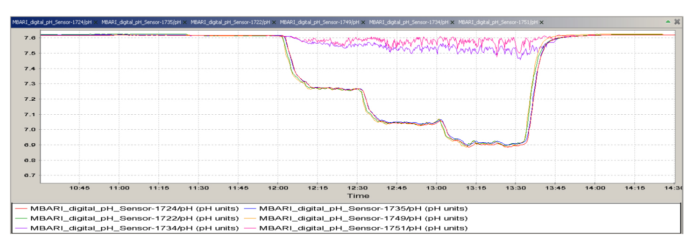

Figure 12: Internal and external FOCE pH measurements using the ESW system

VII. CONCLUSION

The Enriched Seawater System was successfully developed through a series of planned experiments to address a variety of scientific and technical issues. Once the scientists and engineers had completed the preliminary series of in situ experiments, our first ESW system worked but showed that it could be improved. We learned that our initial thoughts, although a more difficult path to execute, were critical to the proper operation of CO_2 enrichment to all potential in situ science experiments.

Data collected with the FOCE system demonstrated that the ESW can fully support in situ ocean acidification research needs and based on the measured flow rates through the FOCE system the ESW provides approximately four weeks of suitable CO_2 enriched seawater and delivers it with precision (+/- 0.01 pH units). These results of course depend upon the structure and quality of the in situ experiment and the controls in place that demand enriched seawater from the ESW. Depending upon these parameters and variables, we believe that the ESW system is capable of supporting even finer pH control of an enclosed experiment.

The next phase of the ESW is to add another suite of instruments to measure oxygen and to add an additional port for introducing sodium sulfite as a way to manipulate dissolved oxygen concentrations. This additional capability will allow the ESW to support experiments looking at the respiration index[8] and metabolic thresholds that may limit survival for ocean animals. This work is critical to understanding and defining the expansion of "dead zones" and provide modelers the necessary data to predict the alternation of these O_2 to CO_2 ratios and how biota will be forced to migrate or otherwise adapt to future oceanic conditions.

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