Engineering Development of the Free Ocean CO_2 Enrichment (FOCE) Experiment

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Abstract - **Globally, the burning of fossil fuels for energy production produces over 25 gigatons of CO_2 per year and this material is released directly into the atmosphere. While approximately half of the CO_2 has remained in the atmosphere long-term, most of the rest has been absorbed by the surface ocean. This has resulted in a lowering of the surface ocean pH by about 0.1 units since the beginning of the industrial revolution and if society is able to stabilize atmospheric CO_2 levels at twice their pre-industrial concentrations will result in a lowering of surface ocean pH by 0.25 units. While many are asking the question of whether we should pursue direct ocean CO_2 sequestration, the FOCE experiment is asking what will be the impact of the pH change on the ocean. In order to address this question, MBARI science and engineering have designed a small-scale in situ CO_2 enrichment experiment to assess the chemical and biological impacts in a manner analogous to the land-based Free Air CO_2 Enrichment (FACE) experiments. This prototype design is testing the ability to control pH within a fixed but freely exchanging volume of sea water. The technology concept for the experiment is based on a small ring structure using a central valve to direct the flow of pH altering fluid. The initial phase of the project uses concentrated HCl mixed with sea water and includes directional and volume control to achieve a desired pH offset. Control feedback is obtained by using pH sensors in the center of the control volume. Other aspects of the design that address the inherent time delays and noise of the associated pH signal are also discussed. Test results will show the capability of the system to maintain close loop control of pH in a given volume. Sea trials then demonstrate the ability of this initial system at a selected site to control pH to specified average level over a given amount of time. Further discussion includes systems in-situ results analysis, corrective actions, upgrades, and the anticipated next phase for FOCE including the use of CO_2 addition to change the local chemistry.**

I. INTRODUCTION

Ocean CO_2 sequestration concepts and questions are an important societal question, and provide interesting experimental opportunities for science researchers and the engineering staff at the Monterey Bay Aquarium Research Institute (MBARI). Debate has proliferated from the early idea proposed by Marchetti in 1977 [1] with little consideration to testing the theories about the technology and associated environmental concerns. With easy access to the deep ocean, along with teams of science and engineering at the same facility, MBARI decided to venture into in-situ experimentation and provide some insight into the questions being posed. The prevailing ideas in favor of ocean sequestration work from the principle that the ocean is a big place and can absorb a tremendous amount of CO_2. This is true, but it is also true the ocean is currently holding 50 times the atmospheric burden of CO_2. The chemistry of seawater is slightly basic which makes the uptake of CO_2 a passive process. However, as CO_2 is absorbed, the ocean pH must drop until the natural processes of rock weathering restores the ocean to it's pre-industrial pH value.

The current situation is that a third of the anthropogenic CO_2 emissions are absorbed by the ocean annually, this equates to 7 giga-tons per year. As the atmospheric levels of CO_2 increase the chemical disequilibrium will create a similar response in ocean absorption. Eventually the ocean will absorb 80% to 90% of the worlds anthropogenic CO_2. At the moment it is estimated that there is about 500 giga-tons of anthropogenic CO_2 in the world's upper ocean waters. The result is a pH change of -0.1 in the upper ocean that will continue to decrease over this century another -0.2 units if current rates of CO_2 emissions continue [2].

The Free Ocean CO_2 Enrichment (FOCE) experiment was created to provide a test platform for addressing issues associated with pH change in the ocean. FOCE has been designed to create a selected lower pH environmental condition, control it within discrete limits, and allow for in-situ multi-discipline science experiments while also conducting monitoring observations. FOCE will provide a knowledge base for predictive experiments to better understand the impacts of a lower pH ocean.

II. FOCE CONCEPT

To date MBARI has performed a series of small scale CO_2 release experiments. These experiments have focused on the chemistry and dynamics of liquid CO_2 at a variety of depths and temperatures. Studying CO_2 hydrate formation and dissolution has helped establish the dissolution rates and equilibration fundamentals. The same experiments have correlated the amounts of CO_2 released and the observed pH disturbances of the surrounding water. Other studies have observed the impacts on the local biota [3]. In the early experiments using pooled CO_2 as the source problems were quickly observed with extreme pH variations of -2.0 units.

On land, there are analogous experiments in CO_2 enrichment routinely carried out on a large scale called the Free Air CO_2 Enrichment (FACE) [4]. One example of is the experiment shown in Fig. 6. The towers release CO_2 into the local air at controlled rates to bathe the local vegetation in anticipated levels of CO_2 that simulate the conditions for the later part of this century. Release rates are controlled using wind speed and direction. One FACE site releases about 1,000 tons CO_2 per year.

Fig.1: A FACE (Free Air CO_2 Enrichment) experiment in Wisconsin.

The FOCE system concept is based upon the success of the FACE systems. The specifications were modified to address the environmental differences of being in the ocean, such as, working with an incompressible fluid, current, chemistry, mixing dynamics and closed loop control variables. The initial concept can be seen in Fig. 2. One key decision was to use hydrochloric acid (HCl) in place

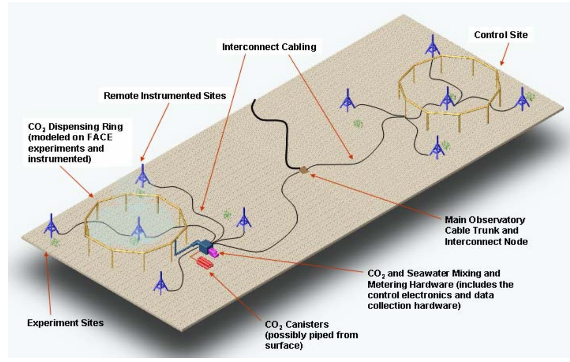

Fig.2: FACE Concept as part of a cabled observatory

of CO_2 for the early experiments. Using HCl is convenient and quickly confirmed our initial concepts for adjusting sea water pH. Once the test concept is proven the design will allow for easily switching over to CO_2 in the future. A primary science requirement was for continuously monitoring pH and to use it as the primary variable for input control. This approach presented several challenges since the dynamics of pH change is dependant on temperature, pressure, and time for either acid or CO_2. Additionally, it was recognized that a variable time delay exists in the system based on the FOCE system scale. Small currents or a large control area would have significant delays. The delays are compounded by a need to manage the buoyancy of acid or liquid CO_2. To address the first issue concerning the effect of variable current speeds the experiment was limited to 10 cm/sec minimum and 30 cm/sec maximum as part of this technology demonstration. These current speeds would allow the system to have enough time to react and obtain a perceptible pH change. Continuously pumping a premix of acid and sea water minimizes the differential in buoyancy. By restricting the magnitude of the pH change, the FOCE prototype could demonstrate the feasibility of the concept without substantial engineering investment.

The FOCE prototype is a scaled down version of the concept in Fig. 2, intended to provide proof of the concept while accommodating the system engineering in a rapid fashion. This approach allowed the team to build, integrate, tank test, and obtain results from an at sea deployment within 3.5 months. Using a small length of wet mateable cable the system is tied to ROV *Ventana* for power and uses Ethernet for system command, control and data logging.

III. FOCE TECHNOLOGY

The FOCE design is comprised of a series of subsystem components; FOCE Frame, Directional

Control Valve, Mixers and plumbing, Controls, pH Instrumentation, and Science Instrumentation. Each subsection was designed and built to be as simple as possible while being assured of later integration. This made the rapid program approach more manageable. Also, the selection of subsystem components was a trade-off of delivery times and cost estimates. Compromises were made to use what was mostly on hand or could be readily manufactured with the machine tools and equipment at MBARI. This prevented long lead items from delaying the project and guaranteed the system would be ready by the scheduled deployment date.

A. The FOCE Frame

The frame is a simple 6061 aluminum weldment with cross wire bracing, Fig. 3. It consists of two sets of horizontal rings set 0.5 meters apart. The inner ring is 1 meter in diameter and the outer ring is 2 meters in diameter. The 0.5 meter by 1 meter diameter defines the pH control area. Eight mount points are equally spaced for perimeter pH probes. The center post holds 3 pH probes mounted equidistant vertically to provide the control inputs for the system. Four vertical struts hold an upper set of rings approximately 1.5 meters from the bottom of the frame. Eight bays hold plastic crates providing places for the HCl tanks. Above the top ring is a flotation pack. This configuration allows the prototype to be treated as an elevator system which is easily deployed and recovered using standard operational practices.

B. The Directional Control Valve

Passive control for upstream release of the HCl was selected to keep the electronics and equipment simple. Although later designs will use solenoids and electronic control it was determined that a mechanical weather vane would suffice, Fig. 4. The valve is required to respond to the ambient current and direct the to-be-injected acidified seawater flow to the upstream plumbing side of the FOCE frame. The vane turns a rotor in currents as low as 5 cm/sec appropriately directing flow to 2 adjacent sectors on the frame out of a total of 8. An interior stator has a single grooved input port arrangement and 8 o-ringed output ports corresponding and leading to the 8 sectors of the frame. The material selected for valve construction was polyetheretherketone (PEEK). A combination of machinability, dimensional stability, tolerance to low pH fluids, high ambient pressures, salt water environment, minimal friction/stiction of the rotor assembly, reasonable sealing of the dynamic seals and good response to ambient currents and

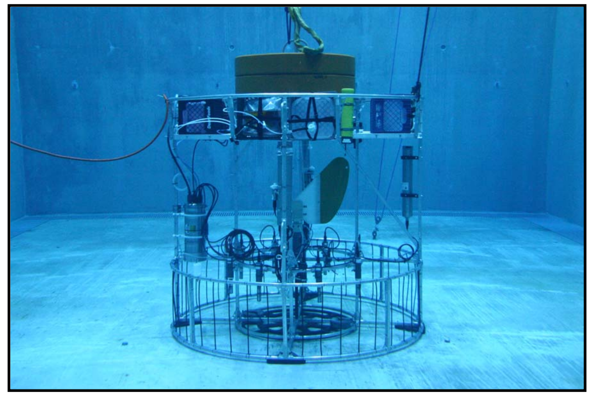

Fig. 3: FOCE Prototype in the MBARI test tank

deployment parameters made PEEK a good choice. PEEK also provided a strong attachment point for the large vane to the rotor. A simple preliminary analysis of drag in 10-30 cm/sec seawater yielded a vane of about 1600 cm. sq. Another requirement was near zero response to gravity or buoyancy when deployed on what most certainly would be a non-level seabed. The bearings are Torlon for axial loads and Zirconium Oxide (ceramic) for radial loads to keep friction as low as possible. The port seals selected are silicon encapsulated with teflon (FEP) which gave a good sliding seal with minimal friction. The port seals required several trial configurations of varying tolerance before a first article was completed. The teflon worked well to reduce friction but the cold-flow tendency of this material was found to create changing conditions with time.

Fig. 4: Directional Valve Assembly in FOCE Frame

C. Plumbing

A system of pumps and tubing was attached to the FOCE frame to deliver the HCl solution from the cubitainers thru the central directional valve and out the emitter tubing located near the seafloor. For the acid delivery, eight 5 gallon (20 liter) plastic cubitainers were united at a common manifold that was then connected to a Cole Parmer peristaltic pump head. This pump head was driven by a variable speed electric motor. Seawater was delivered to the system by an identical Cole Parmer peristaltic pump head and motor assembly. The inlet for the seawater pump was located near the top of the FOCE frame. To measure pumping rates and delivery volumes, a Gems hall effect turbine flow rate sensor (MEPS FT-110 series) was placed in-line downstream to each peristaltic pump. Real-time data from these sensors was then used to monitor seawater/acid mixing ratios. The seawater and acid lines were joined at a second manifold that provided adequate mixing prior to delivering the solution in a single line to the central directional valve. The plumbed components of the FOCE system were inter-connected with nylon tubing (0.25” OD, 0.16” ID). At the outer ring of the frame where the acid solution was emitted to the ocean, the nylon tubing was connected to 0.25” OD PVC garden soaker hose arranged in a vertical array, Fig. 5. The choice of soaker hose permitted a large emitter surface area and minimized system backpressure at high pumping rates. The soaker hose also promoted rapid and turbulent mixing with ambient bottom currents.

Fig. 5: Soaker hose was selected for HCl release after testing a variety of methods

D. Sensors

The FOCE structure was outfitted with eleven Seabird pH probes (SBE model 18). Eight pH probes were fixed to the 1 m dia. ring 0.5 m above the bottom with the tip of the probe approximately 25 cm from the seafloor. Data from these probes was logged internally to two Seabird CTDs (SBE 19plus, 4 pH probes per CTD). The three remaining pH probes were clustered at the center of the control volume along with a Falmouth 2” micro-CTD. The data from these 3 sensors was relayed to the ROV control room in real time and provided the necessary pH feedback for control of the acid/seawater delivery.

Additional instruments were also deployed and recorded to obtain background information. One pH sensor was on the ROV Ventana and recorded background pH information during the entire experiment. An InterOcean Systems S4AD current meter was placed 0.5 meters from the seafloor and approximately 32 meters away from the FOCE frame to measure current speed and direction during the duration of the two day experiment. The current meter was programmed to log data in two modes: continuously (once per second) and one minute averages for five minutes with a sleep cycle of 5 minutes. Real time current data was provided by the ROV. This data was used to set the flow ratios on FOCE as a feed forward input in the control loop. Standard CTD data on the FOCE frame and the ROV were also collected to establish the environmental conditions and differences between the two systems.

One additional sensor was taken along and used to sample the waters independently from the FOCE frame. A custom sensor arrangement called the ‘pH cell’ was mounted on the ROV swing arm, Fig. 6. The sampling snorkel was positioned at a few different spots by the ROV manipulator. This device was used to sample and verify the equilibrium rates

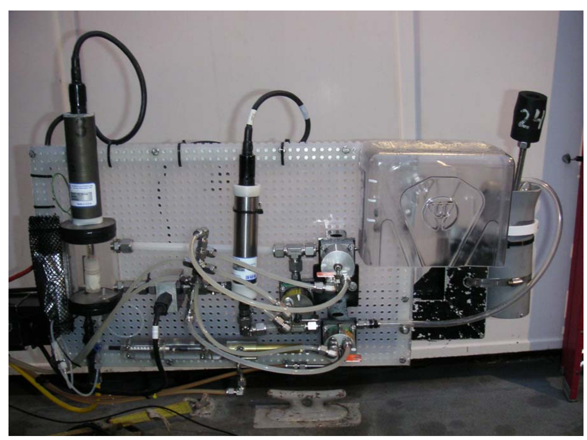

Fig. 6: The pH Cell on the ROV Ventana swing arm

of the HCl concentrations used in the first FOCE deployment. This data was very important to determine the difference between pH equilibrated water and acidified enriched water. This data will be used to modify system parameters around environmental conditions for future FOCE deployments.

E. Modes of Operation and Software Architecture

FOCE is controlled using a very simple design concept, Fig. 7. Due to long time delays in the system control outputs are slowed down by using box car filters and sampling at fairly low rates. This is beneficial since the pH sensors are sensitive and prone to noise from turbulent mixing. The filtering also uses a simple set of bounds based on the capability of the system to adjust pH. These values

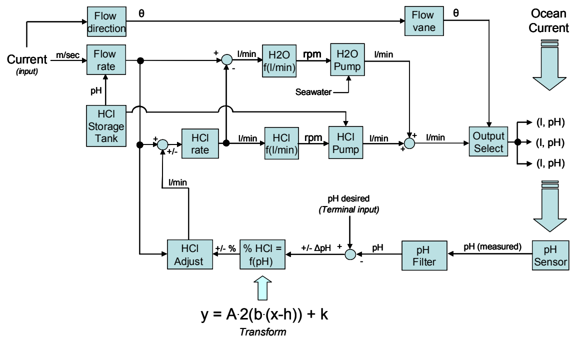

Fig. 7: The Controls Concept Diagram for pH feed back and Current feed forward inputs

are set in the graphical user interface (GUI). The ratio of sea water to acid mixing is based on the estimated current. The delta of pH from set point is then fit to a common curve. A percentage scalar is then determined and used to adjust the acid to sea water pumps ratio in an inverse manner. Most system parameters can be adjusted on the GUI. A system diagram shows the component and values the user can adjust, Fig. 8. The control software and diagrams were created in LabVIEW™. Using this approach, the software was quickly constructed and lab bench tested. A key feature of the system is the ability to set the pH value desired. Using the average of the central pH probes the system seeks the value selected. The real time display shows the filtered values of the three pH sensors being incorporated in the control loop. The two pumps can be readily seen and the operative ratios are settable from this page. The relative adjustment of these parameters is modified by the estimated current input, or feed forward estimates for system delay and mix ratio of HCl to sea water. Figure 9 is the real time graph of the pH probes and the resultant output of the system. The red, blue, and green lines are the individual pH probes. The yellow line is the averaged value of the pH probes and the estimated average value of pH for the control volume. The graph in Fig. 9 shows a step response to an HCl input through the control volume. The analog gauge representations show the real time output values of the HCL and sea water pumps. Above them are red bar graphs which give the ratio in percent. Figure 9 shows one pump at 100 percent while the other is at 0 %. Operational and control data is collected at a frequency selected by the

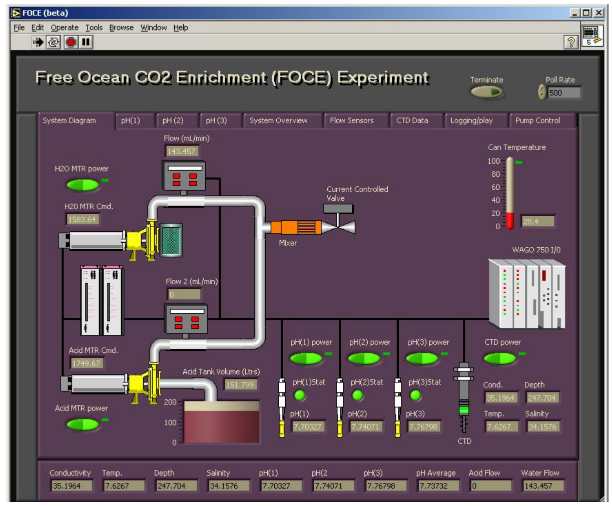

Fig. 8: System diagram and parameter controls page

operator. This setting is independent of the filter sample frequency. The system time is matched with the network clock used for the other instrumentation on the ROV. This aids the post-dive data and technical analysis of the experiment.

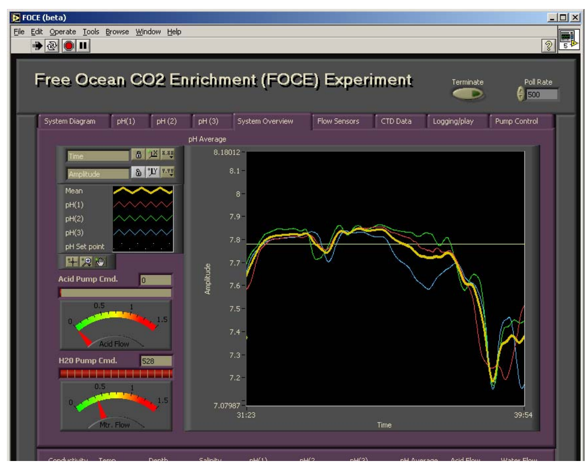

Fig. 9: Real time graphical display of system output

IV. PERFORMANCE / RESULTS

Tank testing of the FOCE system was performed two weeks in advance of the scheduled deployment date. This allowed for fine tuning of the system and making necessary corrections to be sea worthy. A hydraulic ROV thruster was used to create an artificial current in the test tank. The system was placed at a 10 meter depth in the MBARI salt water test facility and allowed to respond as it would deployed at sea. The directional valve worked as designed, porting the acidified sea water flow to the desired up stream side of the frame. The control system also performed as desired, controlling the pumps at the levels specified and mapping to the control curve as defined by engineering. Some minor plumbing changes and tuning were performed in preparation for the field trials.

At sea testing took place on April 12th and 13th, 2005, Fig. 10. The test site selected was within the oxygen minimum zone on a fairly flat area of the Monterey Bay off the coast of central California. Records had indicated the average currents would be in the specified range and the oxygen minimum meant the pH was already low in those waters which would test the systems ability to further depress the local pH. The elevator style deployment went as planned with the system landing with in meters of the desired landing site. The system was connected to the ROV using the ODI™ wet mate connector. The system was brought up and exercised several short duration pH control experiments. The system and all sub-components worked as predicted with the pH change being controlled at +/- .03 units. Troubles were encountered when the local currents went to near zero and eventually completely slacked. The acid enriched water buoyancy issues created a pool of low pH water which was not cleared until the currents picked up again. This was not a performance issue for the FOCE prototype, as the conditions and results were known.

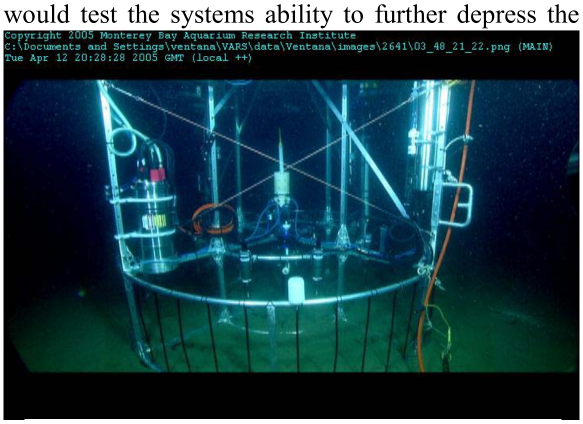

Fig. 10: FOCE deployed in the Monterey Bay

V. CONCLUSIONS AND FUTURE WORK

Follow-on efforts are underway at the time of this writing. Further deployments this year are planning to incorporate current meter data dynamically to adjust mix ratios. The pump flows will be increased to address a wider range of currents. Additionally, the system designs have begun to switch over to solenoids for long term autonomous control. Results have shown thus far that the FOCE initial design is viable. Adjustments for acidified sea water buoyancy in slack currents are still to be addressed. It is still to be determined how much effort should be spent on this issue. In the context of front-line oceanography, usable results the first time out are always a reason to smile. Now that we have met the first hurdles we have more time to work on several improvements. Among them are: a current meter for dynamic input and an electro-mechanical valve design more sensitivity to current direction low ambient flow rates.

Further testing is planned to expand the FOCE systems concepts into more challenging areas of operation. The first task is to begin addressing the large scale issues. These are dominated by delivery of large amounts of CO_2 for long term testing. The FOCE frame structure will need to be modified for trawl resistance and interfacing with cabled or moored observatories. These are currently well understood issues. The second area is to bring the system to shallower depths and more dynamic water masses. Theoretically, the problems are very addressable since the process of water ebb and flow helps the system reaction times. The water masses moving past the test site then dominate the amount of CO_2 required. However, these problems are well defined in terms of the chemistry so the larger issues become experiment funding and permitting. These issues are being actively pursued.

ACKNOWLEDGMENTS

David and Lucille Packard Foundation.
New Energy and Technology Development Organization (JAPAN).
US Department of Energy (DE-FC26-00NT40929)
Thank you to the FOCE team and Pt. Lobos / ROV Ventana crews

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