Initial results from a 4 km ocean CO_2 release experiment

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Introduction

Direct injection of CO_2 into the ocean is one idea among several carbon dioxide sequestration proposals under consideration to offset the increase of anthropogenic greenhouse gases in the atmosphere. This tactic raises important questions concerning the impacts of pH changes and elevated CO_2 levels for marine ecosystems and the role that ocean sequestration should play in national and international carbon management strategies. While ocean sequestration could reduce the level of atmospheric emissions, it would add to the accumulating burden of fossil fuel CO_2 in the ocean. And while there has been considerable debate regarding rising levels of CO_2 in the atmosphere and whether they constitute a "dangerous anthropogenic interference" with climate, there has been no such debate regarding acceptable oceanic CO_2 levels. In order to address these issues and provide advice to the various world-wide governmental bodies so that policy decisions can be made based upon sound science, new types of *in situ* experimental investigations are required.

For the past 8 years, we have conducted small-scale experiments on the purposeful release of CO_2 into the ocean using MBARI's advanced remotely operated vehicle (ROV) technology. Apparatus and techniques for the transport and release of 0.4 to 45 kg quantities of CO_2 per dive have been developed and we have used this technology to pursue fundamental chemical, physical, and biological studies associated with ocean CO_2 sequestration[1-4]. This technology has also allowed us to conduct several *in situ* experiments mimicking some of the ocean CO_2 sequestration scenarios which have been proposed and to begin the process of understanding the impact of CO_2 on the benthic environment[5-9].

We report here several recent advances in the refinement and development of new technology for experimental releases of CO_2 in the deep sea, and the initial results from an international experiment conducted at 3940m depth in Monterey Bay.

Experimental

56L CO_2 accumulator. For this experiment the 56L CO_2 accumulator[10] was thoroughly re-built. A new carbon fiber reinforced fiberglass barrel was fabricated and the aluminum end-caps and piston were replaced with ones made from titanium to alleviate problems with corrosion. The end-caps and piston were redesigned to eliminate voids on the seawater side, while increasing the depth of the recessed cavity on the CO_2 side to allow for an internal cooling loop. The extended length of the CO_2 end-cap also allowed for a second O-ring seal to solve the leakage problems encountered earlier.

Benthic flume. In order to have more operator control over the plume created during the release experiments, a 'benthic flume' was constructed (Fig. 1). It consisted of a trough for CO_2 150 cm long, 40 cm wide and 25 cm deep; a thruster (driven by a computer controlled brushless DC motor) to generate a variable seawater current along the CO_2 trough; and a wave generator paddle. Both the wave paddle and the thruster were controllable in finite increments by the experimentalist in real-time. A clear panel on the front, and an opaque panel on the back, helped to channel the seawater flow through the flume and aided in viewing of the CO_2 pool under the various stresses. Power and control of the benthic flume was achieved via the ROV by using an underwater mateable connection.

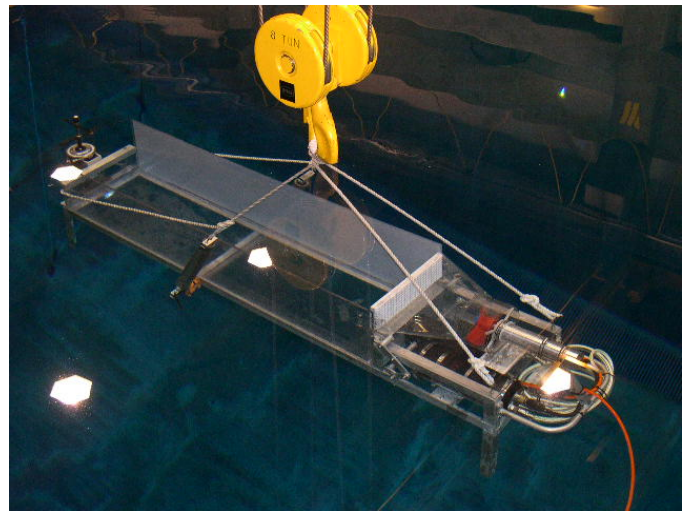

Figure 1. The benthic flume being lowered into the 10m deep test tank at MBARI. The red thruster propeller is visible at the right end of the trough. For the purposes of this test a three axis velocity meter was mounted at the far left-end.

pH probes and calibration. SBE18 pH sensors (Seabird Electronics, Inc., Bellevue, WA 98005) were used. While these sensors have a nominal depth rating of 1200m, we have found that when they are slowly deployed to depth, they can be used as deep as 4000m. The pH electrodes were calibrated using seawater solutions where the pH had been previously adjusted using concentrated HCl or NaOH to ~6 and ~8 as measured by an IQ240 ISFET pH electrode (IQ Scientific Instruments, Inc., San Diego, CA 92127) that was calibrated using commercially available NBS pH standard solutions.

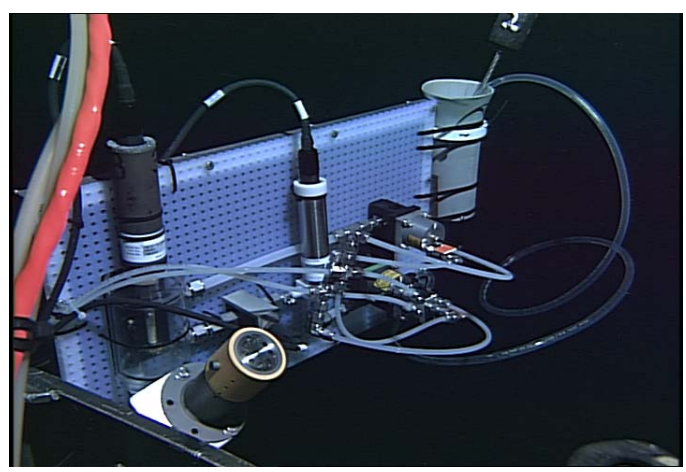

Figure 2. The seawater re-circulation chamber is visible at left with the Seabird SBE18 pH electrode extending from the top. The recirculation pump is the silver cylinder in the middle of the image. Hydraulically activated quarter-turn valves were used to open and close the chamber and to collect ambient seawater samples.

Seawater recirculation chamber. A small volume (~300 mL) chamber (Fig. 2) was equipped with both a pH sensor and a temperature sensor so that samples of CO_2 enriched seawater could be collected and re-circulated. This allowed the kinetics of the CO_2 hydration reaction to be studied. A Seabird submersible pump was used to fill, flush and re-circulate seawater in the chamber. Pumping rates on the order of 0.9-1.2L/min were achieved at depth.

Results and Discussion

Maximization of CO_2 delivery volumes. Delivery of liquid CO_2 in previous experiments was often hampered by less than theoretical yields. Investigation of this phenomenon revealed that the cylinder was often filled with warm water on the seawater side. Heat from this water was conducted through the piston and into the liquid CO_2, thus warming the CO_2 and possibly allowing for gas pockets to form. In order to maximize the amount of liquid CO_2 delivered to the sea-floor, we changed our filling protocol to include pre-filling the seawater side with cold water, and installed an interior copper tube cooling loop on the CO_2 side. Subsequently, all CO_2 deliveries have been within 1-2% of the theoretical delivery volume at depth.

Experimental control of the benthic environment. In previous experiments, we relied upon the ambient current conditions on the sea-floor. Often brisk currents might perturb the experiments, causing noticeable ripples on the liquid CO_2 surface or we might encounter near stagnant conditions, and there was little we could do to modify or control this. With the benthic flume, we can now direct a controlled flow of seawater across the surface of the liquid CO_2. Current speeds of 0.1-1.2 knots are possible and can be adjusted by the ROV pilot in real-time. Additionally, the wave paddle can be controlled in real-time as well to beat from 0.1 to 2 Hz (Fig. 3).

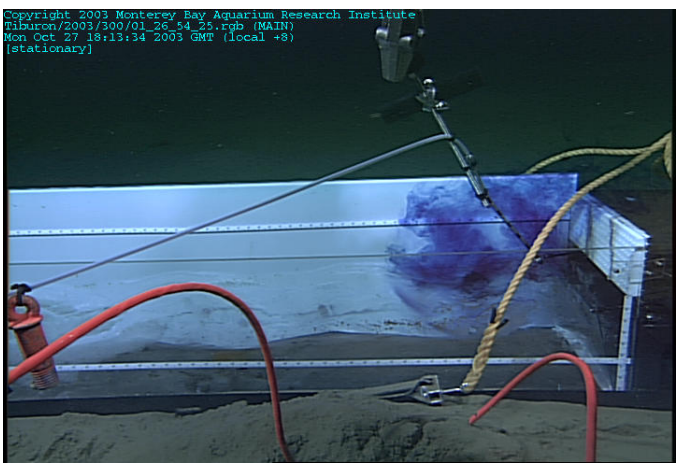

Figure 3. Dye-injection into benthic flume above the liquid CO_2 surface. Sinusoidal waves made by the action of the wave paddle can be clearly seen as the dye cloud drifts above the CO_2-SW interface.

CO_2 hydration kinetics. It is known that the kinetics of the CO_2 hydration reaction are quite slow at atmospheric pressure and room temperature. The half-life of this reaction at 25ºC is about 18 seconds[11]. At lower temperatures, an even longer half-life is predicted (Fig. 4). For example, at temperatures typical of the deep-sea (1.5-2.0ºC), we expect a half-life on the order of 270-300 seconds. However, given that the change in partial molar volumes of the reaction is negative, we predict that the high pressures in the deep-sea will have a positive impact on the reaction rate.

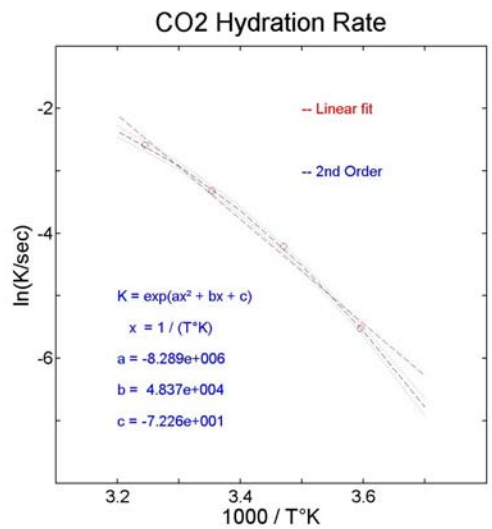

Figure 4. Kinetics of the CO_2 hydration reaction at one atmosphere. Both a linear and a second order fit are shown. The second order equation was used to predict the reaction half-lives at temperatures typical of the deep-sea.

Conclusions

The first ocean CO_2 sequestration experiment at 4 km depth has now been conducted. The benthic flume worked well allowing us to control both the ambient current velocity at the CO_2-seawater interface and to generate regular waves within the liquid CO_2 pool. Both capabilities should aid us in our continued studies of the properties, behavior and impact of liquid CO_2 in the deep-sea.

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