

Progress in Direct Experiments on the Ocean Disposal of Fossil Fuel CO₂

Peter G. Brewer (brpe@mbari.org; 831-626-6618)
Monterey Bay Aquarium Research Institute
7700 Sandholdt Road
Moss Landing CA 95039

Introduction. My laboratory has now been engaged in carrying out small scale controlled field experiments on the ocean sequestration of fossil fuel CO₂ for about five years, and the field has changed enormously in that time. We have gone from theoretical assessments to experimental results, and from cartoon sketches of imagined outcomes to high-resolution video images of experiments on the ocean floor shared around the world. It seems appropriate therefore to give a brief review, albeit one very much from a personal perspective. Although I made my first measurement of the CO₂ content of oceanic waters in 1965, it was not until 1996 that I seriously considered the issue of ocean CO₂ disposal as a possible means of countering the growing problem of climate change, and of meeting the needs of emerging greenhouse gas policies. Two factors combined to create this change in research direction.

The first was the realization (Brewer, 1997) that the oceanic fossil fuel signal (Brewer, 1978; Gruber et al., 1996) resulting from air-sea gas exchange had now reached critical proportions. The so-called “passive uptake” of atmospheric CO₂, almost universally regarded as a great boon to mankind, now approximates 25 million tonnes of CO₂ per day. And this massive flux is taking place directly into the surface ocean, where all photosynthesis occurs, and most coral reefs exist. Were we to propose this surface disposal as an “active” industrial process it is difficult to know what the societal reaction might be. So large is now this accumulated signal that the fossil fuel CO₂ component of surface ocean waters is a “major ion” of sea water in its own right. We have decreased the pH of surface ocean waters by about 0.1 pH units today – enough so that any high school student with a good pH meter could easily tell the difference between sea water from the 19th century and that from today. We have consumed more than 15% of the carbonate ion in surface ocean water today; and we are rapidly changing these figures. The problem is that we are using only a small fraction of the vast chemical capacity of sea water. The slowness of the oceanic vertical circulation is responsible for this; and the predictions are that this circulation will diminish in intensity from changes in the hydrologic cycle.

Why not consider bypassing the atmospheric disposal step with its attendant global warming? - and put CO₂ in the deep ocean directly as was first suggested over twenty years ago by Marchetti (1977). We already have over 100 years experience with surface ocean CO₂ disposal, and the impacts in the deep ocean would be far more benign. Note

that I said “consider” for what I recommend is an active and objective research program, not a rush to judgement.

The second factor was the emergence of an important technology that enabled an experimental attack on these problems. Early in 1996 we had carried out (Brewer et al., 1997) a controlled experiment to create methane hydrates in the deep sea by direct injection. We used MBARIs remotely operated vehicle (ROV) *Ventana* to transport gas to 910m depth, and to open valves to create hydrate formation in water and sediments, while imaging the results with the vehicle camera. CO₂ will readily form a hydrate under oceanic conditions (see Fig.1), and it was a logical next step to attempt this. Our first effort (Brewer et al., 1998), used helium gas to expel liquid CO₂, resulting in all kinds of chemical complexity. Rapid advances in technique then lead to a successful series of experiments (Brewer et al., 1999) ranging from 300m to 3627m depth, with an astonishing range of observed physico-chemical behaviors, and the first hints of very minimal biological impacts.

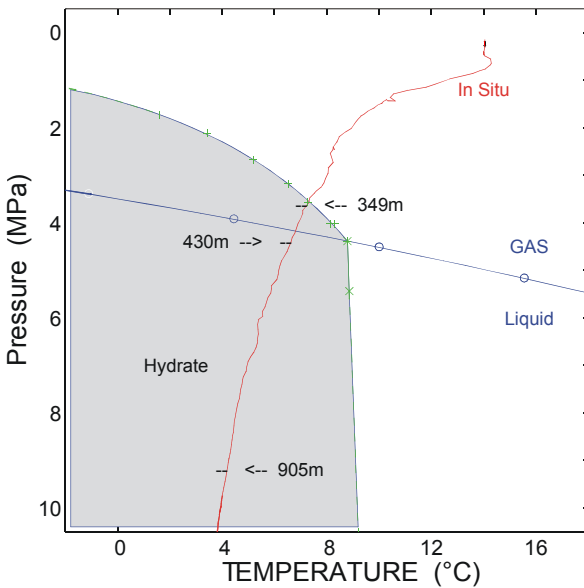


Fig. 1. Phase diagram showing the CO₂ hydrate formation boundary in sea water, overlain with a temperature profile from off the central California coast. From Brewer et al. (1999).

The ability of CO₂ to form a hydrate, and its remarkable compressibility relative to sea water so that a density reversal occurs at depth, are well known features and need not be reviewed in detail here.

At the governmental level there is a pressing need to meet the challenge posed by the United Nations Framework Convention on Climate Change, and the research directions and accomplishments outlined above are consistent with these goals (Brewer, 2000).

Objective. Our objective is to carry out a wide selection of small-scale studies of fundamental chemical, physical, and biological processes so as to provide important data that shed new light on the ocean CO₂ sequestration problem as quickly as possible. In this way we avoid incurring the large engineering costs, and environmental concerns, that would accompany larger releases. We do this in active collaboration with other scientists

both nationally, and internationally. By this approach, and through open publication of our results we hope to stimulate others to replicate our experiments, and to provide new challenges and discoveries in the classic science pattern. It is in this way that scientific consensus is achieved. The need for this is illustrated by the following anecdote.

In November 2000 I attended a meeting in Washington, D.C. at which we were given a briefing by a State Department spokesman as to why the UNFCCC talks in The Hague had broken down. I asked why some form of active energy waste management in the form of geologic or deep-ocean CO₂ disposal was not on the table for discussion. The reply was that no scientific consensus yet existed on these topics, and until this was so they would not arise for policy discussion. That is our objective.

Approach. There are many forms of ocean CO₂ injection that have been advocated. Shallow gas injection to form a dense sinking fluid (Haugan and Drange, 1992), injection of ultra-cold liquid CO₂ to form a dense ice skin-hydrate phase (Aya et al., 1998), formation of a lake of CO₂ on the sea floor (Harrison et al., 1995), and dissolution of a rising plume of liquid CO₂ (Alendal and Drange, 2000) are among the options that have been proposed. We have now carried out field experiments in each of these areas.

Our basic approach has been to use ROV technology as the scientific platform (see <http://www.mbari.org/dmo/vessels/vessels.htm> for a detailed description). For work shallower than 1,500m we used an ROV equipped with a HDTV camera to observe the CO₂ released, and the video tape recorded from this camera provides a permanent record of the work. The system captures images with a specially modified Sony HDC-750 high-definition television camera which digitizes the picture data and formats it to the SMPTE 292M HDTV interface standard with 2:1 interlace. The resolution of the images is 1035 pixels vertically and 1920 pixels horizontally which is about five times the resolution of conventional video. The image data is recorded with a Panasonic HD2000 high-definition video tape recorder without any further transcoding steps.

Liquid CO₂ injections are carried out by expulsion from a reservoir by a piston, activated on command from the vehicle control room. For the shallow releases a small (~500 ml) volume steel cylinder was used. For the deep experiments approximately 9 liters of liquid CO₂ were contained in a commercial accumulator (Parker A4N0578D1) installed horizontally in the tool sled frame. The accumulator was connected to a set of valves and fittings, which permitted loading of the cylinder with liquid CO₂ from standard gas cylinders prior to the dive. Procedurally, after the first filling, an accumulator gauge pressure of about 850 psi was observed, with the piston set at maximum accumulator capacity. The gas delivery cylinder was then warmed (to compensate for expansion cooling) on transfer of the contained CO₂. A second filling was then carried out. The filled accumulator was vented to about 750 psi as it warmed to room temperature to prevent overpressure. The system was configured to permit open contact between seawater and the ocean side of the accumulator piston. As the vehicle dove, and pressure increased, the decrease in volume of the contained liquid CO₂ was compensated for by active piston motion to maintain pressure equality. Camera inspection of the pressure gauge during the dives showed the expected drop in accumulator pressure as the P-T

boundary for liquid CO₂ was approached (in practice at about 400m depth). As the differential pressure across the piston dropped a few strokes of the hydraulic pump were used to maintain positive pressure inside the accumulator. A system check was carried out, by opening the quarter-turn CO₂ release valve, at several depths during deployment, thereby venting small amounts of liquid CO₂

Project Description. The description above gives some experimental details of work already accomplished. In the most recent phase of our work we have tackled four new themes.

1. In close collaboration with I. Aya, K. Yamane, and R. Kojima, from the Ship Research Institute (SRI) (Japan) we have field tested concepts (Aya et al., 1998) of a cold release (-50°C) of liquid CO₂, at 500m depth to simulate the release from a tanker of liquefied gas. A pressure vessel surrounded by an evacuated jacket was used to contain the sample, which was transported to depth by the ROV. The cold CO₂ was released by removing the end cap with the vehicle arm, and then actuating a piston to drive the liquid vertically downwards. The mass of liquid was at once shrouded by an ice-hydrate coating, and sank rapidly due the high density of the cooled liquid phase. By rapidly diving the ROV it was possible to track visually the sinking mass for about 40m, where it soon yielded to heat transfer from the ocean, slowing its descent and eventually increasing in buoyancy so that it rose upwards again while dissolving and breaking up just below release depth. This co-operative international experiment provided the first practical test of oceanic release of CO₂ under conditions representing liquefied gas carrier transportation.
2. We have experimentally determined the dissolution rate of a rising stream of liquid CO₂ droplets (Peltzer et al., 2000). In this experiment we pioneered the use of HDTV for precise imaging of a droplet stream moving in three dimensions. We constructed an imaging box (Figure 2), mounted on the front of the ROV, with valves for controlled release of small quantities of CO₂. The box was open at top and bottom for unrestricted flow, and the opaque rear wall served to screen out visual clutter from marine snow. The side walls contained the droplets from lateral motion and provided easier tracking. A numerical scale taped to the rear wall provided an accurate dimensional check. Figure 3 shows a small droplet cluster imaged as it rises from release at 800m depth.

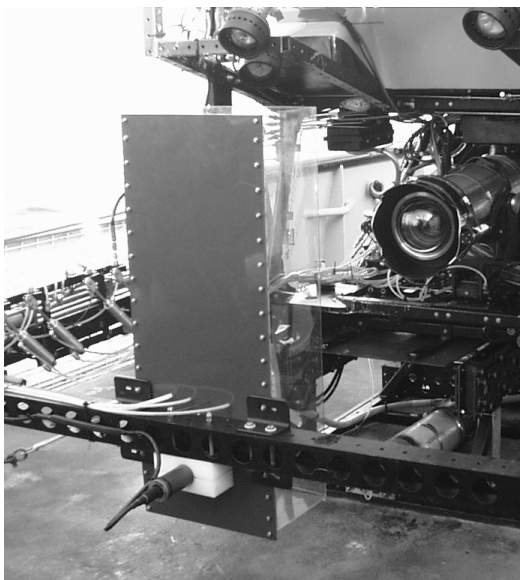


Fig.2. The imaging box used for tracking the droplet stream mounted on the front of the ROV "Ventana". The HDTV camera can be seen on the vehicle. The opaque rear of the box is shown, with gas lines entering.

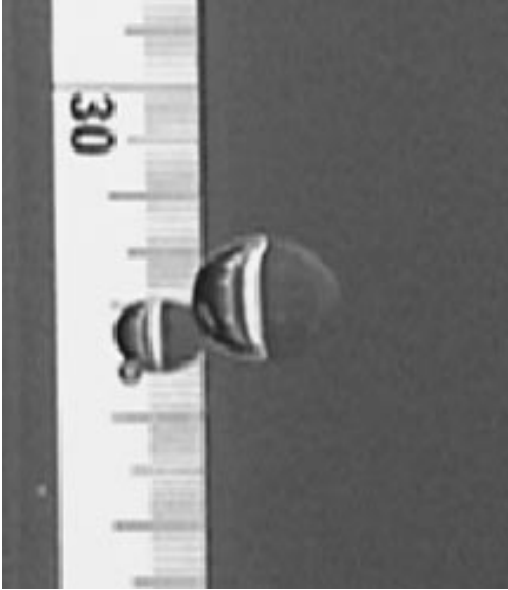


Fig 3. Close up image of a small cluster of CO₂ droplets in motion, with the numerical scale in view. From the accurately observed time change of droplet size a dissolution rate can be calculated. From Peltzer et al. (2000).

The dissolution rate measured was very close to $3\mu\text{mol}/\text{cm}^2/\text{sec}$. By similar techniques we have experimentally determined the neutrally buoyant surface for liquid CO₂ in sea water as being at 2712 dbars, or 2675m depth in the region of the Pacific off central California.

3. In a successful collaboration with S. Kirby and L. Stern (USGS), and W. Durham (LLNL) we have very recently carried laboratory fabricated specimens of CO₂ hydrate to 1032m ocean depth in a novel pressure vessel. This was opened at depth, the hydrate specimens removed, and their dissolution rate measured with a time lapse video camera. Analysis of these data is now under way.
4. In collaboration with J. Barry and M. Tamburri we have initiated a program of biological experiments (Tamburri et. al, 1999). Our first studies were conducted at shallow (625-250m depth) bracketing the hydrate formation boundary (Fig. 1) so as to be able to compare animal responses with, and without, the hydrate coating that is presumed to greatly slow the dissolution rate. An odor attractant stream was used to attract animals to the site, and a valve was then switched to introduce CO₂ saturated fluids into the attractant stream. In practice these early experiments were principally of value to develop essential technique. We learned to integrate a pH sensor with our ROV, and to gain experience with animal behavioral studies. We have now begun to extend these studies to greater depth. Figure 4 shows an image of a blob of liquid CO₂ on the sea floor at 3000m depth; that is close to the practical limit of the depth range where a release is gravitationally stable. The size of the blob is approximately 8 cm diameter, and a pH electrode is visible at the top of the image, held in the ROV arm. A holothurian is observed close by. The dissolution rate of liquid CO₂ at these depths, so far into the hydrate phase space, is far slower than at shallower depths and the lifetime of the observed blob is several days. Thus animals can approach close by with no observable change in behavior.

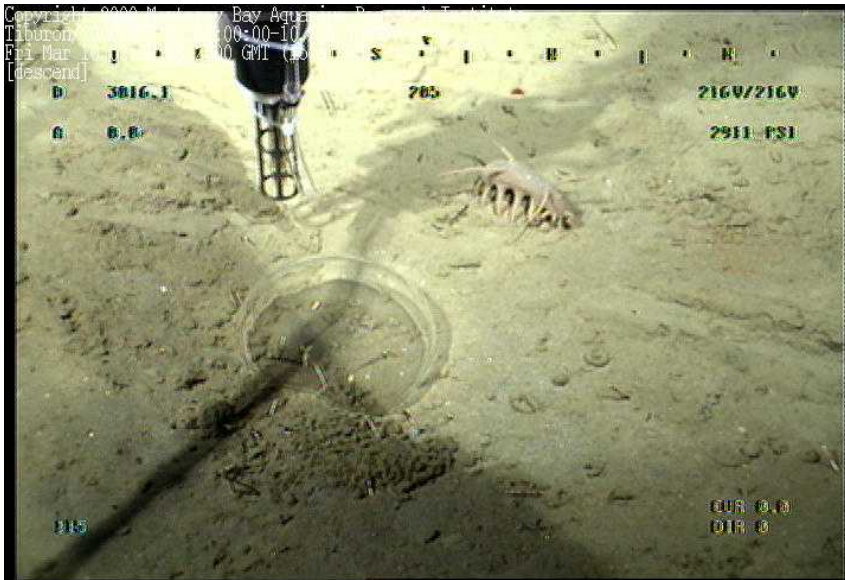


Fig.4. Image of a holothurian on the sea floor at 3000m depth, close by a blob of liquid CO₂ about 8cm in diameter. A pH electrode is visible at the top of the image, held in the robotic arm of the MBARI ROV “Tiburon”.

Results. We have outlined above many of the results emerging from our work. The singular value of these studies is the creation of a set of novel, viable, in situ experimental techniques for directly probing the fate of fossil fuel CO₂ injected into the deep ocean. From these studies we have explored the hydrate phase boundary, and the remarkable changes that occur across it. We have determined the rise rate of droplets of liquid CO₂ of about 1cm diameter in the depth range 800- 400m to be very close to 12 cm/sec, and the dissolution rate to be 3 $\mu\text{mol}/\text{cm}^2/\text{sec}$. We have determined the neutrally buoyant pressure horizon to be 2712 dbars, and a CO₂ release at this level would neither rise to shallower depth (and thus undo work expended to transport it), nor reside on the sea floor where a new set of biologic and geologic questions arise. The dissolution rate at this depth is not well known, but our early results suggest at least a factor of 5 slower than in the 800-400m depth range examined earlier.

Application. The application of our experimental results is to directly inform on the near field fate of fossil fuel CO₂ released at depth in the ocean. The application to studies designed to minimize cost and environmental effects, and maximize safety is very clear, and this will guide our future work.

Future Activities. We plan to continue our experiments with a wide range of national and international colleagues. In particular we will focus on biological effects, on tracking the release of a neutrally buoyant, or near neutrally buoyant, plume, and on the fate of a small “lake” of CO₂ on the sea floor with a particular focus on the effects of hydrate formation and of sedimentary interactions. We have a particular commitment to the creative use of novel technologies for deep sea science, and will deploy a time-lapse video camera for imaging the long term fate of material and biological interactions. And we will utilize in situ a laser Raman spectrometer, carried by the ROV, for obtaining novel spectroscopic information on the status of hydrate formation, and CO₂- hydrate-sediment interactions.

References

- Alendal, G and H. Drange (2000) Two-phase near-field modelling of purposefully released CO₂ in the ocean. *J. Geophys. Res.* In press.
- Aya, I., K. Yamane, S. Namie, and H. Nariai (1998) Proposal of self sinking CO₂ sending system: COSMOS. *Proc. 4th Intl. Conf. On Greenhouse Gas Control Technologies.* In press.
- Brewer, P.G. (1978) Direct observation of the oceanic CO₂ increase. *Geophys. Res. Lett.*, v. 5, 997-1000.
- Brewer, P.G. (1997) Ocean chemistry of the fossil fuel CO₂ signal: the haline signature of "business as usual". *Geophys. Res. Lett.*, v. 24, 1367-1369.
- Brewer, P.G., F.M. Orr, Jr., G. Friederich, K.A. Kvenvolden, D.L. Orange, J.F. McFarlane, and W. Kirkwood. (1997) Deep ocean field test of methane hydrate formation from a remotely controlled vehicle. *Geology*, v. 25, 407-410.
- Brewer, P.G., F.M. Orr, Jr., G. Friederich, K.A. Kvenvolden, and D.L. Orange. (1998) Gas hydrate formation in the deep sea: In situ experiemnts with controlled release of methane, natural gas, and carbon dioxide. *Energy & Fuels*, v. 12, 183-188.
- Brewer, P.G., G. Friederich, E.T. Peltzer, and F.M. Orr, Jr. (1999) Direct experiments on the ocean disposal of fossil fuel CO₂. *Science*, v.284, 943-945.
- Brewer, P.G. (2000) Roger Revelle Commemorative Lecture. Contemplating Action: Storing carbon dioxide in the ocean. *Oceanography*, v. 13, 84-92.
- Gruber, N., J.L. Sarmiento, and T.F. Stocker (1996) An improved method for detecting anthropogenic CO₂ in the oceans. *Global Biogeochemical Cycles*, v. 10, 809-837.
- Harrison, W.J., R.F. Wendtland, and E.D. Sloan, Jr. (1995) Geochemical reactions resulting from carbon dioxide disposal on the sea floor. *Appl. Geochem.*, v. 10, 461-475.
- Haugan, P.M. and H. Drange (1992) Sequestration of CO₂ in the deep ocean by shallow injection. *Nature*, v. 357, 318-320.
- Marchetti, C. (1977). On geoengineering and the CO₂ problem. *Climate Change*, v.1, 59-68.
- Peltzer, E.T., P.G. Brewer, G. Friederich, and G. Rehder (2000) Direct observation of the fate of oceanic carbon dioxide release at 800m. In: *Preprints of Symposia, Division of Fuel Chemistry, American Chemical Society*, v. 45 (4), 794-798.
- Tamburri, M., E.T. Peltzer, G. E. Friederich, I. Aya, K. Yamane, and P.G. Brewer (2000) A field study of the effects of ocean CO₂ disposal on mobile deep-sea animals. *Mar. Chem.*, v. 72, 95-101.