

# PROGRESS IN DIRECT EXPERIMENTS ON THE OCEAN DISPOSAL OF FOSSIL FUEL CO<sub>2</sub>

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## ABSTRACT:

Over the last three years we have carried out several experiments on the direct injection of experimental quantities of CO<sub>2</sub> into the deep ocean, using ROV technology to carry out the experiments and image and record the results. In this paper I review the techniques, and the progress that has been made in understanding the behavior of CO<sub>2</sub> both within, and outside, the hydrate phase boundary. Where possible I introduce new results, and I pose some questions for future work.

**Key Words:** CO<sub>2</sub> disposal, hydrates, ROV

## INTRODUCTION:

The topic of ocean disposal of fossil fuel CO<sub>2</sub> was first discussed by Marchetti [1] over twenty years ago. Since that time a great many policy studies [2], theoretical calculations [3], and laboratory experiments [4] have been carried out, but remarkably very few direct ocean experiments have been attempted. This situation has recently changed with the recognition that ROV (Remotely Operated Vehicle) and research submersible technologies could be adapted to this class of experimental work.

So far as I can tell the first use of submersible technology to investigate the behavior of CO<sub>2</sub> at great ocean depths was the experiment carried out by Honda et al. [5] in 1990. They used the manned submersible "Shinkai 6500" to carry down a block of solid CO<sub>2</sub> in a transparent acrylic cylinder, visually observed the changes taking place. They were able to see the density reversal of sea water and CO<sub>2</sub> as the fluids were subjected to pressure. The observation of a natural seep of CO<sub>2</sub> rich geochemical fluids by Sakai et al. [6] in 1990 further stimulated interest in the strange behavior of liquid CO<sub>2</sub> within the hydrate phase boundary. But a systematic program of field investigation with controlled release of material under specified conditions did not begin until 1996 [7].

The first of this class of experiments that we carried out were to investigate the formation of methane hydrates [8] in sea water and in sediments. We made use of the ROV *Ventana* to carry down a tank of methane gas, and assembled a set of hydraulically activated valves which could be opened by command from the ships control room to release gas at the desired depths. Our success in this first experiment, and our interest in CO<sub>2</sub> sequestration with a hydrate as the sequestered form, then quickly lead us to attempt the more difficult problem of development of ocean CO<sub>2</sub> injection techniques.

In our first experiment [7] we attempted simply to extend the work on methane by adding a small quantity of He to the CO<sub>2</sub> tank, thereby creating a pressurized gas bubble which would act to expel the liquid CO<sub>2</sub> from the container. While we were partially successful in this, and a form of CO<sub>2</sub> hydrate at a depth of about 568 m (T= 4.4°C) was indeed made, we soon realized that we had a problem. The finite solubility of He gas in liquid CO<sub>2</sub> resulted in an unusual mixture that did not closely approximate a true CO<sub>2</sub> disposal scenario. We then developed a set of cylinder and piston arrangements [7, 9] to contain and deliver the CO<sub>2</sub>, and all subsequent experiments have used a form of this protocol.

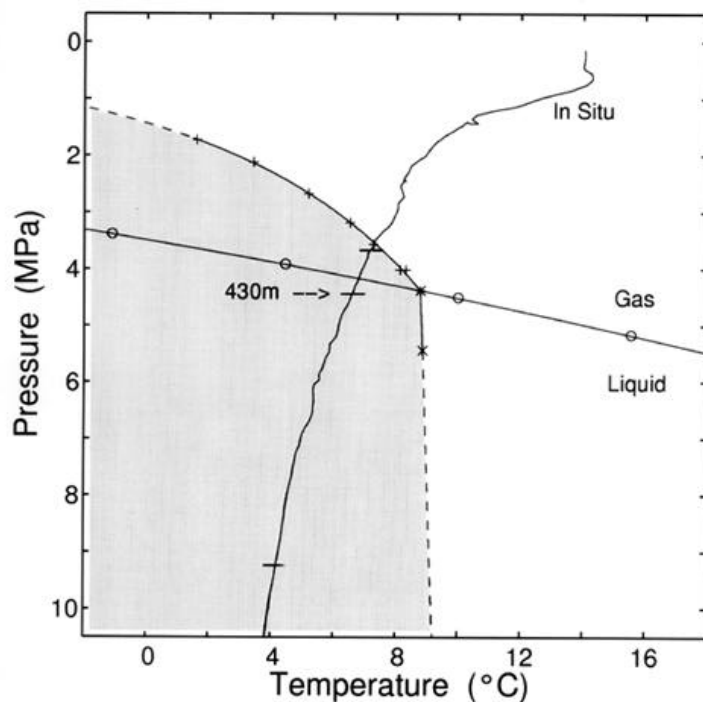
We have now carried out about 8 separate ROV dives for the purpose of investigating the underlying science controlling the behavior of CO<sub>2</sub> injected into sea water for the study of CO<sub>2</sub> sequestration. These dives have covered the depth range of 250m to 3627m, and they have uncovered important effects and processes which must be considered in implementing a successful sequestration program. This strategy of work at sea should proceed in parallel with laboratory studies, and these two strategies will be essential for full understanding.

## RESULTS FROM OCEAN EXPERIMENTS

What have we learned from the sequence of small-scale field experiments carried out so far? I will elect here to discuss the results in order of depth, from shallow to deep, rather than in the chronological order in which the experiments were carried out. This should be easier to follow. In all cases the work

was carried out in the ocean near Monterey Bay, California, for reasons simply of proximity to our research Institute. The usual oceanic conditions relating Pressure-Temperature-Salinity-Density in this region are quite typical for the temperate world ocean, and for convenience we will simply use this example as if it were the general case.

In Figure 1 I show the Pressure-Temperature diagram for this region (taken from ref. [9]), with the phase boundary for the CO<sub>2</sub> gas-liquid transition, and the CO<sub>2</sub> hydrate phase boundary overlaid. This diagram importantly defines the effects observed, and it exerts a powerful control on CO<sub>2</sub> sequestration.



**Figure 1.** Phase diagram for carbon dioxide in sea water showing the gas-liquid/hydrate boundary as a function of temperature and pressure. The curve marked “In Situ” represents a typical temperature pressure curve for the waters off northern California where the experiments were carried out. From ref.[9].

### CO<sub>2</sub> above the hydrate zone

Above a depth of about 300m, and at local *in situ* temperatures CO<sub>2</sub> will still be in the gaseous phase. A gas bubble injected here will buoyantly rise, and dissolve within a few tens of meters. Estimates of CO<sub>2</sub> bubble dissolution rates, and plume dynamics simulating a shallow depth release, have been made by Drange and Haugan [10]. We have carried out small-scale *in situ* experiments by releasing CO<sub>2</sub> gas into a box about 1.5m high with about 0.5m sides, open to the ocean at both ends, and carried on our ROV so as to be quantitatively imaged by the camera. The function of the box was to laterally contain the bubble plume so that it could be imaged while freely rising. The vehicle was then navigated so as to match the rise rate of the bubbles. The injection was arranged so that bubbles of about 1cm diameter were produced. At these shallow depths bubble dissolution was indeed rapid.

CO<sub>2</sub> is extraordinarily soluble, up to about 3 weight per cent, at low temperature and even modest pressures [4], and since the partial molal volume in sea water less than the molecular weight, and is close to 33 cm<sup>3</sup>/mol, then the density of CO<sub>2</sub> saturated sea water is high. Haugan and Drange [11] proposed using the density of such a plume to aid in sequestration. We have attempted to reach near saturation with gaseous CO<sub>2</sub> *in situ* experimentally (see accompanying paper for this meeting by Tamburri and Brewer), but find that this hard to achieve. In practice a fluid, denser than sea water and noxious to marine animals, can be quite readily achieved. But mixing with the surrounding ocean quickly results in adjustment to local density and a shallow plume will be created.

### **CO<sub>2</sub> gas within the hydrate zone**

There exists a small region in Fig. 1 within which CO<sub>2</sub> remains as a gas, but can form a hydrate on contact with sea water. This narrow zone is of little practical significance for disposal purposes, but it must be recognized in experimental technique. In carrying out our sequence of *in situ* experiments the transition of the contained CO<sub>2</sub> from gas to the liquid state emerges as a difficult problem. The sudden change in volume can result in pressure reversals across gauges and check valves, and if this is not quickly compensated for then water intrusion into the apparatus can occur. This creates hydrate formation within the valves and supply lines resulting in experimental failure.

We have carried out one experiment on CO<sub>2</sub> gas injection within the hydrate zone, and a bright white snow like flocculant mass of hydrate was instantly formed.

### **CO<sub>2</sub> liquid below the hydrate zone: 350m – 2600m.**

This depth interval of the ocean has attracted much interest as a sequestration zone. The large-scale physical circulation of the ocean results in waters with the oldest formal <sup>14</sup>C age being located here [12]. Although at these depths the density of liquid CO<sub>2</sub> is less than that of sea water, the density of CO<sub>2</sub> hydrate is significantly greater. Thus many researchers have investigated whether sinking behavior of released CO<sub>2</sub> can be achieved [13]. Our numerous field experiments, with a wide range of injection rates, have always yielded a rising hydrate mass [14]. We attribute this to the formation of only a thin film of hydrate, around a nucleus of CO<sub>2</sub>, in which diffusion is so slow that water and gas cannot be transported and create a film of growing thickness. Thus in all field experiments so far the net effect is to achieve a rising plume. This then undoes much of the work expended in transporting the liquid CO<sub>2</sub> to depth.

The next question is whether the hydrate film is sufficiently soluble in the surrounding sea water that some significant dissolution, providing mass transfer of CO<sub>2</sub> in the dissolved state to the ocean water column, occurs during the rising period. We have attempted to investigate this in two ways. We have attempted to measure the pH gradient close to the hydrate film covering a mass of liquid CO<sub>2</sub> held in an inverted 4 liter beaker [14]. We hypothesized that a boundary layer, saturated in dissolved CO<sub>2</sub>, might form and sink downwards from the exposed hydrate surface. However, once a simple three layer (CO<sub>2</sub>-hydrate- sea water) system was formed no pH gradient could be detected within the limits of the measurement (about ± 0.005 pH units). A signal from a frothy hydrate-water mixture was initially detected, but this relaxed back to zero gradient as CO<sub>2</sub> rich brine initially formed drained from the system.

Since these static data appeared to show a very slow dissolution rate we then attempted the more difficult dynamic observation of tracking a rising plume directly. Models of CO<sub>2</sub> release [10] from sea floor pipelines consider this strategy. If the dissolution rate of a rising plume is quite fast then effective transfer to the ocean can occur. If the rate is slow relative to the rise rate then the hydrate-coated bubbles will rise until they approach the hydrate phase boundary, often many hundreds of meters above. This would result in wasted effort in the deep injection, and sequestration at depths where the ventilation ages of the water masses are quite short [15].

In order to do this we used the open-ended box described earlier, mounted in front of the vehicle, to contain the plume. We released small quantities of liquid CO<sub>2</sub> at 800m depth, and then attempted to fly the vehicle upwards at the same rate as the rising bubble stream. A meter scale was attached to the box for accurate reference, and the images were recorded digitally with a HDTV camera.

Our first and immediate observation was that collision between bubbles close to the injection point was frequent, and that colliding bubbles stuck strongly to each other, apparently minimizing surface energy through hydrate film contact, and creating unusual shapes. These were thus easy for the pilots to recognize and maintain visual contact with.

Our very preliminary analysis of these results shows a rise rate of about 6 m/minute. The results were somewhat biased (upwards) by boundary flow of trapped water along the walls of the rising box. Again our very preliminary analysis of these results shows very slow dissolution rates at depth, with the size of the bubbles only noticeably changing after several hundred meters of transit through the water

column. Some material apparently remained intact until the hydrate phase boundary, about 450m above the release point. We intend to analyze frame grabs from this experiment carefully, and give a full account at a later time.

### **CO<sub>2</sub> liquid in the deep ocean**

We have carried out only one experiment [9] at depths below 3000m, where the release is gravitationally stable due to the high compressibility of liquid CO<sub>2</sub>. We released a total of about 8 liters of liquid CO<sub>2</sub> at a depth of 3627m. Here we observed extraordinary volume increases within a few hours due to the apparent sinking of crystals of dense CO<sub>2</sub> hydrate (CO<sub>2</sub>·6H<sub>2</sub>O) formed at the interface. This transport of hydrate to the bottom of the reaction containers pushed the remaining liquid upwards, and caused multiple spill-overs of the experimental material on the sea floor. The liquid CO<sub>2</sub> on the sea floor showed a high degree of immiscibility with sea water, and did not appear to penetrate or react with the sediments. A solid block of hydrate was formed within a few hours, and this was left on the sea floor at the end of the experiment. We do not know the lifetime of this material, but since the hydrate stability conditions for pressure and temperature are far exceeded it is only the chemical potential for CO<sub>2</sub> in the under-saturated ocean that drives dissolution.

Clearly the achievement of gravitational stability in the deep ocean, and the rapid and apparently complete conversion to hydrate on short time scales are very desirable features for effective sequestration. This depth zone of the ocean appears to offer the greatest potential for future study. In addition, the environmental effects may be relatively benign (see paper by Tamburri and Brewer in this symposium). A large fish, and a sea cucumber, swam close by the experiment with no apparent avoidance reaction.

### **The depth zone not yet explored**

Below a depth of about 5000m the density of liquid CO<sub>2</sub> should become so great that it exceeds the density of the solid hydrate. In this case the hydrate should form as a skin floating on the liquid surface [3]. We have not yet carried out such a field experiment to test this, although the protocols we have described should work well.

### **ACKNOWLEDGEMENTS**

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### **REFERENCES:**

- [1] C. Marchetti, "On geoengineering and the CO<sub>2</sub> problem", *Climate Change*, Vol. 1, (1977) pp.59-68.
- [2] E.A. Parson, and D.W. Keith, "Fossil fuels without CO<sub>2</sub> emissions", *Science*, Vol. 282 (1998) pp. 1053-1054.
- [3] R. Ohmura, and Y.H. Mori, "Critical conditions for CO<sub>2</sub> hydrate films to rest on submarine pond surfaces: a mechanistic study" *Environmental Science and Technology*, Vol. 32 (1998) pp.1120-1127.
- [4] I. Aya, K. Yamane, and H. Nariai, "Solubility of CO<sub>2</sub> and density of CO<sub>2</sub> hydrate at 30 Mpa", *Energy*, Vol. 22 (1997) pp. 263-271.
- [5] M. Honda, J. Hashimoto, J. Naka, and H. Hotta, "CO<sub>2</sub> hydrate formation and inversion of density between liquid CO<sub>2</sub> and H<sub>2</sub>O in deep sea: Experimental study using submersible "Shinkai 6500". In "Direct ocean disposal of carbon dioxide", N. Handa and T. Ohsumi, Eds., Terrapub, Tokyo, pp. 35-43.
- [6] H. Sakai, T. Gamo, E. Kim, T. Tsutumi, T. Tanaka, J. Ishibashi, H. Wakita, M. Yamano, T. Omori, "Venting of carbon dioxide-rich fluid and hydrate formation in mid-Okinawa trough backarc basin", *Science*, Vol. 248, (1990) pp. 1093-1096.
- [7] P.G. Brewer, F.M. Orr, Jr., G. Friederich, K.A. Kvenvolden and D.L. Orange, "Gas hydrate formation in the deep sea: In situ experiments with controlled release of methane, natural gas, and carbon dioxide", *Energy & Fuels*, Vol. 12 (1998) pp. 183-188.

- [8] P.G. Brewer, F.M. Orr, Jr., G. Friederich, K.A. Kvenvolden, D.L. Orange, J.F. McFarlane, and W. Kirkwood, "Deep ocean field test of methane hydrate formation from a remotely operated vehicle", *Geology*, Vol. 25 (1997) pp. 407-410.
- [9] P.G. Brewer, G. Friederich, E.T. Peltzer, and F.M. Orr, Jr., "Direct experiments on the ocean disposal of fossil fuel CO<sub>2</sub>", *Science*, Vol. 284 (1999) pp. 943-945.
- [10] H. Drange and P.M. Haugan, "A feasibility study of dissolution and sequestration of CO<sub>2</sub> in the ocean", The Nansen Environmental and Remote Sensing Center, Bergen, Technical Report No. 54, (1992) pp.61.
- [11] P.M. Haugan, and H. Drange, "Sequestration of CO<sub>2</sub> in the deep ocean by shallow injection", *Nature*, Vol. 357 (1992), pp. 318-320.
- [12] M. Stuiver, P.D. Quay, and H.G. Ostlund, "Abyssal water carbon-14 distribution and the age of the world oceans", *Science*, Vol. 219 (219), pp. 849-851.
- [13] G.D. Holder, A.V. Cugini, and R.P. Warzinski, "Modeling clathrate hydrate formation during carbon dioxide injection into the ocean", *Environmental Science and Technology*, Vol. 28 (1995), pp. 276-278.
- [14] P.G. Brewer, E.T. Peltzer, G. Friederich, I. Aya, and K. Yamane, "Experiments on the ocean sequestration of fossil fuel CO<sub>2</sub>: pH measurements and hydrate formation", *Marine Chemistry*, In Press.
- [15] W.J. Jenkins, "Tritium and <sup>3</sup>He in the Sargasso Sea", *Journal of Marine Research*, Vol. 38 (1980), p. 533-569.