

## HYDRATE FORMATION DURING CONTROLLED RELEASE OF CH<sub>4</sub> AND CO<sub>2</sub> IN MONTEREY BAY

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### INTRODUCTION

We have initiated a program of research into gas hydrate formation in the deep sea by controlled release of gas into natural sea water and marine sediments with the object of investigating the formation rates and growth patterns in natural systems, and the geochemical stability of the reaction products over time. Here we present a brief account of the experiments we have performed to date, we describe the novel experimental apparatus and procedures developed by our group for *in situ* oceanic work, and comment briefly on the significance of our results.

Laboratory experiments on the formation of hydrates are well known (1,2,3) and the techniques typically involve rocking or shaking the reactants in a pressure vessel, and initiation of the reaction with ice crystals or by supercooling. The experience of laboratory researchers is that significant (> 24 hours for methane) induction times delay the onset of hydrate formation (4), and several mechanistic theories have arisen to explain this lag in terms of the activation barrier associated with cluster formation. The growth of hydrates in nature does not involve shaking the reactants, nor is supercooling or the presence of ice crystals part of the deep sea natural environment, and therefore we approached our first *in situ* experiment with genuine curiosity as to whether the reaction would proceed via simple injection of the gas within the time frame of a few hours available to us for observation. We report here that we have repeatedly observed the formation of hydrates in a few seconds from methane, methane+ethane+propane, and CO<sub>2</sub>, under various oceanic conditions, and have begun a program of time series observations of material left in place in our natural laboratory on the sea floor for an extended period of time.

### EXPERIMENTAL METHODS

We have made use of Remotely Operated Vehicle (ROV) technology, and specifically the ROV *Ventana* (5,6) operated by the Monterey Bay Aquarium Research Institute from the research vessel *Point Lobos*, to carry out our experiments. The basic vehicle has a depth rating of 1,850 m and is powered by a 40 hp electro/hydraulic power pack. The vehicle is linked to the surface by a Kevlar armored tether with five copper conductors and an optical fiber core of ten elements which carry all control and telemetry signals. Imaging is provided by a Sony DXC-3000 three-chip color video camera with a Fujinon 5.5 to 40 mm zoom lens through which we observed and recorded the experiment. A Conductivity - Temperature - Pressure sensor (CTD; Sea Bird Instruments) is mounted on the vehicle and data is telemetered in real time to the control room.

Below the main frame of the vehicle is an open tool sled structure which housed the gas tank for the methane, and mixed gas experiments. The basic system is similar to that described earlier by us (7). A pressure regulator set to 0.7 Mpa above ambient pressure and a needle valve that limited the flow rate to about 125 ml per minute were in line. Gas was distributed to the reaction chambers by four hydraulically actuated pistons (Allenair) operating quarter turn valves that were controlled directly by us through the *Point Lobos* control room interface. The valves and reaction tubes were mounted on an aluminum box frame carried on the front of the vehicle and positioned for optimum viewing. The reaction tubes were vented to the outside ocean by an overflow tube at the top of the cylinder, arranged so as to trap a small gas bubble at all times while allowing for pressure equalization. A peristaltic pump was attached to all reaction cylinders to flush sea water at the local temperature and salinity through the apparatus prior to gas injection. The gas flow schematics are illustrated in Fig. 1.

For CO<sub>2</sub> release we faced the problem of dispensing a liquid at the pressures and temperatures encountered. Two systems were used: overpressuring the liquid CO<sub>2</sub> with a bubble of He gas to expel the fluid from a vertically mounted tank; and use of a hydraulically activated piston to expel the liquid CO<sub>2</sub> from a pressured reservoir. Once the CO<sub>2</sub> was expelled the gas flow, valving and reaction vessel were identical to that for methane.

The gas was expelled into acrylic reaction cylinders (60 x 4.5 cm; volume 954 cm<sup>3</sup>) mounted vertically on the frame; a second reaction chamber with a plane viewing surface, and large enough to contain a temperature probe of five thermistors was also constructed and used in the later experiments. The chambers contained either sea water alone, or were partially filled with sediments of varying grain sizes. No provision was made for sample recovery on board ship at this time, and

the observations were purely visual, although the environmental conditions for the experiment are well defined by the CTD sensor.

## OBSERVATIONS

### *Methane Hydrate Formation*

In our first experiment ( January, 1996) we used pure methane gas ( Linde); the thermodynamic boundary for methane hydrate formation posed by the local hydrographic (P,T,S) conditions in Monterey Bay is close to 525 m water depth. We paused at about 500m to inject a small amount of gas as a precaution to clear the lines, then drove *Ventana* to a depth of about 910m and switched on the peristaltic pump to flush the system of trapped sea water and achieve T,S equilibrium with the external medium ( approximately 3.9°C; 34.42‰ ). Once the system had flushed we injected methane gas by bubble stream through a 10 µm porous frit at the bottom of the reaction cylinders. Methane hydrate formation occurred within a few seconds, seen easily as a bright reflective bubbly mass at the gas/water interface at the top of the tube. The hydrate formed as a white rind on the gas bubble surface that appeared to separate the water and gas from further rapid reaction unless some mechanical disturbance occurred. The reaction was reproducible; an injection into a second reaction cylinder produced an identical result. No significant induction period was observed, nor was anything other than gas and natural sea water present.

Of the two remaining reaction cylinders one contained about 20 cm of coarse sand, and the other a similar amount of fine grained mud. Here the hydrate formation was again first seen at the top of the tube. But the pores of the coarse sand matrix were soon observed to be flooded with hydrate, which sealed off further gas flow. The effect was to create cracking and then lifting of a major piece of the solidified sand column. Gas flow through the fine mud caused channels to open up since the capillary pressure for the gas to enter the pore spaces was higher than that required to displace the sediment. White hydrate masses quickly formed on the walls of the channels and gas created void spaces with an appearance and effect quite different from the coarse sand matrix. On recovery of the vehicle the hydrates formed in our experiment dissociated during transit to the surface, and we were not able to recover specimens for analysis.

### *CO<sub>2</sub> Hydrate Formation*

In a second dive with an almost identical experimental arrangement (water, and sediment containing, reaction cylinders) we observed hydrate formation with CO<sub>2</sub>. Here the local thermodynamic boundary for CO<sub>2</sub> hydrate formation occurs at about 350m water depth. We added a small amount of helium gas to the CO<sub>2</sub> cylinder prior to the dive so as to create an overpressure to drive the liquid CO<sub>2</sub> out of the primary reservoir. *Ventana* was then driven to about 568 m, and gas injected as before. White hydrate "whiskers" appeared at the frit within a few seconds, and a mass of hydrate coated bubbles formed quickly at the upper gas/water interface. Any induction period for hydrate formation was so short as to be negligible.

Our inspection of the performance of the apparatus at depth, and leakage of gas around valves, lead us to believe that our stratagem of using He to overpressure the CO<sub>2</sub> had in fact created a CO<sub>2</sub>/ He gas mixture, and that this particular experiment cannot therefore be strictly interpreted as pure CO<sub>2</sub> hydrate formation. Since He does not form a hydrate under any conditions the overall effect is likely to be small. Interestingly all CO<sub>2</sub> hydrates formed were buoyant, and rose rapidly through the sea water to rest at the interface between gas and water. The density of CO<sub>2</sub> hydrate is substantially greater than sea water, and the buoyancy is an indication of trapped unreacted liquid CO<sub>2</sub> ( plus a small amount of dissolved He) in the formed product. Visual inspection, by close camera focus, of the bubbles of hydrate confirmed the presence of a liquid layer inside the hydrate sheath. Injection of CO<sub>2</sub> into the sediment containing cylinders produced a sequence of results very close to that observed for methane.

### *Mixed Gas Experiment*

An experiment with a methane (90%) ethane (5%) and propane (5%) mixture was also carried out. Here the presence of propane as a hydrate Structure II former significantly shifts the hydrate boundary to shallower depths than that for methane alone; moreover the presence of propane is widely regarded as acting to reduce any induction period for hydrate formation. Since we have observed a very short formation time for CH<sub>4</sub> hydrate, the differential effect of using this gas mixture was insignificant and equally rapid hydrate formation on bubble surfaces was seen.

### *Liquid CO<sub>2</sub> injection*

In an effort to create pure CO<sub>2</sub> hydrate without the complexity of probable He contamination in the mixture, we rebuilt the gas release apparatus so as to contain liquid CO<sub>2</sub> in a piston actuated cylinder. Care was taken to apply pressure from ROV system hydraulics to the open side of the cylinder throughout the dive so as to maintain a positive pressure over ambient and thus avoid pressures in the incorrect sense on the gas regulator. Here we dove to about 910m, and released CO<sub>2</sub> into the apparatus. At this depth only the liquid CO<sub>2</sub> phase is present. No fine pore frit, but a simple

small bore tube, was used for sample introduction in this experiment for fear of plugging the apparatus completely. The effect was to create globules of liquid  $\text{CO}_2$  which, after sticking temporarily to the release port, rose slowly to the upper interface. There it appeared that a fine film of accreting hydrate gave a pearly appearance to the external surface of the globules, which did not coalesce but remained as separated units.

#### *Thermal Signatures*

In a modification of our apparatus we replaced one of the cylindrical reaction tubes with a plane faced larger unit for better viewing. In this unit we placed a heat flow probe constructed by the Woods Hole Oceanographic Institution's Alvin group. This consists of a metal rod about 1 m long with five thermistors each separated by about 10 cm. Readout from the probe was fed directly to the control room for real time monitoring of the experiment. Working with pure  $\text{CH}_4$  gas in sea water we observed the temperature rise from the heat of formation during hydrate creation on bubble surfaces at the gas/water interface. Disturbance of the upper boundary by bubble flow created a mixed layer several centimeters deep which served to dissipate the heat, and it was not possible to gain a more quantitative estimate of the amount of hydrate formed.

On termination of the experiment and on raising *Ventana* to shallower depths we immediately observed a temperature drop due to quasi-adiabatic expansion cooling of the unreacted gas in the head space. Adiabatic cooling of the sea water itself is much smaller, but can be evaluated since the equation of state for sea water is well known (8). The temperature drop associated with gas expansion continued on raising until the hydrate decomposition point was reached. This point was not identical with the external oceanic boundary condition for dissociation due to the lower temperature at equal pressure within the apparatus, but it was clearly defined by a sharp break in the temperature trend due to cooling from the heat of dissociation.

#### *Longer Term Observations*

We intend to make longer term studies of the *in situ* stability of the hydrates we form than can be afforded within the confines of a one day dive schedule. This has meant devising a means to leave the apparatus on the sea floor for an extended period, and to return to it periodically for inspection and sampling of the trends. We have begun this process by constructing a square frame designed to sit above the sea floor and to hold the reaction tubes in place at a level where they can be viewed by the vehicle camera on return visits. This requires some means to first form the hydrate, then sever the connecting gas lines, pick up the frame with the vehicle robotic arm, and place it away from *Ventana* so that we can exit the site. Return to the location is provided for by deploying an interrogatable acoustic beacon nearby.

We have completed the first step and have left in place both  $\text{CH}_4$  and  $\text{CO}_2$  hydrate containing reaction cylinders at about 905 m depth at the "Clamfield" site in Monterey Bay. Revisits to this site after approximately 3 days, and 3 weeks, showed very little change in the hydrate structures we first formed. The cylinder containing  $\text{CH}_4$  hydrate, unreacted gas, and sea water, was characterized by a bright white bubbly appearance. The bubbles with hydrate rind had not significantly coalesced or changed dimensions in the 3 week period. The  $\text{CO}_2$  hydrate system, again containing liquid  $\text{CO}_2$ , hydrate and sea water, had the aforementioned appearance of pearly globules that remained as distinct entities separated by their hydrate sheath for the full observation period to date.

#### DISCUSSION

From the experiments we have carried out to date we can make some interesting conclusions about the manner and characteristics of hydrate formation in the deep sea, where the reaction medium contains the normal assemblage of suspended particles, bacteria, and trace gases which characterize the natural environment. Firstly we have repeatedly made hydrates of several gases, each within the period of a very few minutes or seconds, by the simple technique of direct gas injection with no shaking or ice nucleation step whatsoever. The initial manifestation of this was the creation of hydrate coated bubbles at the gas/water interface; but hydrate also formed in seconds to minutes within the pore spaces of marine sediments where no provision was made for gas trapping. We surmise that passage of the gas bubbles around the sediment grains caused sufficient surface renewal that hydrate formed in a similar manner to the more easily visualized upper boundary, but with smaller unit size granules. No significant induction or lag period was observed for hydrate formation for any gas yet injected in this manner.

Once formed the hydrate structures appeared quite stable. That behavior is consistent with the idea that the hydrate rind on bubble surfaces separates the inside gas from the outside water well enough that further growth must occur only slowly by diffusion of the reactants through the hydrate skin. Unless some defect or fracturing of the hydrate rind occurs, this appears to be the rate limiting step.

Growth of hydrate in marine sediments is critically dependent on the grain size of the material. In a coarse material (sand) flooding of the pores results in cementing of the sediment into a massy unified

structure within seconds, yet yields no hydrate nodules of the kind often reported in nature (9). These nodular structures were observed in the process of forming in the flow channels carved by gas in experiments in fine grained mud, and the contrast between hydrate formation in the coarse and fine matrices was dramatic.

Our work with CO<sub>2</sub> hydrate has yielded results relevant to the proposed disposal of CO<sub>2</sub> in the deep ocean (10). For instance the ease with which CO<sub>2</sub> hydrate forms will pose a challenge to deep injection facilities concerned with plugging of the system; and the observation of the relative stability of the hydrate coated globules restricts interaction between disposed CO<sub>2</sub> and the surrounding ocean water. Furthermore, CO<sub>2</sub> hydrate did not separate spontaneously from unreacted CO<sub>2</sub>; instead it formed a mass of intermediate density between sea water and liquid CO<sub>2</sub>. Our observations were consistent with the description by Sakai et al. (11) of the natural venting of CO<sub>2</sub> rich fluids on the ocean floor.

Our experience with CO<sub>2</sub> hydrate formation is that the liquid CO<sub>2</sub> used experimentally requires excellent technique to handle. Post cruise analysis of our experiment carried out with He overpressure indicated by formal calculation (using the Peng-Robinson (12) equation of state) that the gas injected was indeed a CO<sub>2</sub>/He mixture, since under the conditions we used (about 4.4<sup>0</sup> C, 1800 psia) to prepare the gas reservoir then about 10 mol% He will dissolve in the liquid CO<sub>2</sub>. Release of this at our *in situ* experimental conditions will form a mixture of about 20 volume % liquid phase, and 80 volume % vapor, accounting for our observations.

Once formed from sea water/gas (or liquid) contact, the hydrates are stable over a period of several weeks, and quite possibly very much longer indeed, even though sea water and unreacted gas or liquid are separated only by a thin hydrate film. The initial attempt we made to study this was successful in separating the experimental apparatus from the vehicle, and leaving it in place. In future experiments we will leave hydrates within sediment matrices for later recovery, and arrange for greater sea water/hydrate contact, since water flow around the hydrates was quite restricted in the present system.

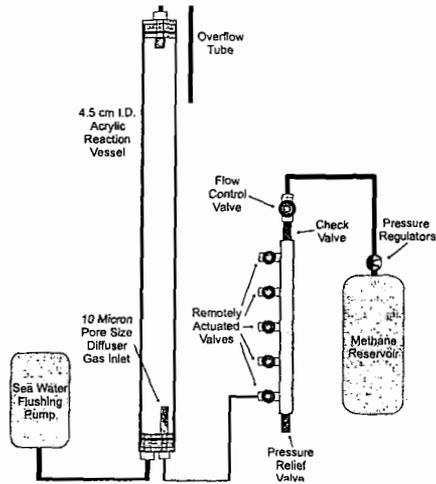
Finally we are devising means for surface recovery of the experimental material for laboratory investigation, and wish to apply the knowledge we have gained to a variety of important geochemical and gas disposal problems.

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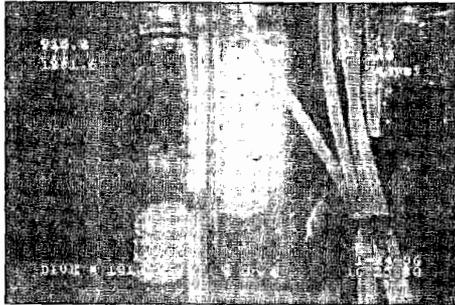
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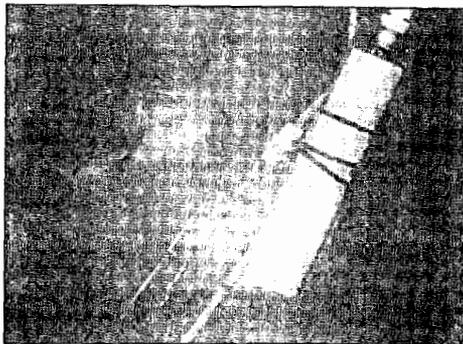
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1. Line diagram of the experimental apparatus used for hydrate generation from the ROV *Ventana*; the various pieces are not to scale.



2. Image of methane hydrate formed at the upper gas/water interface. The hydrate rind on bubble surfaces is plainly seen. The digital information on the screen gives (top, upper left) depth, and date and time (lower right). The reaction cylinders are 4.5 cm. diameter.



3. Image of both methane (right, white) and carbon dioxide (left, gray) hydrates approximately 3 weeks after initial formation in experimental apparatus left on the sea floor. The granular appearance of the methane hydrate is retained; the less rounded blobs of liquid carbon dioxide have a thin veneer of hydrate that apparently prevents surrounding sea water from further reaction.