

Hydrate Formation from Gaseous CO₂ and Water

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Economics of creating CO₂ hydrate on a large scale favor use of gaseous rather than liquid CO₂ as input to the production process. We accordingly studied systems using deionized water and CO₂ gas to reduce formation pressures and costs of hydrate production to the greatest extent possible. Three research avenues were explored: utilization of hysteresis effects, use of dissolved Snomax (a protein from the bacterium *Pseudomonas syringae*), and development of a continuous flow reactor (cfr) utilizing vigorous mixing of water and CO₂ gas. Hysteresis effects produced pressure reductions of 14–50%. We demonstrated a method of transferring benefits from the hysteresis effect to a CO₂ water mixture that had not yet undergone hydrate formation. Snomax at 10 ppm by weight produced about a 5% reduction in hydrate formation pressure. We designed and operated a prototype cfr with partial success at producing CO₂ hydrate. The hydrate phase diagram is based on hydrate decomposition pressures and should not be used as an indicator of formation pressures.

Introduction

We discussed hydrate formation from water and liquid CO₂ in earlier reports (1, 2). Economic considerations led us to explore use of gaseous CO₂ for creating hydrate. If large scale hydrate production is selected as a methodology to facilitate disposal of anthropogenic CO₂, costs for compressing the compound can be minimized by using the gas versus the liquid. Spencer (3) estimated that the power requirement more than doubled for injecting liquid CO₂ directly into the deep ocean, compared to injecting hydrate formed at 12.8 bar and 0 °C, for a macroalgal farm. Spencer more recently repeated the computation for a shifted synthesis gas power plant (4).

The kinetics of CO₂ hydrate formation was discussed by Malegaonkar et al. (5) and by Chun and Lee (6). Computed values of the rate constant K^* differed between the two studies by factors of 28–69. Malegaonkar et al. ascribed the differences to their usage of particle diameter vs particle radius by Chun and Lee as well as a failure by the latter authors to take account of the temperature change occurring as hydrate particles form.

The literature concerning CO₂ hydrate apparently contains very few examples showing detailed pressure–temperature conditions associated with hydrate formation (a number of papers, however, provide this information as regards hydrate dissociation). Noda et al. (7) graphed nine data points representing hydrate formation and lying within the relevant region of the phase diagram. They also showed 12 data points from Vlahakis et al. (8) as representing hydrate formation data, but the text of this reference (p 10) indicated that the points probably represented hydrate decomposition. Blackwell (9) provided 10 data points representing hydrate formations, but the information only consisted of temperature values while pressure was held constant at 55 bar during her studies. Neither of these authors investigated hysteresis phenomena, nor were data available allowing for estimates of variability involved in hydrate formation. To provide these kinds of data, we concluded it was desirable to establish our own database of hydrate formation pressures and temperatures. These data then served as a basis for recycling experiments to obtain information concerning hysteresis. Accordingly, our objectives were to (1) obtain a data set of moderate size, using relatively simple experimentation, showing temperatures and pressures required for hydrate formation from gaseous CO₂ and water and (2) investigate possibilities for reducing hydrate formation pressures from values obtained in the above data set; possibilities to include utilizing the hysteresis effect, evaluating usage of Snomax (a protein used for stabilizing ice crystals), and evaluating effects from vigorous agitation.

Materials and Methods

Apparatus. Pressure chambers used for most of the work described herein were hollow cylinders, prepared by drilling and polishing polycarbonate rod to yield an internal diameter of 2.22 cm (Figure 1). Wall thickness was 1.43 cm. Each end was capped with stainless steel bushings, drilled, and tapped to accommodate 1/4 inch stainless steel tubing and fittings. We tested each chamber to a pressure of 68.9 bar.

Small holes were drilled laterally in some chambers to accommodate 171–20 temperature sensors, transmitting data to a Mark 15 Readout Module (Martek Instruments Inc.). Deionized water was used for experiments reported herein. Two experiments using seawater yielded results typical of values obtained with deionized water. Pressures in most experiments were controlled by Reducing Regulators (Aqua Environment Co., Model 415A). Compressed CO₂ from a commercial source was 99.9% pure with composition as described by North et al. (1).

Two of these cylindrical chambers were coupled together to establish feasibility of utilizing the hysteresis effect to lower hydrate formation pressures. A single cylinder served to evaluate the utility of Snomax and also served as the hydrate receiver in the experiments testing the cfr.

An entirely different apparatus was assembled to evaluate effects from vigorous agitation on hydrate formation. The critical element in this apparatus was the Johnson Fluidic Venturi, utilized in experiments producing hydrate from streams of water and gaseous CO₂ (Figures 2 and 3).

All experiments were conducted in a walk-in cold room at Caltech's Kerckhoff Marine Laboratory. The cold room air temperatures fluctuated through an approximate range of 0.2 °C above and below the preset value.

Procedure. Preliminary experiments indicated that bubbling CO₂ through water yielded more satisfactory results (i.e. hydrate formation at lower pressures for a given temperature and a more easily recognized end point) than

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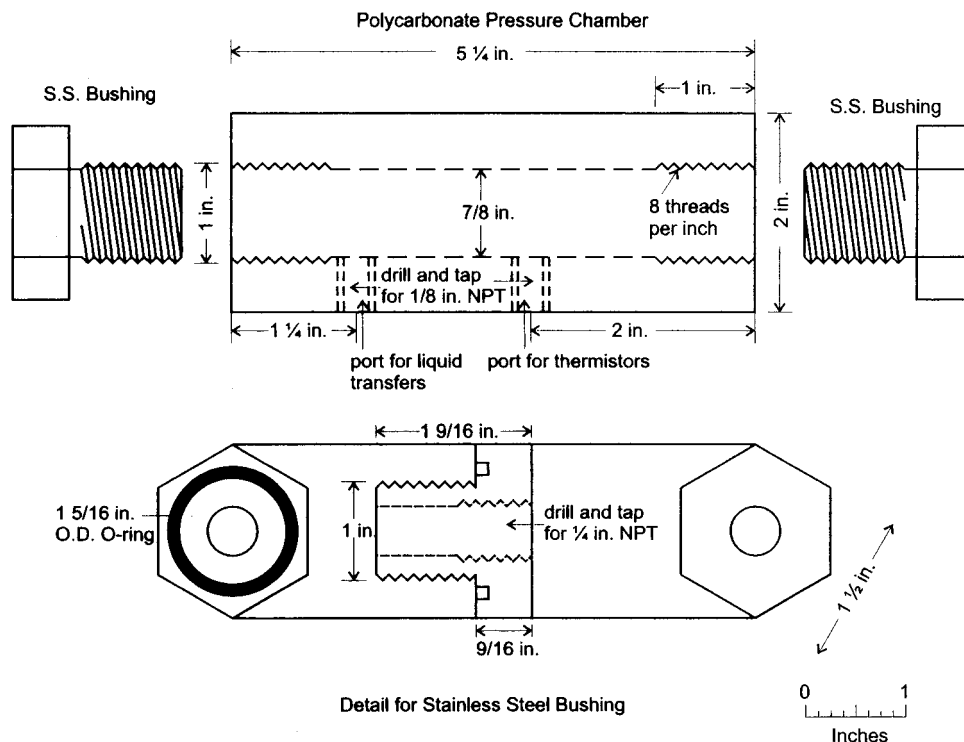


FIGURE 1. Diagram of the polycarbonate pressure chamber used in our experiments.

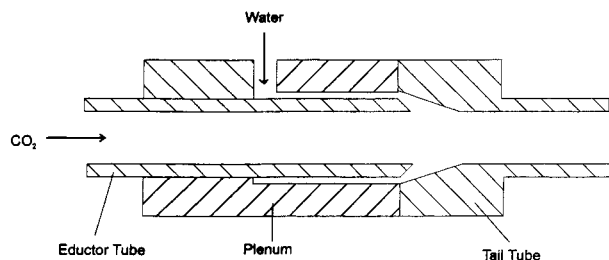


FIGURE 2. Diagram of the Johnson fluidic venturi used to create agitation for converging streams of water and CO₂. The diagram is for illustration only and does not show proper dimensions.

injecting water into gaseous CO₂. The cylindrical chamber was held rigidly with the long axis oriented vertically. CO₂ was injected into the chamber through a hypodermic needle sealed into the bottom bushing. The chamber was typically filled with about 20–25 mL of water, which was sufficient to immerse a temperature probe with about 1 cm of overlying water. This left about 1 cm of CO₂ gas at the top of the chamber. CO₂ was bubbled through the water column prior to each experiment, for 1/2 h, to remove dissolved air.

Hydrate always formed initially at the water–gas interface. The forming solid altered appearance of the water surface from shining (due to light reflection) to dull. With practice and care, the hydrate formation pressure could be determined to an accuracy of about 0.069–0.138 bar. In a typical experiment, pressure was raised in a chamber by bubbling gaseous CO₂ through the water column to a level corresponding to the hydrate decomposition point, as inferred from the phase diagram, utilizing the temperature setting of the cold room. A cooling period followed till the internal and external temperatures were similar. Bubbling recommenced until the first indication of a hydrate crust appeared at the gas–liquid interface. This activity was termed the primary run.

Hysteresis effects were determined by recycling operations after a completed primary run. Pressure was carefully reduced until the hydrate crust completely decomposed. Pressure

was then raised by bubbling until crust again formed (the secondary run). This cycle was repeated for a tertiary run. Further recycling typically yielded formation pressures similar to the tertiary run, so hysteresis was essentially complete after a tertiary run (and occasionally after a secondary run).

Utilizing hysteresis effects involved coupling together two cylindrical chambers to allow the contents of one (the “nucleator”) to be transferred to the other (the “reactor”). Prior to the transfer, hydrate was formed in the nucleator by recycling and decomposition 3 times. The presumably fully “nucleated” water was then transferred to the reactor chamber which held an equal amount of water as well as dissolved and gaseous CO₂ at about the hydrate decomposition pressure. The pressure in the reactor, prior to the transfer, had never been raised to a level where hydrate might have formed. The experiment tested hysteresis characteristics of the 50/50 mixture of “fully nucleated” and “partially nucleated” water (i.e. whether the mixture would exhibit hydrate formation pressures of a tertiary run).

The experimentation testing effects of Snomax on hydrate formation pressures involved comparing data sets involving control formations with sets using deionized water containing Snomax at three differing concentrations (1, 10, and 100 ppm by weight). The Snomax granules were ground to a powder and dissolved in water at temperatures just above 0 °C. Snomax is a commercial product from Genencor, used to prevent melting of snow at ski resorts for a few degrees above 0 °C. The product is a protein obtained from cell walls of a bacterium *Pseudomonas syringae* (10).

We tested effects of violent agitation on hydrate formation by using the Johnson fluidic venturi to mix water and gaseous CO₂. The venturi required input streams of both reactants for proper operation, so we assembled accessory equipment that served as a continual flow reactor (cfr). Preliminary studies with a small venturi constructed especially for our studies produced an output stream of water and air full of small bubbles with estimated diameters up to 1 mm. The measured flow rate was 0.36 L/s. This rate could accommodate about 120 g/s of CO₂, producing 1.7 T/h of hydrate, assuming that all the gas was fully converted. The unit sucked

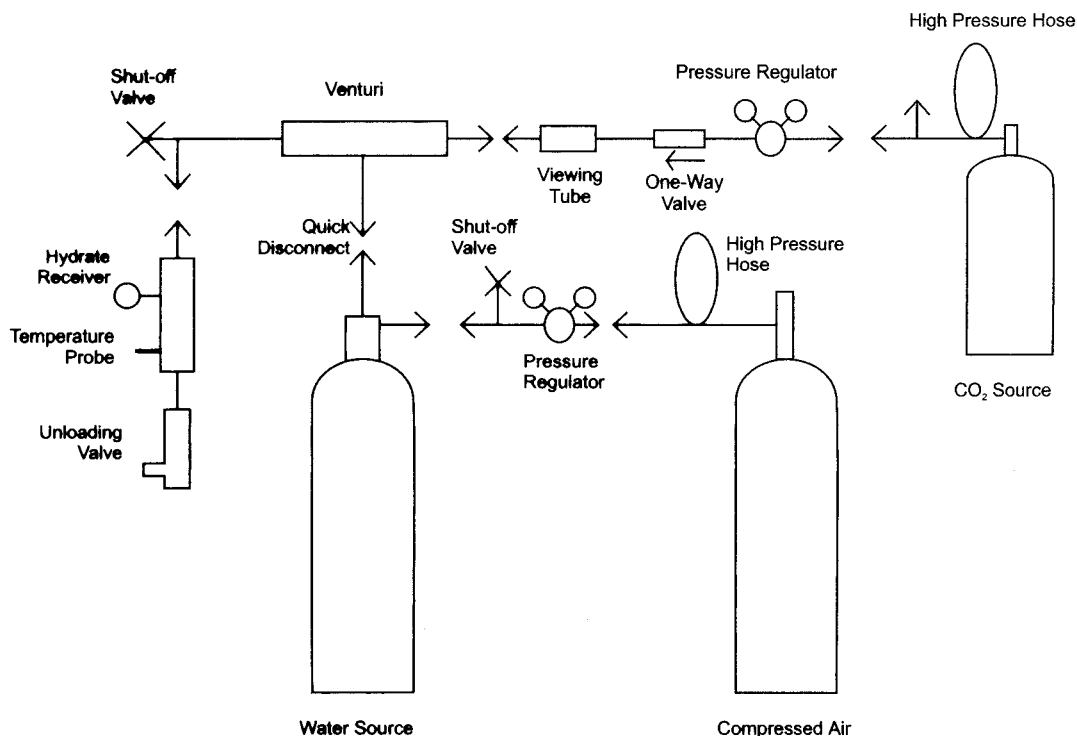


FIGURE 3. Diagram of apparatus used with the Johnson fluidic venturi to determine effect of vigorous agitation on hydrate formation from streams of water and CO₂. Scuba diving tanks were used for the source of high-pressure air and water supply.

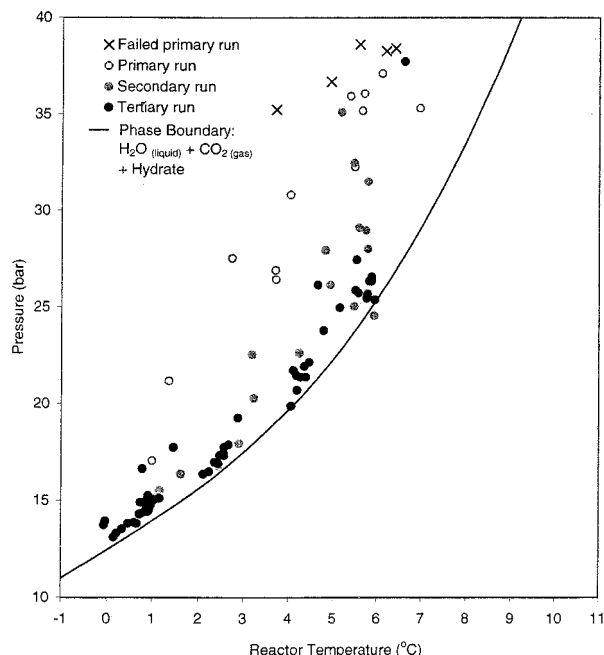


FIGURE 4. Hydrate formation pressures vs temperature, showing data for primary, secondary, and tertiary runs (the latter two categories arising from hysteresis effects).

atmospheric air through the eductor tube with water entering the plenum at 6.9 bar. The fluidic venturi thus might be able to produce hydrate with a CO₂ input pressure well below the hydrate formation pressure. Capacity of the assembled cfr sustained performance for an operational time up to 70 s, determined by using water and compressed air. Under experimental conditions, however (i.e. using deionized water and gaseous CO₂), most of the runs producing hydrate terminated almost instantaneously because the receiving container became choked with solid hydrate.

TABLE 1. Percent Reductions in Hydrate Formation Pressures Due to Hysteresis Effects and Percent Differences between the Hydrate Formation Pressure and the Decomposition Pressure of the Same Run

cold room temp, °C	run	% reduction	% difference
5.0–5.4	A	25	59
4.7–5.4	A	29	68
	B	19	39
	E	29	63
	F	33	72
	G	38	63
3.4–4.9	A	15	83
	B	40	75
	C	32	61
1.7–2.2	A	50	131
	B	39	67
	C	39	87
–0.3–0.2	A	14	32
	B	31	71
	C	40	95

Results and Discussion

Obtaining a Data Base and Hysteresis Data. We conducted 19 primary runs, forming CO₂ hydrate at cold room temperatures ranging from 5.4 to –0.3 °C. Five of these runs were classed as “failed primaries” because no hydrate formed during the primary run which of necessity terminated when the pressure inside the experimental chamber reached the maximum pressure present in the CO₂ source cylinder.

A plot of a number of runs at various temperatures revealed considerable variability with only two instances where hydrate formed at the phase boundary line (Figure 4). The remaining data were segregated according to whether a given run represented a primary, secondary, or tertiary type of run. An occasional secondary run formed hydrate at a pressure characteristic of a tertiary run and vice versa. Pressure reductions due to hysteresis effects were usually substantial (Table 1; temperature differences were not taken

TABLE 2. Results from 11 Experiments Using the Johnson Fluidic Venturi To Determine Capability of Agitation To Produce Hydrate from Water and Gaseous CO₂^a

expt. no.	bar			remarks
	A	B	C	
1	25.2	24.8	22.4	unsuccessful, flow not frothy (i.e. no CO ₂ input)
2	21.8	18.2	21.4	unsuccessful, neglected to include unloader valve
3	29.8	29.2	12.1	hydrate produced
4	26.5	22.4	21.7	small amount of hydrate produced
5	32.1	11.4		unsuccessful, CO ₂ input line probably clogged with hydrate
6	6.3	6.5	6.4	unsuccessful, CO ₂ input line probably clogged with hydrate
7	31.0	23.8	23.8	unsuccessful, CO ₂ input line probably clogged with hydrate
8	30.1	16.3	13.8	hydrate produced
9	29.0	24.1	21.4	unsuccessful, CO ₂ input line probably clogged with hydrate
10	31.4	19.9		unsuccessful, unloader valve kept P low in hydrate receiver
11	32.7	32.4	32.4	hydrate produced

^a Ambient temperature was 1 °C. Cited pressures represent values at the (A) water input, (B) CO₂ input, and (C) hydrate receiver input. Cracking pressure for the unloader valve was 16.5 bar except for experiment 11, which was 31.0 bar.

into account when computing percent differences in hydrate formation pressures; for some but not all cases, the result would be to overestimate the overall hysteresis effect). The percentage pressure reduction achieved by hysteresis appeared to be independent of temperature.

Utilizing the Hysteresis Effect. Schroeter et al. (11) noted "the hysteresis effect is a result of the metastability of hydrate compounds" following decomposition of the hydrate crystals. Utilization of metastable compounds (i.e. hydrate nuclei) would involve transferring a batch of nuclei under pressure to a solution of water and CO₂ that had not undergone hydrate formation, hoping that the mixture might enable hydrate formation at a significant pressure reduction from values characterizing a primary formation.

We conducted this type of experiment using water from a chamber (the "nucleator") that had undergone three cycles of hydrate formation and dissolution at hydrate formation pressures of 25.6, 25.2, and 24.1 bar. A second chamber (the "reactor") contained water at 20.0 bar and supersaturated with CO₂. The "nucleated" water was then transferred from the nucleator to the reactor to produce a 50/50 mixture of fully nucleated and partially nucleated water. Hydrate was then formed in the mixture and then decomposed, passing through six cycles. Hydrate formation pressures for the six cycles were 22.7, 22.1, 22.5, 23.4, 23.4, and 23.0 bar. We concluded that a hysteresis effect had been transferred from the nucleator to the reactor. Further experimentation is needed to determine the minimal ratio of nucleated to reactor water that can still produce a substantial hysteresis effect. A large scale hydrate reactor could presumably transfer hysteresis effects by simply recycling a portion of the product to the reactor input at an appropriate pressure.

Effect of Snomax on Hydrate Formation Pressure. It seemed possible that a protein such as Snomax that influences structure of pure water might also enhance structuring of water cages prior to hydrate formation and/or perhaps stabilize the hydrate entity after formation. Experimentation consisted of determining hydrate formation pressures over a narrow range of temperatures for three concentrations of snomax. The data suggested that Snomax tended to depress the hydrate formation pressure moderately (Figure 5). A Snomax concentration of 1 ppm did not produce as great a depression as 10 ppm. Degree of depression by Snomax at 100 ppm was similar to the effect obtained at 10 ppm. Shifting the temperature from 3.4 to -0.1 °C did not change results. A 10 ppm solution of Snomax reduced the hydrate formation pressure by approximately 0.69 bar. While this represented only a 5% reduction in hydrate formation pressure, it might prove desirable if large-scale hydrate production is ever attempted.

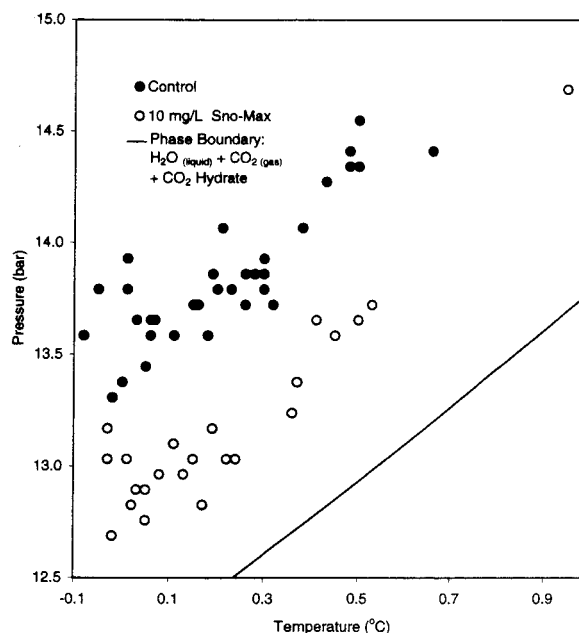


FIGURE 5. Hydrate formation pressures vs reactor temperatures, representing tertiary runs, using a Snomax supplement of 10 ppm vs a control run. Cold room temperature was about 0 °C.

Studies Using the Johnson Fluidic Venturi. A series of 11 tests at various pressures yielded CO₂ hydrate during four runs (Table 2). Four of the unsuccessful runs very likely failed because small amounts of water backed up into the CO₂ line (despite a one-way valve in that line that was intended to prevent such mishaps), completely blocking passage by the CO₂ gas.

The four successful runs with the venturi indicated that vigorous agitation would be a very useful feature in a system designed to produce CO₂ hydrate from gas and water. Hydrate formation was almost instantaneous, completely clogging any flow out of the hydrate receiver for runs 3, 8, and 11. Hydrate also filled the tail tube of the venturi. Little, if any, pore water appeared to have been trapped within the aggregate of hydrate crystals. Kinetics were apparently very rapid and probably dominated under conditions prevailing inside the tail tube. The system apparently produced hydrate in the region of intense mixing as water and CO₂ entered the tail tube. The pressures shown in Table 2 were usually greater than desired for an operational cfr (although the CO₂ input pressure for run 8 was close to that characterizing a tertiary run). Our objectives, however, were to demonstrate the benefit of vigorous agitation in a gas-water system (not

necessarily to demonstrate the optimal conditions for creating large amounts of hydrate) and to show that hydrate could be successfully produced in an operational cfr.

Acknowledgments

We are grateful to Mr. Wayne Talmiter of Genencor for providing a sample of snomax for use in our investigations. Assistance from the staff of the Kerckhoff Marine Laboratory is acknowledged with gratitude. The research was supported by a grant from the Electric Power Research Institute.

Supporting Information Available

Tables of pressures and temperatures and relations between time, pressure, and temperature. This material is available free of charge via the Internet at <http://acs.pubs.org>.

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Received for review July 20, 1998. Revised manuscript received January 29, 1999. Accepted February 5, 1999.

ES980736K