LABORATORY FORMATION OF NON-CEMENTING, METHANE HYDRATE-BEARING SANDS

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ABSTRACT

Naturally occurring hydrate-bearing sands often behave as though methane hydrate is acting as a load-bearing member of the sediment. Mimicking this behavior in laboratory samples with methane hydrate likely requires forming hydrate from methane dissolved in water. To hasten this formation process, we initially form hydrate in a free-gas-limited system, then form additional hydrate by circulating methane-supersaturated water through the sample. Though the dissolved-phase formation process can theoretically be enhanced by increasing the pore pressure and flow rate and lowering the sample temperature, a more fundamental concern is preventing clogs resulting from inadvertent methane bubble formation in the circulation lines. Clog prevention requires careful temperature control throughout the circulation loop.

Keywords: gas hydrate, hydrate formation, dissolved phase

NOMENCLATURE

cc Cubic centimeters
φ U.S. Sieve size designation (phi)

INTRODUCTION

Forming gas hydrate, a crystalline solid, in sediment alters the host sediment’s mechanical properties. In coarse sediment, where gas hydrate tends to form in existing pore space, the impact of hydrate formation depends not only on how much gas hydrate forms, but also on where it forms within the pore space [1-3]. Hydrate-rich, coarse-grained sediments are thought to be of particular value as an energy resource [4], and these high-hydrate-content sediments are generally thought to behave as if the hydrate is a load-bearing member of the sediment [5, 6]. To be most relevant for constraining mechanical properties in the field, laboratory-formed, hydrate-rich sands should exhibit the same behavior.

Load-bearing hydrate systems are thought to occur when hydrate forms in the absence of a free gas phase [7]. This has been accomplished extensively in the laboratory using Tetrahydrofuran [8-10]. Because the solubility of methane in water is low, however [11, 12], hydrate formation purely from methane dissolved in water flowing through porous material is a slow process and has not been as frequently attempted [13, 14].

To accelerate the hydrate-formation process, Priest et al. [1] formed methane hydrate from a limited supply of methane bubbles in an otherwise water-saturated sample. This method required ~7 days, and while this is faster than the several weeks required for the purely dissolved-phase formation of Spangenberg et al. [13], the Priest et al. [1] method is limited to pore-space hydrate saturations below ~40%. Above this level, there is too much free gas initially to fully transform into hydrate.

We propose to combine the Priest et al. [1] and Spangenberg et al. [13] methods. By initiating hydrate growth using the Priest et al. [1] method, we establish an initial hydrate saturation relatively quickly. To increase the hydrate saturation, we then adopt the Spangenberg et al. [13] approach

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and circulate methane-rich water through the sample. The flow of water through a hydrate-bearing sediment has also been shown by Ebinuma et al. [15] to migrate grain-cementing hydrate into load-bearing configurations. While promising in theory, the practical application of this approach is prone to hydrate clog formation in the growth chamber’s inlet and outlet lines, which limits the capacity for additional hydrate growth in the sample. Here we examine the formation process in greater detail, offering suggestions for optimizing hydrate formation rates.

**APPARATUS**

We form methane gas hydrate using a flow loop (Fig. 1). A Polyscience circulator controls the growth chamber bath temperature. An Isco pump is used to maintain a baseline pressure in the system. A Quizix pump is used to maintain a constant water flow rate through the system. We use a glass-bead-filled interface chamber to saturate the circulating water with methane. With the exception of the Isco and Quizix pumps, the system is housed in a fume hood.

Line pressures are measured by both pumps and by pressure sensors in the growth chamber’s inlet and outlet lines (1.6 and 2.8 mm-inner diameter, respectively). Temperatures are measured via thermocouples on the outer surface of the interface chamber, in the growth chamber bath, and inside the growth chamber near the sample’s top and bottom. Star-oddi DST micro autonomous sensors measure pressure and temperature within the sample itself near the sample’s top and bottom. Each sensor is 8.2 mm in diameter, 26 mm long.

**PROCEDURE**

To begin an experiment, the 5-cm diameter, 240 cubic centimeter (cc) sample vessel is loaded with damp F110 quartz sand. To limit migration of sand out of the chamber, the sand is sieved to remove the < 90 µm grain size fraction (3.5φ sieve), and 61 µm mesh-size screens with 119 µm mesh-size screen backings are placed over the inlet and outlet ports. Assuming a target porosity of 36%, the sand is pre-moistened to have ~18% pore-space water saturation. The sand is spooned into the sample chamber and tamped to create ~ 1cm-thick layers. The Star-oddi sensors are placed at measured depths near the bottom and top of the sample. The thermocouples are driven into the damp-sand sample as the top endcap is seated on the growth pressure vessel.

The pressure-temperature path for an experiment is shown in Figure 2. The pressure vessel is first placed in the temperature-controlled bath at 16°C, evacuated, and charged to ~4.2 MPa with methane gas. This methane pressure is calculated to provide ~20% pore-space hydrate saturation and methane-saturate the water that will eventually fill the remaining pore space.

Gas pressure is allowed to stabilize overnight before the system is pressurized to 11.7 MPa by injecting water with the Isco pump at 0.3 cc/min. Approximately a third of the injected water is introduced at the base of the sample before finishing the pressurization process by injecting from the flow inlet at the top of the sample. This two-sided injection is intended to retain free gas bubbles within the sample’s interior, rather than press gas to one end of the sample [E. Rees, personal communication], and takes ~ 3.5 hours to complete. Beginning with damp, rather than dry, sand yields well-distributed gas bubbles upon water injection [18].

To form hydrate, the sample is cooled to ~4.2°C and held at 11.7 MPa by adding water as needed by the Isco pump. The rate of water consumption dwindles to < 0.01 cc/day within ~120 hours. After 120 hours, a heater tape attached to the

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**Figure 1** Flow loop schematic. Water absorbs methane at room temperature $T_r \approx 23°C$ as the water drips past ~250 µm-diameter glass beads in a methane head space in the gas water interface chamber. Methane-rich water then flows into the growth chamber, where hydrate can accumulate in a sand pack held at temperature $T_l$ (9 – 11.5°C) by the growth bath controller. While the pressure control pump holds the sample outlet pressure at 11.7 MPa, the flow control pump cycles water through the system at a constant rate between 0.1 and 1 cc/min.
growth chamber flow outlet line is turned on, and the sample is warmed to \( \sim 12.5^\circ C \) before water flow through the sample is initiated. At this temperature, circulating water tends to dissolve small blockages that form in the inlet and outlet lines during the initial hydrate synthesis. Once flow is established, the sample is cooled to the target temperature of 9 to 11.5°C. Water circulates through the system at a constant rate of 0.05 to 1.0 cc/min (Fig. 1). Prior to entering the growth chamber, water passes over \( \sim 250 \mu m \)-diameter glass beads in a 100 cc methane-charged headspace in the interface chamber. The interface chamber is nominally held at 11.7 MPa at a room temperature of 23°C. When circulating water passes through the interface chamber, the process of dripping through the glass beads exposes a relatively large surface area of water to the pressurized methane in the interface headspace, facilitating uptake of methane by the water [M. Rydzy, personal communication].

Water exits the bottom of the interface chamber and passes to the top of the hydrate growth chamber, which is nearly submerged in the temperature-controlled bath. Circulating water cools as it passes through the sample chamber, then exits through the heater-tape-warmed drain line and completing the circuit to the pumps. By leaving the inlet line and sample chamber top exposed and out of the hydrate-stability field, we seek to reduce hydrate formation in the inlet line and top endcap of the growth chamber.

To conclude an experiment, flow loop valves are shut so the sample is in communication only with the Isco pump. The sample bath temperature is raised to 16°C, 1.5°C above the hydrate stability temperature at 11.7 MPa. As hydrate dissociates, the Isco pump records the pore water volume change at constant pressure.

**RESULTS**

In each test, the Isco pump records the volume of water injected during the initial hydrate formation, prior to initiating circulatory flow. This represents the volume change associated with methane gas in the sample converting to methane hydrate. The volume of water injected is equal, within our uncertainties, to the volume of gas and water taken on by the Isco during hydrate dissociation. This balance indicates the circulating methane-rich water does not appear to generate a measurable volume of new hydrate. Instead, the circulating water frequently forms hydrate clogs in either the inlet or outlet lines around the growth chamber.

**DISCUSSION**

Eliminating flow-line clogging due to hydrate formation from methane bubbles is a priority. Even in the absence of bubbles, however, choosing a sample temperature and flow rate requires balancing competing factors. Here we discuss bubble mitigation strategies, then present considerations for choosing flow rate and sample temperature conditions.

**Bubble Mitigation**

Spangenberg et al. [13] use a relatively high supersaturation ratio (Fig. 3, green square), and though they experienced a clog initially, the clog...
was removed by heating and did not reappear once the sample had again cooled to the target temperature. The saturation ratio itself is therefore not likely to be the variable controlling the onset of clogging in our system. A more reasonable explanation is bubble formation, with subsequent rapid hydrate formation.

Figure 4 illustrates the path circulating water takes in terms of methane solubility. The peaked curved (blue) denotes the equilibrium number of moles of methane per kilogram of solution that water can hold in the dissolved phase (data from Duan et al. [19]). The solubility peak occurs at 14.5°C, the phase boundary for methane hydrate at 11.7 MPa. At temperatures cooler than 14.5°C, hydrate is stable and excess methane in the circulating water can come out of solution to form additional hydrate. For temperatures warmer than 14.5°C, excess methane can come out of solution to form free gas bubbles.

The closer the interface chamber is in temperature ($T_1$ in Fig. 4) to the hydrate stability temperature, the more methane can be absorbed by the water. Upon leaving the interface chamber, however, the water sits in a precarious equilibrium. If the circulating water cools below 13.5°C prior to entering the sample, methane can come out of solution to form hydrate and clog the line (Fig. 4). If instead the circulating water warms at all relative to the interface chamber temperature of 23°C ($T_1$ in Fig. 4), methane can come out of solution as a free gas. Bubbles formed in this way can be swept to the sample inlet, potentially becoming trapped in the 61 or 119 µm mesh-size screens. These screens are likely sites for rapid hydrate formation from trapped methane bubbles.

In our system, bubble formation is likely triggered in a 50-cm length of metal pipe connecting the interface chamber outlet to the growth chamber inlet (see Fig. 1). This pipe crosses the heating-venting region of the bath temperature controller (lower right in Fig. 1). The exhaust from the bath cooler elevates the temperature along the tubing length by 3°C relative to the temperature at the interface. To minimize the time water spends in this length of pipe, we use a pipe with only a 1.6 mm internal diameter. Even so, water still spends one minute or more in the metal pipe depending on flow rate. The trade off for using a small internal-diameter pipe is that this provides an efficient geometry for transferring heat from the warm exhaust air to the circulating water. Heat shielding and additional insulation will be required to avoid
bubble formation in this line.

**Flow Rate and Sample Temperature**

Flow rate and sample temperature control how much methane is available for hydrate formation, and how much time the circulating water is in contact with the sample and can accomplish the transfer of methane from the dissolved phase to hydrate. Figure 5 displays a family of curves showing how many cubic cm of hydrate could form per day in a system held at 11.7 MPa, with an interface chamber temperature of 23°C. The curves assume 1% efficiency in converting dissolved-phase methane to hydrate. The formation rates observed by Spangenberg et al. [13] suggest efficiencies may be 1-10%.

Given the solubility curve shape (Fig. 4), the methane content in the circulating water can be increased by cooling the interface to nearly the hydrate stability temperature. Correspondingly, lowering the sample temperature reduces the methane concentration that water can hold in the presence of hydrate. Increasing this supersaturation difference between the interface and growth chambers (Fig. 4) is what increases the amount of methane available per cc of circulating water.

Supersaturation can also be enhanced by elevating the pore pressure. Solubility is only weakly dependent on pressure in the presence of hydrate, but the solubility curve for temperatures above the hydrate equilibrium temperature shifts upward above the hydrate stability temperature as pressure increases [20], increasing the equilibrium methane content in water for a given interface chamber temperature.

As Figure 5 indicates, elevating the flow rate elevates the hydrate production by providing additional water to the sample. It is not clear, however, at which flow rate this added productivity is offset by the diminished time the circulating water spends in contact with hydrate in the growth chamber. Elevated flow rates may also promote channeled flow, which would significantly limit the spatial and temporal exposure of the circulating water to hydrate in the growth chamber.

**CONCLUSION**

Hydrate formation from methane dissolved in water is thought to result in the load-bearing pore-space hydrate distribution most relevant to studies of hydrate-saturated marine sands. Because of the low solubility of methane in water, dissolved-phase formation techniques are likely to be slow. Initiating hydrate growth using less time-consuming formation techniques, such as the gas-limited technique of Priest et al. [1] can be an attractive approach for reducing the volume of hydrate formation that must be accomplished from dissolved phase methane.

To enhance the productivity of dissolved-phase hydrate formation, methane should be combined with water at the highest attainable pressure, near the hydrate stability temperature. Hydrate growth should then be accomplished close to 0°C to maximize the methane available for hydrate formation. Flow rates of ~1 cc/min have been successful, but lower rates may be necessary at higher hydrate saturations [Spangenberg, personal communication, 2010]. For a given system geometry, less efficient pressure, temperature and flow rate parameters me be required in order to avoid bubble formation and subsequent clogging. The flow line leading from the point of highest methane saturation (the interface chamber in this work) into the growth chamber is particularly vulnerable to bubble formation and must not be allowed to warm above the temperature at which methane was saturated into the water. Bubbles
formed in this line can collect at the growth chamber entrance and rapidly form the small amount of hydrate required to block the flow line.

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REFERENCES


