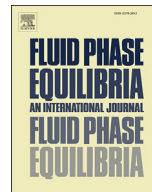




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Novel gas hydrate reactor design: 3-in-1 assessment of phase equilibria, morphology and kinetics

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ABSTRACT

A novel reactor equipped with a bilateral, temperature-control stage was developed to study gas hydrates. The design allowed for tight control of the crystallization substrate temperature, independent of ambient conditions. Methane hydrate formation was investigated on a surface with a uniform temperature and on a surface with a constant temperature gradient. The uniform temperature experiments showed a previously unreported transition point in methane hydrate morphology and displayed closely reproducible film morphologies. A single temperature-gradient experiment showed transitions in morphology with respect to driving force. These transitions were found to be consistently reproducible, and occurred due to a change from continuous crystal growth to polycrystalline, adhesive type growth. The temperature gradient was also used to control the solid–liquid interface position during gas hydrate dissociation, providing a simple and fast method for hydrate-liquid-vapor (H–L–V) equilibrium measurements. The temperature gradient was used to correlate film velocity and supercooling in order to assess apparent kinetics of hydrate growth. Overall, the ability to observe gas hydrate growth on tightly controlled temperature gradients was found to reduce multi-trial methods to a single experiment that: (1) quantifies morphology/growth mechanism transitions with respect to temperature, (2) measures the H–L–V equilibrium temperature at the experimental pressure, and (3) correlates the apparent kinetics with respect to temperature. Thus, the new design was shown to operate as a 3-in-1 reactor, effectively allowing assessment of phase equilibria, morphology and apparent kinetics of gas hydrates.

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1. Introduction

Gas hydrates or aqueous clathrates are crystalline compounds composed of hydrogen bonded water cages enclosing small guest molecules. Aqueous clathrates typically form at high pressures and moderate temperatures [1]. Under certain thermodynamic conditions clathrates can plug oil and gas pipelines, so additives are commonly used to inhibit hydrate plug formation. These additives include thermodynamic inhibitors, kinetic inhibitors and anti-agglomerants [1]. Hydrate plug prevention represents a significant operating cost to the oil and gas industry [2]. Research in this area aims to find alternative, more cost effective hydrate inhibitors [3] and improve the accuracy of measurements with respect to inhibitor effectiveness to reduce excess inhibitor used as a margin of safety [4].

There are several types of hydrate reactors currently used to study gas hydrates [3,5]. Stirred-cell hydrate reactors are widely used for formation/dissociation kinetics [6,7], hydrate particle agglomeration [8,9] and hydrate phase equilibrium experiments [10,11]. Rocking-cells and flow-loops are designed to simulate pipeline conditions while assessing formation/dissociation kinetics, hydrate particle agglomeration and plug formation [12,13]. Unstirred hydrate reactors are used mainly for crystallography [14] and crystal morphology experiments [15].

Observations of hydrate growth aim to provide a visual means of increasing our understanding of the processes that occur upon hydrate formation [14–18]. For example, these studies can lead to insights into how certain inhibitors function [19–23] or characterize hydrate interactions with foreign particles [24,25]. These sorts of measurements can aid in the development of realistic hydrate growth models [18,26].

Morphology hydrate reactors are often used to assess the effect of driving force on hydrate morphology [15,27,28] and to measure apparent growth kinetics through hydrate film velocity [26,29–32].

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In general, these reactor designs consist of an unstirred, pressurized sample cell fitted with sight windows. The temperature of the system is controlled externally via a coolant jacket or bath. This type of design offers little control over crystal growth beyond the target conditions at hydrate formation.

One means of controlling crystal growth is directional solidification. This technique is used when control over the thermal history of a crystallizing sample is desired [33,34]. Typical methods involve pulling a sample slide across a stage with a fixed temperature gradient, using two constant temperature plates spaced apart such that the thermal gradient is constant over the gap. The temperature is set above and below solid–liquid equilibrium at either end of the gap so that the solid–liquid interface remains at some position between the two plates. Dragging the sample across the plates (toward the colder plate) results in crystallization of the sample at a rate equivalent to the pulling velocity; however, this type of apparatus is limited to low pressure experiments due to the moving parts required for velocity control. As such, research in this area has been limited to ice and hydrates that can form at atmospheric pressure [25].

The gradient freeze method is a type of directional solidification that does not require moving parts, where the solid liquid interface is controlled by changing one or both of the boundary temperatures of the temperature gradient. Liu et al. [35] used a gradient freeze stage to control a solid–liquid (ice–water) interface allowing for stationary observation of the interface.

The objective of this work was to design a high pressure vessel that could perform gas hydrate experiments requiring precise, local temperature control and that would allow for stationary observation of a hydrate–liquid–vapor interface. Validation of the reactor was accomplished by observing methane hydrate formation and dissociation on water droplets at constant pressure. It was found that the new design could operate as a 3-in-1 reactor, effectively allowing assessment of phase equilibria, morphology and apparent kinetics of gas hydrates. High resolution images were used to elucidate the growth mechanism of methane hydrates. Novel, economical procedures to study morphology, to assess apparent kinetics and to determine hydrate–liquid–vapor equilibria of hydrates are presented in this paper.

2. Experimental

2.1. Apparatus

A new experimental set-up was designed to control gas hydrate crystal growth at pressures up to 20 MPa (Fig. 1). The central part of the apparatus consisted of a pressure vessel that contained a bilateral temperature control stage (High-Pressure Bilateral Temperature Control Stage or HP-BTCS). The stage controlled the temperature across a sample of water that was pressurized in an atmosphere of a hydrate-forming gas.

A 316 stainless steel cell was fitted with sapphire sight windows and wrapped in a coolant jacket. Several radial ports allowed for gas in, gas out, temperature measurement, pressure measurement and gland seal fittings. Sapphire windows, sealed into a 1^{1/4} inch diameter steel housing (Rayotek Scientific, CA, USA) were oriented on the vertical axis for a ‘bird’s eye’ view of the sample stage. The stage was illuminated from the bottom window with a Schott KL2500 LCD cold light source (Optikon, ON, Canada). Images were acquired through the top window with a PCO.edge 5.5 sCMOS camera (Optikon, ON, Canada). A Nikon AF-Micro-Nikkor 60 mm lens (Optikon, ON, Canada) was used for low magnification images. An Infinity KC microscope and IF series objectives (Optikon, ON, Canada) were used for high magnification images. The pressure vessel was cooled by a Thermo Scientific AC200 refrigerated

circulator (Fisher Scientific, Canada), which was used to circulate a 50/50 (v/v) mixture of ethylene glycol and water through a copper coil wrapped around the external circumference of the vessel. The pressure in the cell was measured by a Rosemount 3051s pressure transmitter (Laurentide Controls, QC, Canada) with an accuracy of $\pm 0.025\%$ of the span. The temperature of the cell was measured with a platinum RTD probe (Omega Engineering, QC, Canada) with an accuracy of ± 0.32 °C. Two Conax Technologies transducer gland seal fittings (Electro-Meters, ON, Canada) were used to seal a total of eight wires through the vessel wall.

2.1.1. High-pressure bilateral temperature control stage

The HP-BTCS was designed to independently control temperature on opposite sides of the stage. Fig. 2 shows a schematic of the HP-BTCS. Both ends of the stage have a thermoelectric cooler (TEC) (TE Technology, MI, USA) to allow heat transfer from the top to the bottom surface of the stage. Copper plates were fastened to the top and bottom of each TEC to uniformly distribute temperature on the top and bottom surfaces. Temperatures of both the top copper plates were measured by fast-response thermistor elements (TE Technology, MI, USA) with a resolution of 0.01 °C and an accuracy of ± 1 °C. A sapphire substrate was used to hold the water sample and bridge the two ends of the stage. The TECs were controlled by two bi-polar PID temperature controllers (TE Technology, MI, USA), with a resolution and a temperature control stability of ± 0.01 °C.

2.2. Methods

A 20 μ L sample of distilled, deionized water was transferred onto the sapphire substrate with a micro pipette. The vessel was then sealed and purged with research-grade gas containing a mole fraction of 99.99% methane (Air Liquide, ON, Canada). For all experiments, the pressure and temperature surrounding the stage were held constant.

2.2.1. Crystal formation history

The water sample was first frozen at atmospheric pressure, then subsequently thawed at a higher pressure in the hydrate stable region to seed hydrate crystal growth. The sample was then heated to 1 °C above H–L–V at the experimental pressure, dissociating the initial hydrate.

2.2.2. Hydrate formation

The HP-BTCS was used to locally cool the water sample to the experimental temperature conditions. Experiments were conducted with a uniform surface temperature (Fig. 3a) and with a constant temperature gradient (Fig. 3b). For temperature gradient experiments, both sides of the stage were cooled to near the H–L–V temperature, then one side was cooled to obtain a set temperature difference across the stage. For both uniform surface temperature and constant temperature gradient experiments, hydrate crystals nucleated within five minutes after the stage was cooled below H–L–V. The stage temperature conditions were held constant (± 0.01 °C) for the duration of hydrate formation.

2.2.3. Hydrate dissociation

For hydrate dissociation, a set temperature gradient was then applied to the sample, with the hot end of the gradient near the H–L–V temperature. The high and low setpoint temperatures were increased simultaneously in 0.1 °C increments. Each step increase in the setpoint temperatures moved the H–L–V isotherm toward the cold side of the stage. Temperature was held constant at both ends of the stage while the hydrate dissociated in the region of the stage above the H–L–V temperature (Fig. 3c).

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