

Full Length Article

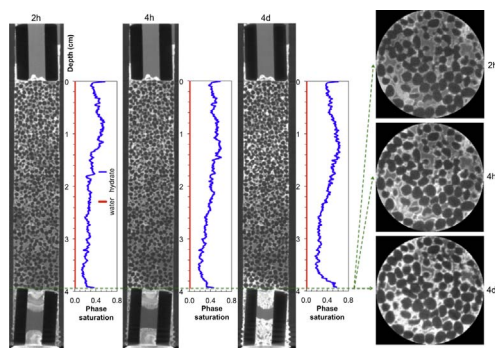
Ostwald ripening changes the pore habit and spatial variability of clathrate hydrate



Xiongyu Chen*, D. Nicolas Espinoza

Department of Petroleum and Geosystems Engineering, The University of Texas at Austin, United States

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Hydrate pore habit
Ostwald ripening
Growth rate
Heterogeneous hydrate saturation
Permeability
Shear strength

ABSTRACT

Clathrate hydrate is a solid crystalline compound that consists of water cages with trapped gas molecules. Methane hydrate in permafrost and marine sediments is estimated to contain 2×10^3 to 4×10^6 Gt of carbon, which makes it both a potential energy source and a liability to global warming. The transport and mechanical properties of hydrate bearing sediments (HBS), and therefore hydrate dissociation through depressurization, thermal stimulation, or CO₂ injection, depend on hydrate pore habit and spatial distribution in sediments. However, the evolution of hydrate pore habit and spatial distribution in HBS are not well understood yet. Here we show experimental evidence of Ostwald ripening of gas hydrate crystals in pores and porous media. We find that (1) hydrate growth rate (under nearly isothermal conditions) versus the degree of overpressurization fits an Arrhenius-type equation, and (2) Ostwald ripening gradually changes hydrate pore habit from grain-attaching to pore-filling and increases hydrate saturation heterogeneity at both pore and core scales. The latter ultimately creates significant spatial variations of permeability and sediment strength. Our results provide insights into kinetics and pore-scale physics that determine the geophysical signature from HBS at various scales. Based on our findings of hydrate occurrence in both gas and gas-water interface, we argue that hydrate growth in natural HBS is not limited to the water liquid phase. Our observation of hydrate pore habit alteration by Ostwald ripening explains patchy saturation and heterogeneous distribution of hydrate in natural HBS, which gives physical insight to improve geophysical hydrate models in porous media.

* Corresponding author.

E-mail address: xiongyu@utexas.edu (X. Chen).

1. Introduction

Naturally occurring methane hydrates are found in continental margins [1–4] and permafrost [5,6] around the world. They are detected by seismic bottom simulating reflectors [7–10], salinity reduction of pore fluids in core samples [11,12], and increases of elastic wave velocity and resistivity in well logs [8,13]. In ocean sediments, natural gas hydrates distribute heterogeneously [8,11] and preferentially grow in coarse sands [9,12].

Hydrates have been synthesized under controlled conditions to determine hydrate growth rate and morphology/habit in great detail [14]. Hydrate growth on water droplets shows that hydrate nucleation is almost instantaneous once the experiment starts [15,16]. Hydrate film studies find that hydrate growth rate increases with undercooling [17,18]. Deep-sea hydrate syntheses in sand also suggest hydrate preferentially form in coarse sands [19,20]. Laboratory observation of hydrate pore habit by 2-dimensional (2D) glass micromodel shows hydrate is mostly pore-filling rather than grain-coating [21]. Three-dimensional (3D) synchrotron X-ray computed micro-tomography (μ CT) experiments show that xenon hydrate crystals coarsen over time, distribute patchily, and coexist with thin water layers (a few microns) around sand grains [22,23]. Ostwald ripening, in which small crystals are consumed by large ones to minimize surface area and free energy [24], has been observed using X-ray diffraction (XRD) during hydrate synthesis in sand [25]. Hydrate pore habit can influence sediment properties, such as seismic velocities [26], permeability [27], sediment strength [28], thermal conductivity [29] and electrical properties [30]. Hence, understanding how pore habit changes with time and space is critical to understanding natural HBS and predicting the effect of induced perturbations.

The objective of this work is to present new evidence of xenon and methane hydrate Ostwald ripening in large pores and in a sand pack. We use three different experiments to quantify isothermal hydrate growth rate and Ostwald ripening, and show how they affect hydrate distribution and pore-scale hydrate habits, and finally discuss implications to transport and mechanical properties of HBS.

2. Materials and methods

We conducted three experiments (all constant mass): (1) xenon hydrate growth in water and gas phases without porous media (Exp1), (2) methane hydrate growth on water droplets (Exp2), and (3) xenon hydrate growth in wet sandpack (Exp3). In previous work [22,31,32], xenon hydrate was also used as an analog for methane hydrate. Xenon hydrate and methane hydrate are both structure I clathrate hydrates [33], and X-ray mass attenuation coefficients of xenon are one order of magnitude higher than those of methane [34] (which makes it easier to differentiate hydrate from water). Table 1 summarizes temperature, initial pressure (P_{ini}), water salinity (S), gas composition and equilibrium pressure (P_{eq}) for the three experiments.

2.1. Xenon hydrate growth in large pore (Exp1) and in sandpack (Exp3)

The two xenon hydrate experiments use a similar apparatus shown in the left of Fig. 1. The apparatus consists of an aluminum pressure vessel (0.86 cm inner-diameter and 7.2 cm length) connected to a gas accumulator. The apparatus is mounted on the stage of a Nikon XTH

Table 1
Conditions of the three hydrate experiments.

	T(°C)	P_{ini} (MPa)	S (wt%)	Gas	P_{eq} (MPa)
Exp1	23.0	2.84	0	Xenon	1.56
Exp2	1.0	7.05	0	Methane	2.83
Exp3	23.3	3.72	10	Xenon	1.75

225 X-ray μ CT scanner. The detector is a 1500 by 1900 16-bit flat panel. At maximum magnification the resolution limit is $\sim 3 \mu\text{m}$. The scanning parameters are 85 kV, 300 μA , 250 ms of exposure with no filters. The energy of 85 kV is a result of optimum gray-level detection, device settings, and improved phase differentiation.

The two X-ray radiographs on the right of Fig. 1 show projections of the aluminum vessel with and without sand. A compressed stainless steel spring, PTFE spacers, and stainless steel sieves permit applying an effective stress of 170 kPa to the 4-cm-long sandpack. The two sieves prevent sand going into the spacers. The mean grain diameter of the sand is 0.7 mm, which yields a capillary pressure between xenon gas and brine of roughly 100 Pa [35]. The effect of this capillary pressure on hydrate growth can be ignored, since experimental and modeling studies find that the capillary inhibition effect on hydrate growth is negligible for pore size larger than $\sim 1 \mu\text{m}$ [36–38].

For both Exp1 and Exp3, the temperature is $23 \pm 1^\circ\text{C}$ (controlled by room AC) and the initial xenon pressure is roughly twice the estimated hydrate-gas-water equilibrium pressure (see Table 1) [39,40]. The aluminum vessel is half-filled with water for the large pore experiment (Exp1). In the case of the sandpack experiment (Exp3), we saturate the small vessel with 10 wt% NaBr brine, and then inject air to displace water from the spacers and the sand in order to reduce water saturation. We utilize brine instead of pure water in the sandpack experiment to enhance the contrast in CT imaging and include salt-exclusion effects. The equilibrium pressure for Exp3 is estimated at 10 wt% salinity (Table 1). The equilibrium pressure will gradually increase as hydrate grows, since hydrate formation excludes salt from solution and increases salinity.

For both Exp1 and Exp3, the experiment starts by opening the valve between the small vessel and the accumulator, such that the high-pressure xenon gas enters the small vessel and hydrate starts to nucleate. The quality of CT images increases with the number of X-ray projections. More frames to average at each projection angle help to cancel out background noise. The optimized projection numbers during a full scan is 2985, which takes 12.5 and 50 min to complete for 1 and 4 frames to average, respectively. In the initial 24 h of the experiment, the sample is scanned every hour and each scan takes 12.5 min; after 1 day, the sample is scanned once a day and each scan takes 50 min to obtain higher quality images.

2.2. Methane hydrate on water droplets (Exp2)

The method details and setup schematic can be found in Jung et al. [41]. Three distilled water droplets (instead of one in [41]) are placed on top of a hydrophobic PTFE plate, which sits inside a pressure cell with a viewing window. The initial diameters of the left, the center, and the right droplets are 1.9, 3.8 and 1.5 mm, respectively. A cooling coil is attached to the bottom of the pressure vessel to maintain the sample at low temperatures (1.0°C). The experiment starts by injecting high-pressure methane gas (7.1 MPa and 1.0°C) into the pressure vessel. During the experiment, a high-definition visible-light camera is used to monitor the pressure vessel. The initial pressure is 2.5 times of the gas-water-hydrate equilibrium pressure (2.83 MPa at 1.0°C) [40]. Since methane hydrate has a lower density than water, the growth of hydrate expands the volume of the droplet. On the other hand, since methane is not pre-saturated with water, the water droplets can evaporate during the experiment. Hence, droplet volume increases implies hydrate formation.

3. Results

3.1. Hydrate growth rate

Fig. 2a and b show xenon hydrate nucleation and growth in a pressure vessel equivalent to a large pore with hydrophilic walls (half filled with water) during 11 days. Fig. 2c shows temperature and

Download English Version:

<https://daneshyari.com/en/article/6632484>

Download Persian Version:

<https://daneshyari.com/article/6632484>

[Daneshyari.com](https://daneshyari.com)