Full Length Article

Simulating natural hydrate formation and accumulation in sediments from dissolved methane using a large three-dimensional simulator

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ABSTRACT

The slow hydrate formation and accumulation process from dissolved gas in nature was simulated at large-scale in sandy sediments using a three-dimensional hydrate simulator. A low hydrate formation rate (0.37% pore volume per day) was achieved by maintaining the supersaturation of dissolved methane and migration velocity of the pore fluid at very low levels. Electrical and acoustic measurements were performed to track the hydrate formation in the sediments. A dynamic hydrate evolution process was observed: Crystallization – migration – accumulation – recrystallization. This evolution process has a critical effect on the connectivity of the pores and the strength of the sediment frame. After the dynamic evolution process, stiff frame-supporting hydrates and patchy hydrates were observed as the final morphologies in the pores, although the variation in the acoustic velocity indicated that frame supporting was the dominating morphology in the pores. Based on this, hydrate saturation values were inversed from resistivity and acoustic velocity models for frame-supporting hydrates. The calculated results showed that the order of hydrate saturation at different sites from the resistivity model was consistent with that from the acoustic velocity model by overestimating the hydrate saturation obtained from the resistivity inversion. Analysis of the spatial hydrate distribution showed that hydrate distribution in the sediments was discontinuous. The concentration, temperature, and fluid velocity profiles play a key role on this discontinuity, which we propose should be considered in detail in future experimental and numerical studies.

1. Introduction

Natural gas hydrates are ice-like crystalline compounds comprised of small guest molecules, such as methane or other light hydrocarbons, trapped in cages of hydrogen-bonded water frameworks under relatively low temperature and high pressure [1]. Owing to their huge numbers and wide distribution, natural gas hydrates are considered a future source of energy. Oceanic methane hydrates in sandy sediments, as well as methane hydrates trapped in permafrost, are primary targets for gas production [2]. In order to recover methane safely and effectively from hydrate reservoirs, great efforts have been devoted to study hydrate formation and dissociation behavior both in the field and in laboratories, as previously reviewed [3,4].

Upward migration of pore fluids with dissolved gas is considered as an important mechanism for many naturally-occurring hydrate reservoirs [5,6]. The excess methane loaded on pore fluids can be converted into hydrate crystals when they migrate from a warm zone to a colder zone. In laboratories, hydrate formation from free gas has been intensively studied [7–13], but there is limited understanding of hydrate formation from dissolved gas in sediments, especially over long

time and volume scales.

Hydrate formation in the absence of free gas has been confirmed by in situ experiments, in which hydrates were formed in several static systems [14–17]. In these works, the pore habit of the hydrates formed from the dissolved gas was observed by direct visual observation [15], computed tomography technology (CT) [16], and indirect electrical seismic measurements [14,17]. It was observed that hydrates formed from dissolved gas exhibited non-cementing habits: Pore-filling or frame-supporting.

In laboratories, attempts have been carried out to simulate the dynamic formation process of natural hydrate reservoirs from dissolved gas and to prepare representative specimens for physical property measurement and evaluation of production methods [18–21]. The artificial synthesis of specimens with high saturation degree was achieved in a laboratory by circulating warm methane-loaded water through cold packed sand in vessels of different volumes [22,23]. However, because of the low solubility of methane in water, these experiments were time consuming. A saturation of ~95% was obtained after two months of the circulation process in a vessel with a pore volume of 37.3 mL [22]. Kinetic studies of hydrate formation in these circulating experiments

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revealed that the rate-limiting step was the dissolution of methane gas into the circulating water to form a methane-supersaturated fluid [23]. Therefore, the hydrate formation rate from dissolved gas can be greatly accelerated by enhancing the methane transfer at the gas–water interface in the dissolving unit. By applying enhancing methods, a hydrate saturation of ~ 90% was successfully achieved in a specimen with a volume of approximately 200 L after about 70 days circulation process [23]. To track the hydrate distribution in large-volume sediments, special tomography techniques have been developed by increasing the number of sensors, such as electrodes, thermal couples, and acoustic dipoles [24–26]. These technologies are able to identify where and when hydrates form or dissociate. The spatial hydrate saturation can be inversed from the measured physical properties of hydrate-bearing sediments via suitable models, such as Archie's equation for resistivity [27] or elastic velocity prediction models for the acoustic velocity [28–31]. As hydrates present different pore habits, caution should be paid to the selection of suitable models for the analysis of the measured data.

As mentioned above, for the fast preparation of representative hydrate specimens, easy availability of the dissolved gas was guaranteed and the methane concentration in the warm fluid was elevated closely to the saturation value, as reported in previous works. However, these requirements may not be achieved in natural environments, especially in shallow sediments far away from the gas source. For the sake of saving time, experimental studies at large volume scales are seldom attempted at very slow hydrate formation rates with less supersaturation of dissolved methane and at very slow upward migration velocities. To broaden the existing experimental data, in this work, very slow hydrate formation in sandy sediments from unsaturated methane-loaded brine was conducted in a modified three-dimensional hydrate simulator (TDHS) with a volume of 196 L built in our laboratory [32], in which the acoustic, electrical, and thermal properties at various locations were monitored in real-time. The aim of this work was to gain insight into the physical properties and hydrate distribution during such a slow hydrate formation process.

2. Experimental section

2.1. Device

A detailed description of the three-dimensional hydrate simulator (TDHS) was provided in our previous study [32]. Fig. 1 shows a schematic diagram of the apparatus, which mainly consists of four parts: The hydrate formation system, the dissolved-gas supply system, the sensors system, and the temperature control system. The most critical segment of the hydrate formation system is a high-pressure reactor with an inside diameter of 0.5 m and effective height of 1 m. The available internal volume is 0.196 m^3 and the maximum allowable working pressure is 32 MPa. Two porous stainless steel plates separate the inner space of the vessel in three parts. The sensors and sandy sediments were packed in the spaces between the two plates.

For the dissolved-gas supply system, a 4.1 L stirring chamber was used as a reservoir to supply the methane-loaded brine. Three quarters of the chamber were used as the methane gas head. Free gas was continuously in contact with brine in this chamber. Its pressure was kept constant by injecting methane from a cylinder through a pressure reducing regulator. A constant-flow pump was used to drive the flow loop in the whole system.

Fig. 2 shows the sensor arrangement in the sediment. Five resistance temperature detectors (RTDs) at different depths were armored in one rod and denoted T1, T2, T3, T4, and T5 from bottom to top. The accuracy of RTDs is ± 0.1 K. Thirty electrodes were configured in six rods named A, B, C, D, E, and F. In each rod, e.g., Rod A, the five electrodes (1,2,3,4, and 5) afforded four measuring sections (A12, A23, A34, and A45) from bottom to top. The electrical resistance of the sediment between the electrodes was measured using a digital electrical bridge. All

24 measuring sites at different depths could be detected within 5 min. The measured four resistance values in one rod, e.g., Rod A, were converted to resistivity values recorded as RA12, RA23, RA34, and RA45 from bottom to top. The uncertainty of the resistivity is ± 0.05%. Seven pairs of acoustic dipoles (V1–V7) with a measuring distance of about 30 mm were inserted in the sediment to detect accurately the variation of acoustic properties due to hydrate formation and evolution. The received signal was digitized with a digital oscilloscope and transferred to a computer for analysis. The uncertainty of acoustic velocity data is ± 0.1%.

It must be noted that the arrangement of sensors was based on a simple assumption that the hydrate distribution was axially symmetric. Although hydrates may distribute heterogeneously in sediments [33,34], the variation of the measured properties was considered in this work to exist only at different heights and radii, because the sediment sample was axially symmetric and the gas was injected through the central port at the bottom. The properties of the sediment between the measured sites were obtained by linear interpolation in the vertical and radial direction.

The hydrate formation system was placed in a cooling room of dimensions 3.5 m long, 2.2 m wide, and 2.8 m high. The refrigeration and heat system enabled the room temperature to be maintained at 258–293.15 K with an accuracy of ± 0.5 K. The dissolved-gas supply system was placed in a relatively warm environment with an air conditioner.

2.2. Procedure

A group of experiment for the formation of methane gas hydrate from dissolved gas was conducted in the TDHS. Quartz sand of 40–80 mesh with a porosity of 0.38 and aqueous brine (NaCl aqueous solution, 3.5 wt%) were used to prepare the sandy sediments. Methane gas with a purity of 99.95% was used as the gas source in the stirring chamber. The experimental conditions are listed in Table 1.

Quartz sand was firstly packed in the reactor and confined by rubber sleeves (in the radial direction) and steel meshes (in the vertical direction). Thereafter, the reactor was sealed and evacuated. Aqueous brine at ambient temperature was injected into the reactor from the bottom at the desired experimental pressure of 7.0 MPa. Then, the stirred vessel was connected to the reactor and the flow loop was initiated. Before cooling down, the brine in the whole system was presaturated rapidly with methane in a fast circulating process (30 h) with a flow rate of about 100 cm^3/min. Methane was quickly dissolved in brine by stirring intensely in the stirring chamber. Afterwards, the cooling room was cooled to the desired temperature. The flow rate was reduced to 50 cm^3/min and the stirring intensity was reduced to a third of the starting value. The pressure in the stirring chamber would drop continuously due to the consumption of methane for hydrate formation in the reactor. Additional methane was supplied to maintain a constant pressure in the stirred vessel and reactor, and the amount of gas supply was recorded. The temperature and pressure were monitored in real time by Monitor and Control Generated System (MCGS). The resistivity was measured every hour and the acoustic velocity was recorded every 12–24 h. The experiment was stopped after 55 days when the recorded electrical and acoustic data were stable and very little methane was being consumed.

2.3. Data processing and inversion

2.3.1. Gas consumption

Based on the recorded pressure and temperature variations in the methane cylinder, the gas consumption during the hydrate formation process was calculated by the Patel-Tejia (PT) equation of state [35]. The equation was developed to improve the prediction result of volumetric properties of fluids, which contains three additional parameters to characterize each particular fluid. The average absolute deviation in