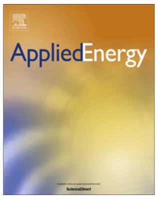
Applied Energy 184 (2016) 482–490

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy



Formation of cyclopentane - methane hydrates in brine systems and characteristics of dissolved ions

Qiu-Nan Lv, Xiao-Sen Li *, Zhao-Yang Chen

Key Laboratory of Gas Hydrate, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, PR China
Guangdong Key Laboratory of New and Renewable Energy Research and Development, Chinese Academy of Sciences, Guangzhou 510640, PR China
Guangzhou Center for Gas Hydrate Research, Chinese Academy of Sciences, Guangzhou 510640, PR China

HIGHLIGHTS

- Formation rate of CP-CH_4 hydrate was measured in NaCl solution.
- Increase of gas flow rate was propitious to accelerate the hydrate formation rate.
- The salinities of remaining liquid first increased and then decreased.
- PXRD analyses indicate that Na^+ and Cl^- adhere to the surface of hydrate.

ARTICLE INFO

Article history:
Received 15 July 2016
Received in revised form 8 October 2016
Accepted 14 October 2016

Keywords:
Cyclopentane-methane hydrate
Hot brine
Bubble
Salinity
PXRD

ABSTRACT

Based on the hot brine in situ seafloor prepared for marine NGHs exploitation, the formation of hydrates and the characteristics of dissolved ions were investigated for the cyclopentane (CP)-methane-NaCl solution (3.5%) system. Both the gas consumption and the solution salinity influenced by two factors – the flow rate of gas (Q_g) and the mass fraction of CP (M_{CP}) -were discussed. On one hand, the gas consumption went up at a lower M_{CP} (3.950 wt%) while dropped down at a higher M_{CP} (8.340 or 18.775 wt%) with the increase of Q_g. Nevertheless, higher mass fraction of CP behaved more favorable for the gas consumption. On the other hand, there would be a similar trend that the salinity of remaining liquid increased firstly and then decreased with the reaction time at any fixed Q_g and M_{CP}, which might be attributed to the adsorption of Na^+ and Cl^- on the surface of hydrate. Furthermore, PXRD analysis of the hydrate was conducted to confirm this explanation. And it was confirmed that the ion of Na^+ or Cl^- did not play any role in the construction of hydrate cages. Meanwhile, CP was enclosed in large cavities ($5^{12}6^4$) while CH_4 was mainly enclosed in the small cavities (5^{12}).

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Natural gas hydrates (NGHs) are non-stoichiometric crystalline, inclusion compounds, formed from water and gas molecules under the condition of low temperature and high pressure. An amount of NGHs occur naturally within or under permafrost regions and marine sediments, and 1 m^3 of pure methane hydrate can be decomposed to produce up to 160–180 m^3 of methane gas. Therefore, NGHs are the potential energy resource with the traits of large reserves, high energy density and wide distribution [1], which is attracted more and more attention.

The researchers have put forward many ways to exploit this huge energy resource, such as depressurization [2,3], to reduce the pressure of NGHs reservoir below the equilibrium pressure of hydrate; thermal stimulation [4,5], to raise the reservoir temperature above the equilibrium temperature of hydrate by injecting stream, hot water or hot brine; chemical injection [6], to change the conditions of hydrate decomposition by injecting chemical additives; replacement of methane by CO_2 hydrate [7], and the combination of the above methods [8,9]. Each method has its advantage and disadvantage. Previous studies have suggested that depressurization is an energy efficient method due to its low energy consumption. However, it has long dissociation time and low production rate. With the development of exploitation process, the temperature of the surrounding media or the rock matrix is significantly reduced, which may lead to the hydrate re-formation, the ice formation and the well blocking [10,11]. As a result, the

---

* Corresponding author at: Key Laboratory of Gas Hydrate, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, PR China.
E-mail address: lixs@ms.giec.ac.cn (X.-S. Li).

http://dx.doi.org/10.1016/j.apenergy.2016.10.035
0306-2619/© 2016 Elsevier Ltd. All rights reserved.

exploitation process is not stable and successive. Thermal stimulation is more efficient and easier to control the exploitation process compared to other methods. However, the heat loss is remarkable in the process of injecting hot water or steam into the NGHs region from the surface of the ocean [12], which would bring huge costs for the exploitation.

A novel technique was proposed to prepare hot brine in situ seafloor for marine NGHs exploitation based on hydrate technology [13], which can be briefly described as follows: with the injection of hydrate formers, hydrates are constantly forming in the device installed in situ seafloor under the high pressure circumstance. Meanwhile, it will float up to the surface of the ocean due to its lower density. The hydrostatic pressure is lower than the phase equilibrium pressure, which lead to the dissociation of hydrates. Consequently, the hydrate formers can be generated, accumulated and recovered from the process. With the consumption of water and the release of the heat from the exothermic reaction, the concentrated hot brine is pumped out from the device and injected into the NGH reservoirs for NGHs decomposition. Compared with the conventional injection thermal exploitation, heat loss can be effectively minimized during the introduction of heat medium (eg. hot water or hot brine) for this novel technique, which is turned to be an excellent approach to exploiting the marine NGHs in future. This technique can also be applied for seawater desalination or combining NGH exploitation and seawater desalination. However, the main challenge towards this technique is the effective way to prepare hot brine in situ seafloor. And the enhancement in hydrate formation rate would be essential for that. It is reported that there are chemical method and mechanical method proposed to resolve it. Introducing the hydrate formers in the formation of hydrate is generally considered as a typical chemical method enhancing the hydrate formation rate [14,15]. Besides, the dissociation enthalpy can be also greatly improved when using hydrate formers. With regard to the suitable hydrate formers, it should have some necessary features such as the non-toxic or low toxicity to the environment, the insolubility in brine and the feasibility in its reuse. Cyclopentane (CP) is found to be an effective hydrate formation additive which can reduce the equilibrium pressure [16–20]. Yet the pure CP hydrate with a low dissociation enthalpy of 82.3 $\mathrm{kJ \cdot mol^{-1}}$ is difficult to form during the initial stage [21]. Therefore, help gas as a guest molecule can be helpful to stabilize the hydrate lattice and accelerate the hydrate nucleation [22,23]. An amount of equilibrium data have been reported that binary CP hydrate can form in the presence of different help gases such as CH_4 [24,25], CO_2 [26], N_2 [25], H_2 [26], H_2S [24], Kr [23] and CH_2F_2 [27] in pure water. Although the hydrate dissociation temperature for the CP-CH_4-water system is lower than that for both CP-CH_2F_2-water and CP-Kr-water system, CH_4 is considered as the suitable help gas in hydrate-based hot brine preparation. The most important reason is that CH_4 is cheaper than the others and it can be obtained from NGHs. Sun et al. [28] studied the effect of CP on methane hydrate formation conditions, and found that CP could shorten the induction time and improve the hydrate formation rate, and greatly reduce the formation pressure of methane hydrate. The dissociation enthalpy of the CP-CH_4 hydrate is as high as 130.25 $\mathrm{kJ \cdot mol^{-1}}$ at 285 K [29]. In mechanical methods, the hydrate formation can be enhanced by stirring [30–32], spraying [33,34], bubbling [35] for any of them can promote the mixing between gas phase and liquid phase. Actually, it was obviously observed that the bubbling could be less energy-consumed compared with the other two methods. CP is used as a hydrate formation additive to reduce the equilibrium pressure and improve the hydrate formation rate in the CP-CH_4-NaCl solution system [36,37]. Nevertheless, the accelerative mechanism of CP is not quite clear, and further identification is needed.

In this work, based on the hydrate formation for CP-CH_4-NaCl solution (3.5%) system in a visible bubble reactor, effects of the flow rate of gas (Q_g) and the mass fraction of CP (M_{CP}) on the gas consumption and the hydrate formation rate were investigated. In addition, the salinity of remaining liquid was analyzed with the argentometric method during the process of hydrate formation. In order to determine the crystal structure of the binary (CP-CH_4) clathrate hydrate, powder X-ray diffraction was measured.

2. Experimental section

2.1. Experimental material

NaCl with the mass fraction of 0.995 was purchased from Guangzhou Second Chemical Reagent Factory, China. The methane with purity of 0.999 was purchased by Foshan Huate Gas Co., Ltd. The CP (purity 0.99 up) was obtained from Chengdu Best Reagent Co., Ltd. All aqueous solutions were prepared by deionized water. The deionized water with the resistivity of 18.25 $\mathrm{m\Omega \cdot cm^{-1}}$ was produced by an ultra-pure water system obtained from Nanjing Ultrapure Water Technology Co., Ltd., China.

2.2. Apparatus

A schematic diagram of the experimental apparatus is shown in Fig. 1. The apparatus made of 316 stainless steel is a hydrate bubbling reactor with water jacket. The cuboid reactor has an inner volume of approximately 40.0 L. The reactor is divided into four segments. Each segment of reactor is fitted with four viewing windows to observe the hydrate formation. The reactor can bear pressure up to 4.0 MPa. The system temperature is controlled by cooling medium injected into jacket from the water bath. The temperature of the water bath can be regulated from (−5 to 40) °C with uncertainty of ±0.2 °C. The temperatures of reactor and gas collecting cylinder are measured by thermoprobes (Pt1000) with uncertainty of ±0.05 °C. The pressure measurement is performed by the pressure transducer, with a range of (0–10) MPa and maximum uncertainty of ±0.02 MPa. The pressure is controlled by a propor tional-integral-derivative (PID) through a pressure regulated valve (Tescom ER3000). The gas flow rate is controlled by a gas flow meter (LineTechM3030) in the range of 0–1 L/min with an accuracy ±1% F.S. CP is injected into the reactor by the proportional pump with a range of (0–60) L/h and accuracy ±1% F.S. The CH_4 and CP are mixed in the static mixer (SK DN15/L), then they are injected into the reactor through a perforated plate distributor (10 cm in diameter) with the pore size of 100 μm. Discharged gas is separated by gas-liquid separator and collected by gas collection cylinder.

2.3. Procedures

Each experimental run is carried out according to the following steps:

(1) The experimental apparatus is washed up cleanly using deionized water and 3.5% NaCl solution (mass fraction). Then, 16 L of 3.5% NaCl solution is introduced into the reactor. Subsequently, the reactor is flushed at least four times with the methane to ensure the absence of air.
(2) The system is cooled down to the experimental temperature (278.15 K).
(3) The temperature of liquid phase is stabilized at 278.15 K for 2 h. Then CH_4 gas is pumped into the reactor from the gas cylinder until the desired system pressure (3.5 MPa). The amount of gas is measured by a gas flow meter and the system pressure is controlled by a PID value.

Download English Version:

https://daneshyari.com/en/article/4916886

Download Persian Version:

https://daneshyari.com/article/4916886

Daneshyari.com