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Methane storage in water frameworks: Self-preservation of methane hydrate pellets formed from NaCl solutions

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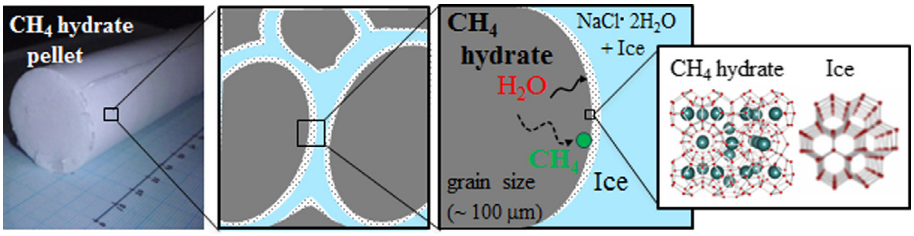
HIGHLIGHTS

- Highly stable CH_4 hydrate pellets were synthesized from NaCl solutions.
- The CH_4 storage capacity of the hydrate was experimentally verified.
- The effects of the liquid phase on hydrate self-preservation were clarified.
- A kinetic model for the self-preservation of a CH_4 hydrate with NaCl is proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

The use of methane (CH_4) hydrate as a CH_4 or natural gas storage medium offers an efficient and green source of energy. In this study, we produced CH_4 hydrate pellets containing NaCl at up to 2.7 wt%, and storage tests were performed to investigate the stability of CH_4 hydrates with NaCl at 253 or 248 K under ambient pressure. Based on assessing mass variations and powder X-ray diffraction analyses, it was determined that the dissociation rate of the hydrate greatly depends on the storage temperature. Below the eutectic point of the water-NaCl system, the hydrate exhibited self-preservation, while specimens readily dissociated at 253 K. The experimental results obtained in this study elucidate the effects of the NaCl solution on the self-preservation of CH_4 hydrates, and allow a kinetic model for this self-preservation phenomenon to be proposed. The results indicate that CH_4 hydrate pellets formed from sea water are a viable CH_4 storage and transportation media below the eutectic temperature.

1. Introduction

Gas hydrates are crystalline host-guest compounds consisting of cages made of hydrogen-bonded water molecules that include guest molecules such as methane (CH_4), other hydrocarbons or carbon dioxide (CO_2). Gas hydrates typically form under low temperature and high pressure conditions, and can contain 160–170 times their own volume in gas under equilibrium conditions [1]. The appearance of gas hydrates in oil and gas pipelines has led to blockages and attendant safety hazards since the early 19th century [2,3]. Natural gas (NG) hydrates containing primarily CH_4 with various other hydrocarbons as guest molecules are widespread in permafrost and in the sediments associated with continental margins. They are now attracting interest as an alternative source of NG [4,5], and may therefore serve as an efficient and green source of energy [6,7].

Various technological applications of gas hydrates have been proposed, related to NG storage and transportation [8], gas separation [9,10], refrigeration [11,12] and desalination [13,14]. However, the commercial deployment of hydrate-based technologies remains challenging. The primary issues are associated with the thermodynamics

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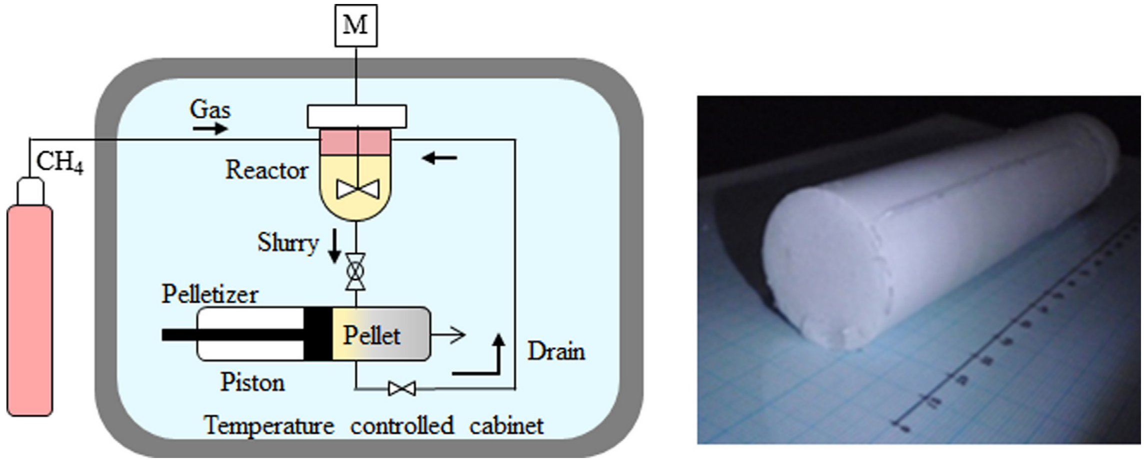

Fig. 1. The experimental apparatus and product. A diagram of the apparatus, including the CH_4 hydrate pelletizer (left) and a typical CH_4 hydrate pellet (right).

and kinetics of gas hydrates. To allow storage under milder pressure and temperature conditions so as to reduce refrigeration costs, thermodynamic promoters such as tetrahydrofuran (THF) have been investigated. At the same time, because of the inherently slow formation of hydrates, there have been attempts to promote their growth rates using kinetic promoters such as surfactants [15,16], other guest molecules [17] or amino acid [18]. In addition, studies of the economic feasibility of storing and transporting NG by means of hydrates have been performed [8] and the results compared with other NG transportation approaches, such as liquid natural gas (LNG) [19–21]. NG hydrate pellet systems has been proposed [22,23], which has been suggested that the system is more cost-effective than LNG systems for the transport of relatively small amounts of NG and transportation between the medium distances of around several thousand km [24]. Also, the applicability of land transportation of NG hydrate pellets was examined [25]. Even though the associated NG hydrate volume would be more than three times that of the LNG for the same amount of NG, the hydrate system can be applied to undeveloped small and mid-sized gas fields thanks to low initial capital cost [26] or total cost reduction by combination the system with existing LNG receiving terminal [27]. Because LNG transport is performed at approximately atmospheric pressure and 110 K, the very slow decomposition of NG (or CH_4) hydrates at ambient pressure and temperatures (just below the melting point of ice; 273 K), referred to as self-preservation [28] or anomalous preservation [29] of the hydrate, is advantageous with regard to energy efficiency. Thus, the effective application of the self-preservation phenomenon is crucial to allowing the storage and transportation of NG or CH_4 by means of gas hydrates.

The self-preservation of CH_4 hydrate, which suppresses the dissociation rate of the hydrate well outside the equilibrium region below 273 K, has been investigated from micro-viewpoints [30–32] and macro-viewpoints [33]. The phenomena at temperatures around 253 K has been investigated for practical application, and it has been revealed that this phenomenon depends on porosity [34,35] and size [36,37] of the hydrates, microstructure [38,39], and ice sheet formed due to the hydrate dissociations [40–42]. The phenomenon also depends on and type of guest molecule [43,44]. As an example, our group has succeeded in storing NG for several months at 253 K using a pelletizing technology [45]. In contrast, it has been reported that a CH_4 hydrate formed from a NaCl solution does not exhibit self-preservation [46,47]. Our group recently revealed that CH_4 hydrate pellets formed from a NaCl solution do not show self-preservation at 253 K because dissociation proceeds both from the outer surfaces of the pellets and from the interior [48]. It is possible that the rapid dissociation of the hydrate results from the presence of the NaCl solution (rather than solid ice) at the storage temperature of 253 K, based on the known ability of NaCl to act as a thermodynamic inhibitor [49,50]. This raises the question of whether or not a CH_4 hydrate can ever show self-preservation in conjunction with NaCl. It is necessary to obtained more detailed information regarding NaCl solutions coexisting with CH_4 hydrates to answer this.

In the present study, we investigated the dissociation of CH_4 hydrate pellets formed from aqueous NaCl solutions at temperatures below and above the eutectic point of a NaCl-H_2O system. The dissociation rates and phase diagram for the NaCl-H_2O system were also examined to better understand the hydrate dissociation mechanism and kinetics. Based on the CH_4 hydrate dissociation model proposed in this paper, the feasibility and environmental impact of CH_4 hydrate pellets formed from sea water are discussed.

2. Material and methods

2.1. Sample preparation

The CH_4 hydrate samples used in this study were formed from 3 or 10 wt% aqueous NaCl solutions, using distilled water (KOGA Chemical Mfg. Co., Ltd., Japan) and NaCl (Wako Pure Chemical Industries, Ltd., Japan). Approximately 0.7 L of each NaCl solution was introduced into a 0.98 L reactor and subsequently pressurized with CH_4 (SUZUKI SHOKAN Co., Ltd.) to 5.5 MPa to form a CH_4 hydrate slurry. A pelletizer based on a unidirectional piston was connected to the reactor and used to mold and dehydrate the slurry to produce pellets with a ϕ 33 mm diameter at temperatures ranging from 273 to 277 K and a pressure of 5.5 MPa (Fig. 1). Hydrate crystals in the slurry were compressed repeatedly by the piston at 15 MPa until the pellet exceeded 100 mm in length. The device was subsequently cooled to 253 K and depressurized to atmospheric pressure to obtain a CH_4 hydrate pellet. The relevant NaCl-H_2O phase diagram is shown in Fig. 2. The details of this procedure can be found elsewhere [52].

2.2. Chemical analysis

The NaCl concentration (or salinity: S) in each sample was obtained based on measuring the electrical conductivity (ES-51, Horiba, Ltd., Japan) of the melt water. The mass of excess water in a CH_4 hydrate pellet (w_{exw}) was calculated as

$$w_{\mathrm{exw}} = w_{\mathrm{aq}} - w_{\mathrm{w}},$$

where w_{aq} is the mass of melt water and w_{w} is the mass of water in the CH_4 hydrate. Here, w_{w} is given by

$$w_{\mathrm{w}} = w_{\mathrm{m}}/M_{\mathrm{m}} \times n \times M_{w},$$

where w_{m} is the mass of CH_4, M_{m} is the molecular weight of CH_4, M_{w} is