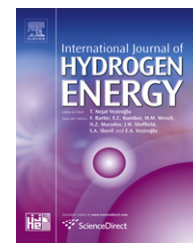


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Engineering investigation of hydrogen storage in the form of a clathrate hydrate: Conceptual designs of underground hydrate-storage silos

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ABSTRACT

This paper describes the conceptual designs of a facility for storing, in the form of a clathrate hydrate, hydrogen produced in an industrial complex area. We recently reported the first engineering investigation of hydrate-based hydrogen storage, focusing on the conceptual design of hydrate production plants applicable for the large-scale stationary storage in urban or industrial complex areas (Nakayama et al., *Energy Fuels* 2010;24:2576–2588). This paper complements the previous study by presenting conceptual designs of underground hydrate-storage silos each to be coupled to a hydrate production plant. Several different types of underground silos each having a 35,000 m³ capacity were planned and designed on a construction-engineering basis, which included (a) a tunnel-type silo consisting of several levels radially arranged around an access shaft, (b) a tunnel-type silo consisting of several levels that branch off from a single access level connected to an access shaft, and (c) a vertically-oriented cylindrical tank-type silo. For each type of silo, we have specified the hydrate loading and unloading equipment as well as the cooling system, and have estimated the construction cost.

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1. Introduction

The possibility of storing hydrogen in the form of a clathrate hydrate, a crystalline solid compound framed by interlinked cages made up of hydrogen-bonded host water molecules, has been a hot subject of research in the last decade. The cages may be occupied only by hydrogen molecules, thereby forming a simple (single-guest-component) hydrate, or selectively occupied by hydrogen and “second guest” molecules, forming a binary (two-guest-component) hydrate. The second guest substance is, for example, a compound such as tetrahydrofuran (THF) that its molecules fit into the larger

cages (5¹²6⁴ cages) of hydrate structure II (sII), thereby stabilizing the hydrate framework and significantly lowering the hydrate-forming pressure as compared to the pressure required for forming a simple hydrogen hydrate. Numerous experimental and theoretical studies concerning hydrogen hydrates have been reported during the last decade, particularly focusing on the possible reduction of the hydrate-forming pressure obtained with various “second guest” substances as well as the hydrogen occupancies in the smaller (5¹²) and larger (5¹²6⁴) cages of simple or binary sII hydrates. A comprehensive literature review about hydrogen hydrates was reported by Strobel et al. [1].

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The hydrogen storage using a clathrate hydrate has both definite advantages and disadvantages as compared to other technical options that simply compress hydrogen gas to a pressure of 35 or 70 MPa (ISO 11439) or liquefies hydrogen gas by cooling it to a temperature of ~ 20 K at a pressure above 1.3 MPa, use metal hydrides or ammonia for chemically storing hydrogen, use carbon nanotubes for physically storing hydrogen, etc. Hydrogen hydrates, particularly simple hydrogen hydrates, can be produced with no use of any expensive or toxic materials whenever the pressure of a binary hydrogen + water system is raised beyond, for example, ~ 230 MPa at a temperature of 273 K, 35 MPa at 200 K, and 0.1 MPa at 163 K [1–3]. Once formed under such pressure–temperature conditions, these hydrates can probably be stored under atmospheric pressure as long as the system temperature is maintained at 170 K or lower, with little time-dependent loss of encaged hydrogen molecules [2]. These production and storage conditions possibly make the hydrate-based hydrogen storage technology more economical and safer than other rival technologies. On the other hand, the hydrate-based hydrogen storage technology has no advantage over the conventional compressed- or liquefied-gas technology regarding the volumetric or mass-based hydrogen storage capacity. According to the neutron diffraction measurements with a simple deuterium (D_2) hydrate reported by Lokshin et al. [2], the D_2 occupancies of the $5^{12}6^4$ and 5^{12} cages under the condition of atmospheric pressure and a temperature of, for example, 140 K are 2.75 and 1.00 molecules per cage, respectively, which indicates that the mass fraction of hydrogen in the hydrate stored at this pressure–temperature condition is 3.03% [4]. In case of a binary hydrogen + THF hydrate stored at atmospheric pressure, the hydrogen mass fraction will only be $\sim 0.2\%$ or even lower [4–6]. Obviously, the hydrogen storage capacity available with ordinary clathrate hydrates does not reach the U.S. DOE targets for onboard hydrogen storage systems (4.5 mass% by 2010 and 5.5 mass% by 2015) [7].

The nature and properties of the hydrogen hydrates described above indicate that hydrogen hydrates are more suitable for stationary hydrogen storage than for mobile applications; this is because, for stationary hydrogen storage, neither the volumetric nor gravimetric storage capacity is the primary concern and, on the other hand, the safety and cost for long-term, large-scale storage are crucial. Our current interest is possible hydrogen storage in large-scale stationary stations in urban or industrial complex areas. The better safety of hydrogen hydrates compared to, for example, highly compressed hydrogen gas, will be of significant benefit in this case. Based on the above opinions, we have performed a feasibility study on the large-scale stationary hydrogen-hydrate storage. A part of this study focusing on the conceptual designs of hydrogen-hydrate production plants has already been reported in a separate paper [4]. The present paper aims to describe the residual part of the study, i.e., the conceptual designs of underground hydrate-storage silos each to be constructed, being contiguous to a hydrate production plant, in an industrial complex area. The advantage of underground storage lies in the possibility of constructing large-scale storage facilities, each exceeding $10,000$ m³ in volumetric capacity, in industrial complex areas wherein hydrogen is produced from various industries. The additional

benefit of underground storage is due to the fact that the daily and seasonal variations in temperature of the surrounding rock masses are relatively small, which is favorable for maintaining the storage-space temperature constant and thereby minimizing the rate of dissociation of the stored hydrate. The construction cost for the underground storage is several times higher than that for a tank storage at ground level. However, in most industrial complex areas in Japan, it is difficult to construct large-scale storage facilities on the densely built-up ground. Therefore, we believe underground storage to be the better choice despite its higher construction cost.

Underground hydrogen-hydrate-storage systems may be constructed in two different types: a tank type and a cavity type. In case of the former type, a vertically-oriented cylindrical tank with proper pressure-resisting and temperature-retention functions, similar to conventional LNG tanks, needs to be constructed underground. In case of the latter type, an underground cavern and/or tunnel are to directly hold the hydrate, depending on the pressure-bearing and temperature-retention capacities of its wall backed up by the surrounding rock masses. In this paper, we examine the feasibility of both the tank-type and cavern-type underground silos for the hydrogen-hydrate storage, specifying their structural designs based on the current state of civil engineering. A construction-cost estimate is provided for each silo design.

2. Specification of the problem

2.1. Storage condition of hydrogen hydrate

In our conceptual design study of hydrogen-hydrate production plants [4], we specified the thermodynamic conditions to be maintained inside the hydrate-forming reactors in each plant for each of the two cases; (a) the production of a simple hydrogen hydrate, and (b) the production of a binary hydrogen + THF hydrate. These conditions as well as the estimated hydrogen-storage capacities (mass basis) of these hydrates are summarized in Table 1. For the detailed reasoning of these operational conditions and the hydrogen-storage capacities, the readers should consult our companion paper [4]. In short, we planned to produce a hydrogen hydrate at an elevated pressure (35 MPa) and at a sufficiently low temperature (140 K), and to store the hydrate at the same temperature, but under atmospheric pressure. Although we presented plant designs for both simple and binary hydrates, we judged, based on some experimental results about the binary hydrates [5,6], the hydrogen storage in the binary hydrate at atmospheric (or a nearly atmospheric) pressure to be impractical (cf. note (34) in Ref. [4]).

Thus, we present in this paper only the storage-silo designs relevant to the simple hydrate. To be consistent with the conditions given in Table 1, each silo is expected to receive the hydrate product continuously conveyed from an adjacent production plant, being under temperature control at 140 K.

2.2. Model location for hydrogen-hydrate storage and its capacity

Although our interest is not necessarily limited to the hydrogen-hydrate storage at a particular location, selecting an

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