

# Enhanced efficiency of salt removal from brine for cyclopentane hydrates by washing, centrifuging, and sweating



Songlee Han<sup>a</sup>, Ju-Young Shin<sup>b</sup>, Young-Woo Rhee<sup>a,\*</sup>, Seong-Pil Kang<sup>c,\*\*</sup>

<sup>a</sup> Department of Chemical Engineering, Chungnam National University, 99 Daehak-ro, Yuseong-gu, Daejeon 305-764, Republic of Korea

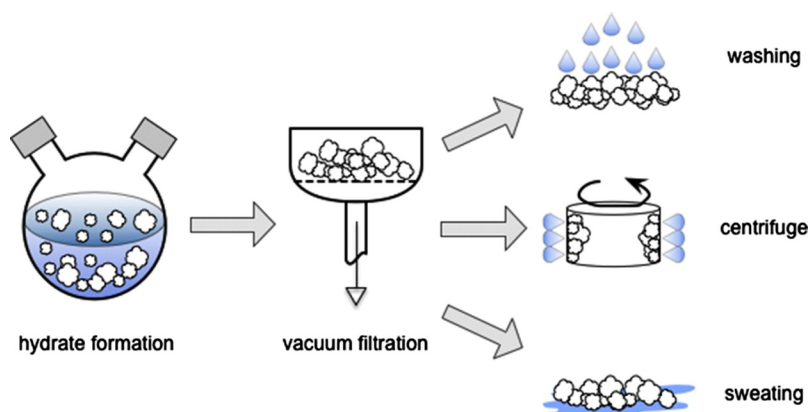
<sup>b</sup> Department of Chemical Engineering, Hanyang University, 222 Wangsimni-ro, Seongdong-gu, Seoul 133-791, Republic of Korea

<sup>c</sup> Climate Change Research Division, Korea Institute of Energy Research, Daejeon 305-343, Republic of Korea

## HIGHLIGHTS

- Cyclopentane hydrate formation in 3.5 wt.% NaCl aqueous solution was investigated.
- Hydration number and conversion of water to hydrate were observed.
- Post-treatments of hydrate using washing, centrifuging, and sweating were tested.
- It was proven that they were effective and efficient ways to enhance salt removal.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 19 August 2014

Received in revised form 19 September 2014

Accepted 21 September 2014

Available online xxxx

### Keywords:

Gas hydrate  
Cyclopentane  
Hydrate formation  
Centrifuging  
Washing  
Sweating

## ABSTRACT

As a concept technology for water desalination, a hydrate-based process involving water-immiscible hydrate former was proposed and is under development [1,2]. In this study, we focused on successive secondary treatment methods to improve the salt removal efficiency when the hydrate-based process was applied for water desalination. At first, hydrate formation reactions were carried out at atmospheric pressure and either 1.0 or 4.0 °C, with simulated brine of 3.5 wt.% NaCl and various concentration of cyclopentane (from 1.0 to 5.0 mol%). Results showed that substantial conversion of water to hydrate was possible as the degree of subcooling became high. A water mixture with 3.0 mol% cyclopentane at 4.0 °C, was subjected to centrifuging, washing, or sweating to achieve additional salt removal. Centrifuging produced the best salt removal efficiency (average 96%). Washing with a suitable amount of freshwater could effectively improve salt removal (to 93%). Sweating for an appropriate amount of time could also reduce the salt attached to the crystal surface more than 95%, but in this case the amount of water produced was proportionally diminished. According to the result, optimized washing method can be a promising candidate to raise the efficiency of the hydrate-based desalination process.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Gas hydrates are solid crystalline compounds formed when water molecules are connected by hydrogen bonds to form three-dimensional

\* Corresponding author. Tel.: +82 42 821 5686; fax: +82 42 822 8995.

\*\* Corresponding author. Tel.: +82 42 860 3475; fax: +82 42 860 3097.

E-mail addresses: [ywrhee@cnu.ac.kr](mailto:ywrhee@cnu.ac.kr) (Y.-W. Rhee), [spkang@kier.re.kr](mailto:spkang@kier.re.kr) (S.-P. Kang).

structures under specific temperature and pressure condition: generally low temperature and high pressure, and the water structures are able to enclose low-molecular-weight guest species [3]. Gas hydrates are considered as a nuisance in the oil and gas industries, because produced fluids contain water, and they are frequently exposed to conditions favoring hydrate formation with light gaseous mixture [4]. This leads to blockage problems in production equipment, especially pipelines, and can become a serious operational issue. Such hydrates are being investigated in order to use them for applications such as energy storage [5,6], CO<sub>2</sub> capture [7] and transport [8], frozen food [9], refrigerant and cold thermal energy [10], and alternative natural gas transport [11].

An attractive potential application for gas hydrates is water desalination. When hydrate crystals form, they consist of distinct water and guest species, so that we can obtain clean water after dissociating the hydrate particles recovered. Based on this possibility, water desalination using hydrates has been investigated during last decade [12,13] and is still being developed at laboratory scale [2]. Gas-hydrate technology for water desalination is theoretically feasible and attractive, but still requires breakthroughs to increase the efficiency of salt removal, and to decrease the cost. Compared to thermal distillation, the freezing (or hydrate) method requires quite low energy consumption, because the heat of vaporization of water is 40.7 kJ/mol, heat of freezing of water is 6.02 kJ/mol, and heat of hydrate formation is only 4.84 kJ/mol (for cyclopentane hydrate [14]). However, a serious challenge to the success of the freezing and hydrate method is the removal of salt attached to the surface of the recovered crystals. Salt is dissolved in water trapped inside the cleavages between crystals, and this salt is the sticking point to commercialization. Therefore, it would appear that the goal of desalination using crystal formation should be changed. It seems that, based on the current technology, the desalination process for obtaining drinking water using gas hydrate and freezing method is inadequate: however, water adequate for industrial use can be recovered from brackish or polluted water. Based on its energy efficiency, it appears that the gas hydrate method could become a competitive process. Cha and Seol [2] aimed to use hydrate technology to recover usable water from wastewater produced in shale-gas fields.

Gas hydrate formation requires water and a hydrate former. In the case of gas species as a hydrate former, hydrate formation requires greatly increased pressure so that the additional equipment and operating costs are needed to achieve it. Researchers have tried to find ways to decrease the hydrate-formation pressure and have reported that CO<sub>2</sub> [12,15], R141b [16] and R22 [17] could be promising candidates for hydrate formation at relatively low pressures. Corak et al. [1] used cyclopentane as a hydrate former because it forms solid hydrate crystals at atmospheric pressure. Cyclopentane exists as a separate liquid phase in water under normal conditions and shows extremely low solubility in water. Thus, it can be recovered simply by decanting after the hydrate crystals are collected and dissociated. They investigated the effect of the degree of subcooling, and of the ratio of cyclopentane to water, on the formation rate. They reported that operation variables are mostly dependent on the degree of subcooling, and a high degree of subcooling seems to produce rapid hydrate formation rate, as well as higher degree of desalination overall.

In this study, we investigated the hydrate-formation process using cyclopentane as a hydrate former, and took the unincorporated cyclopentane into account in the calculations. In addition, we examined the effectiveness of supplementary steps after vacuum filtering to increase the efficiency of salt removal. We washed hydrate crystals with a small amount of fresh water, centrifuged filtered hydrate crystals in order to remove salt trapped in cleavages, and provided sweating time by which hydrate crystals might decrease the salt on the crystal surface. Simple and effective post-processing improved the competitiveness of the hydrate method for desalination. The purity of the water produced and the increased efficiency of salt removal for each step were intensively studied.

## 2. Experiment

### 2.1. Materials

Distilled water was purchased from Merck (HPLC grade), and was further treated using a water deionization system (Thermo Scientific GenPure™). Cyclopentane (98% purity) was purchased from Sigma-Aldrich and used without further treatment. Brine solution was prepared by adding 3.5 wt.% of NaCl (Duksan Chemical, 99.0% purity) to de-ionized water.

### 2.2. Apparatus

A glass crystallizer with a thermocouple was constructed to form cyclopentane hydrate. A round-bottomed two-necked flask (750 ml) containing a magnetic spin bar (40 × 8 mm) was placed in a temperature-controlled cooling bath. The thermocouple was inserted into the solution to measure the temperature throughout the experiment. Each neck of flask was sealed by a silicon lid in order to prevent the coolant from soaking into the crystallizer. To obtain a stable temperature for hydrate formation, the coolant (mixture of 30 vol.% ethylene glycol and 70 vol.% of water) was circulated by chiller (Jeio-Tech, R3040). RPM of magnetic spin bar was controlled using an external immersion stirrer (Sonics, MC303).

A vacuum filter assay device (Wheaton) connected to a vacuum pump (Vacuubrand, ME 8) was used to filter the hydrate slurry. While filtering the hydrate slurry, OMNIPORE membrane filters (10.0 μl JC, Millipore) were applied to the filter assay device in order to separate the hydrates from the remaining liquid. In addition, a vacuum oven (Jeio-Tech, OV 12) was utilized to separate cyclopentane from water when the hydrates were dissociated. Excess water in the hydrate particles was also removed using a cooled centrifuge (Hettich Lab Technology, Universal 320R).

The purity of water was determined by measuring the conductivity of the aqueous solution, using a SevenCompact™ conductivity meter (Mettler Toledo).

### 2.3. Experimental procedure

Equilibrium dissociation temperatures for cyclopentane hydrate at 1 bar have been reported, but the reported temperatures were all different (7.7 °C [18], 6.8 °C [19], 7.11 °C [20]). In addition, there was no available equilibrium dissociation temperature for brine (3.5 wt.%). Corak et al. [1] determined a dissociation temperature of 6.8 °C for 3.0 wt.% NaCl solution, and Zyliftari et al., 5.28 °C for 3.4 wt.% NaCl solution [20]. Therefore, we measured the equilibrium dissociation temperature of cyclopentane hydrate in pure water and in 3.5 wt.% NaCl brine, to confirm the validity of our experimental procedure and to determine the exact subcooling to use. According to our measurement, we selected the equilibrium temperatures of 7.8 °C for pure water, and 6.6 °C for 3.5 wt.% NaCl brine.

First, the cyclopentane and brine (3.5 wt.% NaCl) were introduced into a crystallizer and well mixed using a magnetic spin bar at 700 RPM. Then, the mixed fluid was cooled down to a specific experimental temperature. To induce the formation of cyclopentane hydrate, the temperature was maintained at 1 and 4 °C, at which temperatures the subcooling was 5.6 K and 2.6 K, respectively.

Hydrate formation is a stochastic process and its appearance is thus rather irregular. For this reason, we tried to make the process more reproducible by adding a few small ice particles to the crystallizer at the experimental temperature, which commenced hydrate formation easily. The temperatures of the liquid mixtures, and the time, were continuously recorded throughout the experiment. After particles of cyclopentane hydrate appeared, the crystallizer was left as it was while maintaining the temperature to allow the particles to grow enough. When the temperature of the mixture became stable again,

Download English Version:

<https://daneshyari.com/en/article/623383>

Download Persian Version:

<https://daneshyari.com/article/623383>

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