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Desalination by forming hydrate from brine in cyclopentane dispersion system

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HIGHLIGHTS

- Kinetic experiments were performed to optimize the CP hydrate desalination conditions.
- Excess CP addition into brine and CP dispersion increase the yield of dissociated water.
- Controlled encapsulation/entrapping of residual brine into hydrate phase was attained.
- An inverse correlation between removal efficiency and yield of dissociated water exists.

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ABSTRACT

To make application of hydrate based desalination technology practical, the kinetic behaviors and separation capability were examined for cyclopentane hydrates formed from brine in cyclopentane dispersion systems at 274.1 K/277.1 K with initial salinity of 3 to 5 wt% for water fractions from 20.0 to 90.0 vol% and rpms from 300 to 500. The excess cyclopentane addition into brine and cyclopentane dispersion significantly increased the yield of dissociated water when the removal efficiency stayed around 80%. This implies enhanced kinetics and controlled encapsulation of residual brine into the hydrate phase for brine in cyclopentane dispersion systems. More hydrates formed under lower temperature or initial salinity. Higher rpm could further promote hydrate formation but would adversely affect the removal efficiency. Desalination efficiency was enhanced with washing during vacuum filtration and effects of ratio of washing water/dissociated water on the removal efficiency were considerable. An inverse correlation exists between the removal efficiency and the yield of dissociated water under the same conditions. Lower temperature (274.1 K) and 60% water cut should be optimal for higher yield of dissociated water from brine in cyclopentane dispersion. The ratio of washing water/dissociated water and rpm conditions should be adjusted depending on the situation.

1. Introduction

The shortage of fresh water is an increasingly important issue in many countries and regions around the globe mainly due to growing population as well as agricultural and industrial demand. Currently this problem is addressed by desalination of seawater using the traditional methods including reverse osmosis (RO) technology and multi-stage flash (MSF) distillation. Although these traditional methods are well established and reliable to provide sources of fresh water, there remains a need concentrating on the development of desalination technologies with lower cost and improved productivity and efficiency as indicated in a considerable amount of research effort [1–3]. Clathrate hydrates are non-stoichiometric crystalline compounds that are formed when guest molecules are incorporated into hydrogen-bonded cavities constituted by host water molecules [4]. Hydrate is most commonly acknowledged in the petroleum industry to be able to cause plugging problems in oil and gas pipelines, endangering production operations. On the other hand, hydrate-based technologies represent potential solutions in a wide range of applications including gas separation [5–8] and storage [9,10]. Formed hydrate crystals are free of salt ions, so after separation of hydrates from concentrated salt solution, fresh water can be produced from melted hydrates, making desalination

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process feasible. Hydrate desalination process was also reported to be more economic in energy efficiency compared with thermal distillation [11]. It generally requires high pressure for gas hydrates to form [12,13], however, cyclopentane (CP) hydrate could form under atmospheric pressure at temperatures above the freezing point of water [14]. CP is immiscible with water, easy to separate and recycle. Desalination by CP hydrate would be safer, more convenient and it would also reduce costs for the process to operate without pressurization.

The kinetics of CP hydrate formation was investigated using differential scanning calorimetry [15,16], but the research was limited to high water cut systems. According to Corak's study with CP hydrates at the subcoolings of 5.6 K and 3.6 K [14], when the subcooling is 5.6 K, the kinetics of hydrate formation was faster and in general better purification of water was observed. Smaller ratios of CP to water resulted in lower amount of hydrates formed and higher removal efficiency for high water content systems. The separation of hydrates from concentrated salt solution proved to be difficult [17–19]. The filterability of hydrates and guest molecules with milder formation conditions were further investigated [20]. In an attempt to separate hydrate crystals and concentrated brine more effectively, Park et al. [2] proposed an apparatus equipped with a dual cylinder unit for mechanically squeezing and pelletizing gas hydrates from slurries. While higher efficiency of desalination was obtained by this method than others without washing, the produced pellets may be too small for practical use and the maintenance cost for mechanical abrasion may also be a problem [21]. The applied hydraulic pressure was as high as 50 kg/cm^2 and potentially plugging risks may be introduced by the design of plurality of passing holes. As reported in Corak's study [14], after filtering by vacuum suction, cooled centrifuge was used to further remove excessive water from the solid hydrate phase. In addition to vacuum filtering, supplementary post-treatment steps of washing, centrifuged filtering and sweating were carried out recently in Han's work [11]. Centrifuging proved to be the most efficient way for the removal of remaining water but it is not economical, nor is it available for massive treatment. The washing method, on the other hand, is much easier to implement in practice and was claimed to be a promising candidate for increasing salt removal efficiency with a relatively little effort [11]. However, only primary tests were conducted with respect to the washing method and more detailed studies are required for the development of this technology.

In this work, single-stage hydrate desalination experiments were carried out using brine in CP dispersion systems with different water contents focusing on the improved washing method. It was discovered that excess CP addition into commonly used systems of high water cuts could significantly increase the yield of dissociated water while the removal efficiency was almost the same. More hydrates were formed with lower temperature or smaller initial salinity. Increase in rpm would facilitate formation of more hydrates but would adversely affect removal efficiency. The influences of the ratio of washing water/dissociated water on removal enhancement was investigated in an attempt to address the problem of separation of hydrate crystals and concentrated brine. The results also indicated a trade-off between the yield of dissociated water and the removal efficiency. It is noted that lower temperature (274.1 K), optimal water volume fraction and proper ratio of washing water/dissociated water & rpm conditions should improve the desalination process with brine in cyclopentane dispersion systems. The results should provide fundamental information and useful perceptions for the development of this technology.

2. Materials and methods

2.1. Materials

Deionized water was purchased from Beijing Century Technology Co., Ltd. with electrical conductivity $<10^{-4}$ S·m^{-1}. CP (96% purity) was purchased from Aladdin and used without further treatment. Brine was prepared by adding NaCl (Xilong Chemical Co., Ltd., 99.5% purity) with appropriate weight percent to deionized water.

2.2. Hydrate formation and desalination test

The apparatus used for hydrate formation was briefly a stainless-steel reactor with internal volume of 763 cm^3. One platinum resistance thermometer was embedded in the bottom of the reactor to measure system temperature. A schematic of the apparatus is shown in Fig. 1. The reactor was mounted in an air bath with a view window and is equipped with a speed-adjustable electromagnetic stirrer inserted into the reactor for solution agitation. The uncertainty of temperature measurement is ±0.1 K. The temperature of the air bath is stable within ±0.1 K.

A vacuum filter setup connected to a vacuum pump (Naxi China Vacuum Co., Ltd.) was used to filter hydrate slurry. The salinity of dissociated water was determined by measuring the conductivity of the aqueous solution, using a FiveEasy™ conductivity meter (Mettler Toledo).

The experiments were carried out in batch mode and the procedure was as follows. Prior to the experiments, the reactor was cleaned with deionized water three times and dried, and then the water and oil dispersion with total volume of 400 cm^3 was prepared. The temperature in the reactor lowered and reached desired values before the preparation of dispersion. In order to avoid variations in induction time and for better experimental reproducibility, the dispersion was first placed inside a refrigerator to facilitate the nucleation of hydrate. As soon as hydrate particles became observable, the dispersion was promptly transferred into the reactor and the electromagnetic stirrer started at a preset constant speed. This was considered to be time zero for hydrate formation. The temperatures were recorded by a data acquisition unit and logged into a computer every 1 min.

The experiments stopped when the formation had continued for a desired period of time (8 h) [14,21]. The formed hydrate slurry was then discharged and transferred into the cooled vacuum filter setup in order to separate the hydrate phase and the brine. After initial filtration, the entire Buchner funnel with filter cake of hydrates was weighed. The amount of washing water was determined based on the weight of the filter cake of hydrates, a preset ratio of washing water/dissociated water (g/g) of 0.5 and a constant empirical coefficient. The deionized water for washing was also cooled. Then the filter cake of hydrates was further filtrated when washing water was flushed through the filter cake from the top to the bottom of the Buchner funnel. The hydrates always experienced a loss in weight during the second filtration with washing. This was believed to be mainly caused by the removal of residual brine with washing water. The produced hydrates were then weighed and were left for dissociation at room temperature (298 K) for over 10 h when the CP produced from dissociation was gradually removed due to evaporation. The weight and salinity of dissociated water were determined when the total mass of dissociated water no longer lowered indicating negligible residual CP.

2.3. FBRM analysis

Focused beam reflectance measurement (FBRM) probe was used to identify the sizes of CP hydrate particles. The FBRM probe consists of six lasers [22] which illuminate a small area in front of the probe face. There is a rotating optical lens at the probe tip which can deflect the laser. When it starts working, the emitted laser is reflected if it scans across the surface of a particle. The chord length of droplets or particles can be determined by the product of the measured reflectance time and the laser scan speed with an uncertainty of 0.5 μm, and it is counted at a certain time interval. The chord length distribution can then be determined. Median chord length that stands for the size of the droplet or particle to some extent is obtained from chord length distribution in FBRM software.