



# Investigation of salt removal using cyclopentane hydrate formation and washing treatment for seawater desalination



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## HIGHLIGHTS

- Cyclopentane hydrate formation in seawater was investigated.
- Hydrate formation followed by filtration and washing treatment was carried out.
- Major salt ions were analyzed during hydrate formation, filtration, and washing.
- Salt removal according to conversion and amount of wash water was examined.

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## ABSTRACT

Salt removal via formation of gas hydrate was investigated by experimental measurement of the salt concentration in filtered water and water retrieved from hydrate crystals. Gas hydrate formation was carried out at 277.15 K, using seawater of 3.4 wt% salinity and 3 mol% cyclopentane to water-cyclopentane mixture. Single-stage hydrate formation followed by filtration removed 63% of the salt ions. Successive washing treatment with 274.15 and 277.15 K freshwater was applied with different amounts of washing water, and several major cations and anions in seawater were analyzed in each treatment step. Ions having larger radii showed less salt removal by hydrate formation, and salt removal decreased as the conversion of water to hydrate progressed. However, salt removal was improved by washing treatment to nearly the same degree regardless of the kind of salt ions and the salt removal efficiency improved up to 42% more than that of filtration only. The results presented in this study can be used as basic design values for the development of a hydrate-based desalination process.

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## 1. Introduction

It has become increasingly difficult to secure safe sufficient water because of the pollution of water resources and severe climate abnormalities resulting from explosive population growth and rapid industrialization. Securing abundant clean water serves social, economic, and ecological interests; so a great variety of studies have been performed to solve these problems [1]. From a technical point of view, to obtain sufficient water of the quality desired, it is essential not only to conserve and protect existing water but also to discover new water resources [2, 3]. Accordingly, a variety of desalination technologies has attracted the interest of researchers because seawater is the largest water reserve on Earth (97%), whereas only 0.5% of surface water on Earth is freshwater. The problem with using seawater directly for daily life is that it contains unacceptable levels of organic matter and salinity. Thus, desalination of

seawater is an obvious and good alternative to finding new source of clean freshwater [3].

Existing reliable desalination methods at industrial scale are based on either multi-stage thermal distillation or seawater reverse osmosis (SWRO) filtration. Distillation is a prevailing method, but requires a large amount of phase transition energy, that is the heat of vaporization of water from liquid to vapor, so that it is quite expensive. SWRO method uses membrane to allow the selective transport of water along with polymeric barrier at pressurized condition. Developing the materials for membrane and energy recovery devices, reverse osmosis (RO) process has dropped its energy consumption to around 3.0 kWh/m<sup>3</sup>-produced water [4,5]. According to the literature [6,7], as of 2011, RO filtration method is spreading out the market up to 66% of installed desalination capacity, and nearly all new plants. However, this energy requirement is still higher than other forms of water supply at 0.1 to 1 kWh/m<sup>3</sup>, therefore much of efforts have been made on the development of hybrid systems, such as RO with thermal process or renewable energy source, for improving the economics aspect [8]. Pre-treatment for RO method

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is another important step, due to the nature of membrane design, that is, only one-way flow through membrane. Because the accumulated material cannot be removed from the membrane surface, they easily become fouling, which means loss of production capacity.

Freezing is another attractive method, but still not widely used commercially. This method utilizes the phase change phenomenon of water to solid ice crystal so that the coexisting ions and impurities are excluded, and finally thawing produces purified water. Considering the energy required to induce the phase change of water during boiling (40.7 kJ/mol) and freezing (6.02 kJ/mol), seawater desalination by freezing method is more advantageous. In addition, freezing desalination process has a low operating temperature, which minimizes scaling and corrosion problems, and even inexpensive plastics or low cost materials can be used at low temperature [9]. Gas hydrate formation method for desalination could be one of the novel desalination processes, which is also classified into a freezing, crystallization method. Because of the additional chemicals called guest, such as gas/liquid hydrocarbons and CO<sub>2</sub>, gas hydrate forms at higher temperature than the freezing point of ice, and this leads to an expectation of the improved energy efficiency [10,11]. The hydrate crystals form under suitable temperature and pressure, and are collected to be dissociated by breaking the temperature or pressure. In the next stage, the guest shall be recovered from the dissociated water for further use, and freshwater is produced [12]. Gas hydrate technology is still under development, but when applicable at larger scale, it could be a cheap alternative to the traditional thermal and membrane desalination process [8]. Diminution in energy consumption for water production is the main concern, so in this regard, gas hydrate method as a pre-treatment step for RO process was tried to investigate its feasibility by simulation study [13]. Pre-treated feed by gas hydrate step would reduce the load of salt removal on RO process. According to the report, 90% of salt removal efficiency using CO<sub>2</sub> hydrate formation step and 0.80 of the subsequent RO recovery ratio with energy recovery device showed 2.74 kWh/m<sup>3</sup> of total energy consumption, which is able to compete with the SWRO system with energy recovery device. In addition, the heat of hydrate formation is just 4.84 kJ/mol (for cyclopentane hydrate [14]), thus the energy consumption could be decreased further, comparing the enthalpies of the phase change.

The use of gas hydrates for desalination has been investigated during the last 50 years, and a variety of hydrate formers and formation methods were investigated to obtain improved kinetics and conversion [4,15–18]. In most of the previous works, CO<sub>2</sub> [19], light hydrocarbons [20], and chlorofluorocarbon refrigerants (e.g. R141b and R22 [21–23]) were tried as hydrate formers. However, they would require relatively higher pressure for the operation. Recently, some researchers tried to use cyclopentane as a hydrate former for the desalination process because it forms solid hydrate crystals at atmospheric pressure [24,25] and 280.95 K [26]. Moreover, cyclopentane is nearly immiscible with water and shows extremely low mutual solubility. Therefore, it could be recovered simply by decanting from the liquid-liquid phase mixture after collecting and dissociating the hydrate crystals. Coral et al. investigated the effect of the degree of subcooling, and of the ratio of cyclopentane to water on the formation rate [24]. Like freezing method, however, the water molecules containing salt ions are confined within solid crystals of gas hydrate as well. Thus, subsequent post-treatments are required. In our previous work, we investigated the formation of cyclopentane hydrate in 3.5 wt% NaCl synthetic seawater and observed the hydration number and conversion of water to hydrate [26]. Optimal operation temperature and concentration of cyclopentane were decided from the measured results. Post-treatment of hydrate crystals (e.g., washing, centrifuging and sweating) was also tried in efforts to enhance salt removal efficiency, and we found that optimized washing can be a promising candidate among possible post-treatments, to raise the efficiency of the hydrate-based desalination process.

In this work, the investigation was extended to an experimental hydrate-based desalination process using cyclopentane with real seawater, and the effectiveness of washing method as post-treatment

was examined. While adopting the optimum temperature and concentration of cyclopentane for hydrate formation, and ratio of washing water to produced water, determined in our previous work, the effect of a few anions and cations on the salt removal efficiency in the proposed process was investigated by analyzing the ion concentration in filtered water, and in water retrieved after dissociating the hydrate particles. The salt removal efficiency for each ion, and the proportion of water converted to hydrate, the amount of wash water, and the feed concentration were also examined.

## 2. Experiment

### 2.1. Materials

The seawater samples were obtained from the east coast of Jeju island, Korea (33°33'47.3" North, 126°46'26.2" East) and used as it was without any further treatment. The seawater samples were analyzed to obtain the ion concentration using ion chromatography. Results from a detailed analysis of the concentrations of ions in the seawater samples are presented in Table 1. The presence of other minor ions was neglected. Cyclopentane was purchased from Sigma-Aldrich (98% purity, reagent grade) and used as a hydrate former without further treatment.

### 2.2. Apparatus

A round-bottomed two-necked flask was placed in a temperature controlled cooling bath to be used as a hydrate crystallizer. A thermocouple was inserted into the aqueous solution to measure the temperature of the seawater during the experiments. The contents of the hydrate crystallizer were stirred using a magnetic spin bar. An external chiller was used to control the bath temperature. A vacuum-filter assay device was used to filter the hydrate slurry, and a membrane filter was applied to separate the hydrate crystals from the remaining liquid. A vacuum oven was utilized to evaporate cyclopentane from the water for mass analysis. A detailed description of the hydrate crystallizer and post-treatment experiments was presented in our previous work [26]. The concentration of each ion was measured using ion chromatography (Metrohm, 881 Compact IC pro) with an autosampler (Metrohm, 863 Compact Autosampler). Appropriate ion analysis columns were used for cations (Metrohm, Metrosep C4) and anions (Shodex, IC 82904A).

### 2.3. Experimental procedure

To provide the primary cleaning treatment, the seawater samples were passed through a filter paper to remove floating substances and other particulate. Then, a mixture of seawater and cyclopentane was placed in the hydrate crystallizer and well mixed by a magnetic spin bar. In this experiment, the stirring rate of the spin bar was fixed at 700 rpm for all the experiments. Next, the temperature of the contents in the crystallizer was cooled to a specific experimental temperature. After the system temperature became stable, a few small ice particles were added to the crystallizer to induce the commencement of hydrate nucleation. The temperature over time was recorded throughout the experiment. As the cyclopentane hydrate particles formed, the crystallizer was left as it was for about two hours to grow hydrate crystals. The temperature increased for a moment because of the exothermic hydrate formation reaction, but instantly reverted. At this point, the content of the

**Table 1**  
Concentration of ions in seawater samples.

Total Dissolved Solids (TDS) (mg/L)	Cation (mg/L)				Anion (mg/L)	
	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
34,027.56	10,832.56	605.86	1054.49	1323.08	17,627.38	2548.19

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