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.

ARTICLE INFO

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/m³-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/m³, 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_2, 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_2 hydrate formation step and 0.80 of the subsequent RO recovery ratio with energy recovery device showed 2.74 kWh/m³ 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_2 [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 cost 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. Cycopentane 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^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}
34,027.56	10,832.56	605.86	1054.49	1323.08	17,627.38	2548.19

hydrate crystallizer was a slurry of hydrate particles and liquid consisting of un-reacted water and cyclopentane. Then, the hydrate slurry was separated into hydrate particles and remaining liquid by the vacuum filtration using OMNIPORE membrane filters (Millipore, 10.0 ml JC). The filtered hydrate particles were subjected to further washing using a specific amount of fresh water. Immersion of hydrate particles into distilled water was expected to be an effective surface cleaning method to remove the clinging salt ions to the hydrate particles [26]. The washed hydrate particles were subjected to the vacuum filtration step again. In every step, the remaining liquid and dissociated water from the hydrate particles were collected and analyzed, to obtain the ion concentration. Finally, the removal efficiency of each ion was calculated from the measurement data using following equation.

$$\text{Salt removal efficiency } (\%) = \frac{C_o - C_f}{C_o} \times 100$$

where C_o was the initial concentration of a specific salt ion in the feed, and C_f was the final concentration of the specific salt ion in the dissociated water from hydrate crystals.

There was unreacted or dissociated water and cyclopentane present at each filtration and washing step, so that we had to measure the mass and ion concentration in each samples to confirm the mass balance. Immiscible two-phase liquids consisting of water and cyclopentane were separated carefully by decanting. A small amount of accompanying cyclopentane in the water was removed by evaporation in an oven for 2 h, at 323.15 K. A more detailed description of this procedure can be found in a previous report [26].

3. Results and discussion

In our previous work [26], the equilibrium dissociation temperature of cyclopentane hydrate was determined to be 280.95 K for pure water, and 279.75 K for 3.5 wt% NaCl aqueous solution. We first measured the melting temperature of the cyclopentane hydrate in actual seawater (salinity given in Table 1), and determined it to be 279.45 K. Based on this temperature information, we performed experiments on hydrate formation and washing at 274.15 and at 277.15 K, which provided subcooling of 5.3 and 2.3 K, respectively. This means that the driving force of this system became slightly less than that of the simulated system although the experimental temperatures were the same. In addition, we used the same concentration of cyclopentane (3 mol%) relative to the total moles of the water-and-cyclopentane mixture as in our previous work, because it was found that the addition of 3 mol% cyclopentane was suitable for the formation of hydrate slurry. Hydrate of 3 mol% cyclopentane with seawater was formed at 277.15 K, and the crystals were filtered and collected. A subsequent washing step was done with 2 wt% portion of produced water at 274.15 and 277.15 K. The salt removal efficiencies calculated from these results are presented in Fig. 1. The hydrate formation and initial filtration steps resulted in removal of 63% of the salt ions. Subsequent washing with water at 274.15 and 277.15 K further increased the salt removal efficiency to 72 and 83%, respectively. More salt ions were removed by washing with water at 277.15 K than at 274.15 K. It seems that warmer water affects the surfaces of the hydrate crystals, dissolving ions adsorbed to the crystal surface. Of course, it should be considered that washing with water of higher temperature would also decrease the amount of hydrate crystals. We determined that washing crystals with 277.15 K water was most suitable for further treatment, so that all the subsequent washing steps were done at 277.15 K.

During these experiments, each salt ion in seawater was measured after each filtration and washing step. The removal efficiencies of the respective ions were calculated and presented in Fig. 2. As can be seen in the figure, the filtration step was better at removing small ions and cations. Large anions were less well removed during hydrate formation and filtration steps. However, after each washing step, the salt removal
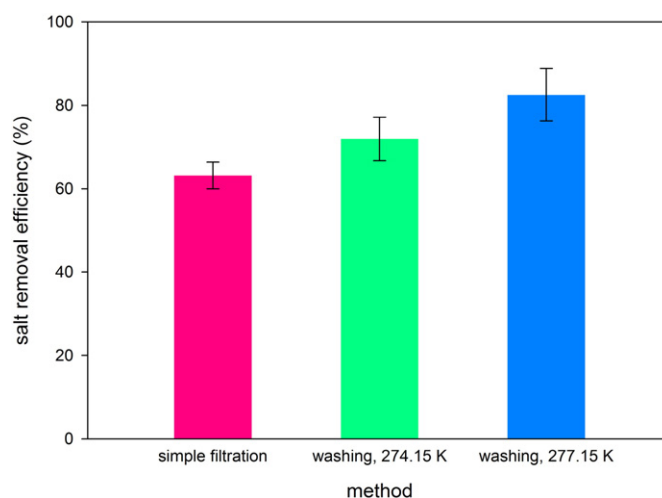

Fig. 1. Effect of washing on salt removal after formation of cyclopentane hydrate: The ratio of washing water to produced water was 0.02.

efficiencies did not show any distinctions related to the ion radius or kind of ion. Nearly similar ion removal efficiencies were obtained after washing step. Park et al. reported the characteristics of cation removal from seawater by gas hydrate formation method [27]. They used CO_2 as a hydrate former and even made use of a newly developed apparatus that could crystallize hydrate particles and simultaneously shape them into pellets. From their results, it was found that the removal efficiency of each cation increased according to its ionic radius. Kang et al. also reported the removal characteristics of cations and anions from seawater hydrate using the apparatus of Park et al., with CO_2 and CH_4 as hydrate formers [28]. After pelletizing, the hydrate particles were dried by wiping the pellet surface with paper tissue. The use of CO_2 as a former gave better results than did CH_4 for salt removal, and the removal efficiency of ions increased according to the ion radius, regardless of surface washing. Given that hydrate formation methods were different, and that our results showed trends different from those in [27,28], we draw the conclusion that the adhesion characteristics of ions to the hydrate surface is diverse, depending on the kind of ion and the hydrate former.

Here, it seems necessary to discuss the morphological difference of hydrates formed from cyclopentane and those formed from gases. Cyclopentane forms structure II hydrates, and the morphology of cyclopentane hydrate is different from that gas formers such as CO_2 and CH_4 (structure I). In addition, the morphology of the crystals formed has a significant dependence on the degree of subcooling. As a general
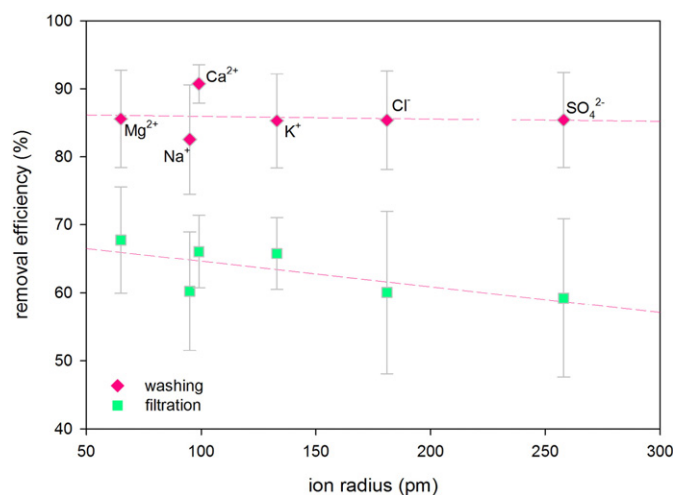

Fig. 2. Removal efficiency of each major ion in seawater according to ion radius: hydrates were formed and washed at 277.15 K, and washing water/produced water was 0.02.

trend, when the subcooling is ≥3.0 K, the shape of the hydrate crystals is typically sword-like or in the form of triangular dendrites. When the subcooling is 2.0–3.0 K, the crystal shape changes to a polygon of skeletal crystals, and when the subcooling is ≤2.0 K, the crystals are large polygons with one side of polygon for the gaseous formers (e.g., CH_4, C_2H_6, C_3H_8 [29] or CO_2 [30]). This trend does not change when applied to an aqueous solution of salts. As for the hydrate formed from hydrophobic cylopentane in seawater, the crystal shape is hexagonal or square at 1.4–4.5 K subcooling, and triangular for subcooling >5.4 K [31,32]. According to this information, the shape of the hydrate crystals formed in Park et al. [27] and Kang et al. [28] would be dendritic, while those formed in this work would be polygonal. Dendritic gas hydrate crystals more easily contain water than polygonal crystals do, as long as the hydrate crystal grows at a suitably low rate. This is because a higher growth rate of hydrate crystal implies increased potential to include more water (and salt ions) among crystals. The salt removal efficiency obtained in this work was about 83% after washing with 277.15 K water, but that of CO_2 hydrate reached nearly the same value when extreme hydraulic pressure (≥70 kgf/cm² [28]) was applied. The possibility of the emulsion formation for cyclopentane-water system should be considered as a matter of course. Throughout these experiments, the mixture of water and cyclopentane formed an oil-in-water emulsion at first; then the hydrate slurry formed as the temperature cooled down to initial temperature. Due to the formation of an emulsion, it may be possible that the cyclopentane is entrapped inside the formed crystals [14]. Accordingly, when the crystal is dissociated to retrieve the produced water, the emulsion can form again, and cyclopentane can be recovered in small drops as well. In future work, a well-developed method for the dispersion of water and cyclopentane should be devised to avoid this situation.

Fig. 3 shows a scatterplot with regression line, of the salt removal efficiency after filtration of hydrate crystals according to the conversion of water to cyclopentane hydrate, reacting at 277.15 K with 3 mol% of cyclopentane. Cyclopentane hydrate can contain 17 mol of water per mole of cyclopentane to form a structure II hydrate, so the theoretical conversion of water to hydrate becomes 52.58%. As can be seen in the figure, the salt removal efficiency declined as the conversion increased. Even though the temperature difference was fixed at 2.3 K, the stochastic nature of crystallization resulted in scattered conversion values from 41.2 to 53.3%, and the corresponding salt removal efficiency also varied from 53.7 to 70.8%. The average conversion and salt removal efficiency were 51% and 63%, respectively. Because we previously found that post-treatment by washing makes it possible to decrease the salt removal efficiency, there is no need to worry about the inclusion or

adhesion of salt ions to hydrate crystals during hydrate formation. Conversion of water to cyclopentane hydrate is relevant not only to the concentration ratio of cyclopentane to water and to the degree of subcooling, but also to the reaction time, reactor shape, and so forth. As mentioned above, we fixed the ratio of cyclopentane to water, the degree of subcooling, and reaction time according to the results from our previous work. Accordingly, we would like to discuss briefly the reactor here. When a large scale desalination process using hydrate formation is to be actualized, the amount of hydrate slurry with a high concentration of hydrate crystals should be increased as much as possible for the best productivity. To accomplish this goal, the ratio of cyclopentane to water, degree of subcooling, and the reaction time had better be increased. However, we already found in our previous study that the suitably adjusted values of each parameter resulted in better salt removal efficiency.

A continuously stirred tank reactor with mechanical stirring is generally employed for hydrate production. Stirring is an important means to obtain better mass contact between water and the gas formers. However, in this work, immiscible cyclopentane formed a two liquid-phase mixture and even an emulsion with water when stirred. A large amount of hydrate slurry with high conversion could be obtained easily in a comparatively short time by using a dispersion tool such as a homogenizer. Compared to ordinary mechanical mixing, a dispersion homogenizer would seem more effective for emulsifying cyclopentane and water. Highly dispersed cyclopentane in water forms a fine emulsion, and this should make it possible to achieve a higher conversion to hydrate crystals. This shape of reactor can increase the rate of hydrate formation, but it is expected that its salt removal efficiency will not be good, according to Fig. 3. Although post-treatment of washing mitigates the effect of inclusion or adhesion of salt ions to hydrate crystals, the amount of wash water and the details of washing (method and equipment) should be deliberated. In other experiments, we found that this type of reactor system does not promote favorable salt removal efficiency, even after washing, when compared to the results using a more typical mixing type reactor. It seems that a carefully developed unique reactor is required to accomplish rapid, large scale production of hydrate slurry. We have begun investigations on the characteristics of cyclopentane hydrate production according to the reactor type, and will present these findings in a later report.

We also investigated the salt removal efficiency of washing treatment according to the amount of washing water. After hydrate formation with 3 mol% cyclopentane at 277.15 K, the slurry was filtered, and then the collected hydrate crystals were washed using fresh water of which the amount was varied according to a specific ratio of wash water to produced water. The results presented in Fig. 4 show that
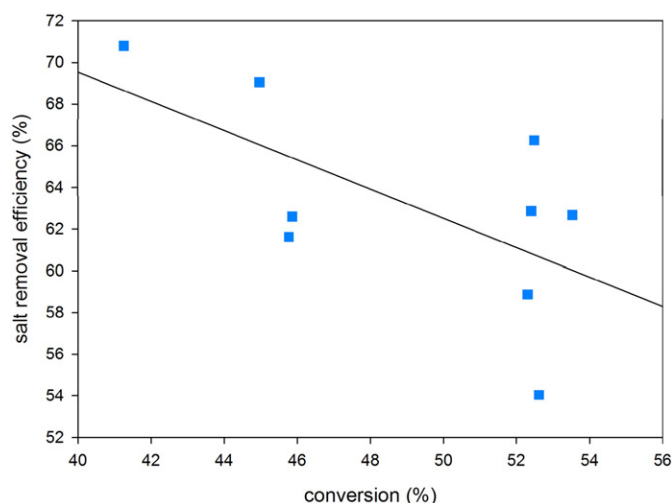

Fig. 3. Salt removal efficiency after filtering the hydrate crystals, according to the conversion of water to hydrate.
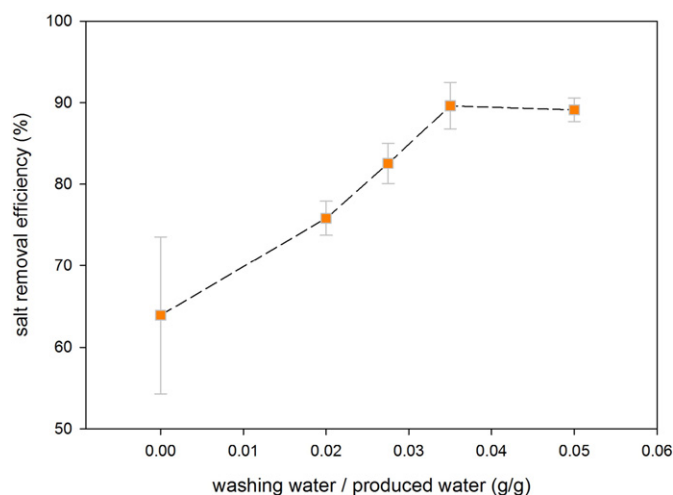

Fig. 4. Effect of the amount of washing water on salt removal after hydrate formation and filtration.

hydrate crystals are cleaned by washing with water. Moreover, the salt removal efficiency was extremely enhanced (up to 90%, 42% improved from filtering only case), compared to that of filtration only. However, the increase in efficiency increase nearly ceases when wash/produced water ratio exceeds 0.035. Thus, to maximize the efficiency of the washing treatment, an appropriately chosen amount of washing water should be applied. This optimal ratio of wash water to produced water is likely to be near 0.03. In general, the amount of wash water should be at most a few percent of the total produced water [33]. Large scale hydrate slurry production with efficient washing should be done to realize a competitive desalination process. For this purpose, equipment suitable for production should take into account the size and type of reactor and filters. In particular, a filter system should be designed that enables the continuous operation with the smallest amount of wash water possible. There are several types of filter systems that can be operated in continuous operation (e.g., rotary vacuum-drum, belt), and other self-cleaning mechanical aids. When selecting the best filtration system from among the candidates, our experimental data could provide important criteria for the decision.

Although the cyclopentane hydrate formation method removes 63% of salt ions (up to 90% with successive washing treatment step), this level of salt removal value is not acceptable for the final goal of seawater desalination, namely acquiring potable water. As reported in the recent literatures [24–28], the salt removal efficiencies reported for gas hydrate formation method ranged from 60% to 93%, depending on the kind of gas hydrate former and post-treatment condition. Therefore, another post-process to complete salt removal is required when the hydrate formation method is applied to obtain drinking water through seawater desalination. Recent trend is to combine methods as hybrid, as mentioned in the Introduction section. Lee et al. [13] carried out the simulation of a reverse osmosis desalination process coupled with a hydrate formation method as a pre-treatment step for reverse osmosis process. According to their result, the gas hydrate formation method as a pre-treatment step is acceptable for a reverse osmosis process if the salt removal efficiency of the gas hydrate process can reach 78% at least. They used energy consumption value as an important criterion for the allowance, so that the economic efficiency of the reverse osmosis desalination process would be improved further, if the energy consumption in the hydrate formation step could be reduced more. To be a competitive desalination process, total energy consumption should be maintained below 3.0 kWh/m^3 and this could be accomplished when the gas hydrate pre-treatment step is operated at 84% of salt removal (1.6 kWh/m^3). The energy consumption by gas hydrate process is reported above 1.58 kWh/m^3 {Javanmardi:2003gd}. The principal reason for energy consumption in the gas hydrate formation method is attributed to the compression need to achieve the conditions suitable for gas hydrate formation. However, liquid cyclopentane can remove this requirement so that the energy consumption is markedly diminished. Another important point is the operation temperature. Considering the seawater temperature, the most favorable operation temperature is as close as possible to room temperature. Gas hydrate formation generally requires relatively low temperature, which is another shortcoming. To overcome this disadvantage, Cha and Seol {Cha:2013dc} introduced a secondary hydrate former (CO_2 gas) so that the operation temperature could be increased to 289.15 K, although the operation pressure remained high (up to 3.0 MPa). In addition, the hydrate formation method could be another meaningful position as a pre-treatment step for RO process. As mentioned before, RO process is susceptible to the feed condition, such as the salinity and solids within water, but on the other hand, gas hydrate method is relatively robust to such condition. Rejection of salt and floating solids by gas hydrate formation at a certain level could make the RO process solid and reliable much more. Therefore, it is worthwhile to carry out the overall simulation of a desalination process using gas hydrate formation as a pre-treatment followed by reverse osmosis, considering the operation conditions in detail. Nevertheless, the gas hydrate formation process could

also be a promising method for recovery or purification of water polluted during oil and natural gas production or of industrial wastewater.

4. Conclusion

A hydrate-based desalination process involving hydrate crystal formation, filtration, and water washing steps was investigated to clarify detailed salt ion removal efficiencies in detail. A single-step hydrate formation reaction of cyclopentane and seawater without any further treatment was carried out at 277.15 K (corresponding subcooling was 2.3 K), 3 mol% cyclopentane, and atmospheric pressure. The total salinity of the seawater was 3.4%, and about 63% of the salt ions were removed by hydrate formation and filtration. The concentration of each cation and anion was analyzed in filtered water and water retrieved from the hydrate crystals, from which the removal efficiency of each salt ion was calculated. To improve removal of salt inclusions in the crystals, or salt adhered to the crystal surfaces; a wash treatment of 277.15 K freshwater was applied after filtration. This washing increased the salt removal efficiency as much as 42%, compared to the result from filtration only, and all of the cations and anions considered in this study were removed at similar levels. The relationship between the salt removal efficiency and water conversion to hydrate was also investigated. As the conversion of water to hydrate increased up to the theoretical limit, the salt removal efficiency decreased by about 15%. Accordingly, it seems that higher conversion is not good from the point of view of salt removal. However, the successive washing treatment was able to eliminate this concern so that large scale production of cyclopentane hydrate slurry using an appropriate reactor may soon be considered. The efficacy of the amount of wash water used in the washing treatment was also investigated in relation to the salt removal efficiency. The salt removal efficiency increased as much as 42% when washing was applied, compared to hydrate formation and filtration, and considering the amount of wash water. It is expected that the experimental data presented in this study will be useful as basic design parameters when the hydrate-based desalination method is embodied into a concrete process. Study on the most effective reactor design and filtration method, as well as simulation of the overall process, is currently under investigation.

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