Master's Thesis

RO PRETREATMENT USING HYDRATE BASED ICE DESALINATION PROCESS

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(Environmental Science and Engineering)

Graduate School of UNIST

2016

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A thesis
submitted to the Graduate School of UNIST
in partial fulfillment of the
requirements for the degree of
Master of Science

Sang-Woo Han

1. 19. 2016 of submission
Approved by

Advisor

Young-Nam Kwon

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This certifies that the thesis of Sang-Woo Han is approved.

1.19. 2016 of submission

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Abstract

There are a variety of methods for seawater desalination, and seawater desalination method through ice-freezing also exists. This study discusses freezing desalination as a new method to combine direct contact freezing and indirect contact freezing. It is the first method as well to generate ices by utilizing CO2 Hydrate itself as refrigerant. This study explores HBID (Hydrate Based Ice Desalination)process.In HBID process, hydrate dissociation energy is used for cooling down water temperature and finally making ice. There are three factors freezing energy of HBID system. Joule-Thomson Effect, endothermic energy of carbon dioxide emission and endothermic energy of hydrate dissociation. The endothermic energy of hydrate dissociation is most dominant proposition as the major freezing energy of HBID system among the three factors.TheHBID process rejection efficiency increased as the NaClconcentration of feed water increased. However, when the NaCl concentration of feed water decreased the produced water quantitydecreased. In case of 10, 20 and 50ppm humic acid solution treatment, the rejection is above 70%. .HBID process is not significantly influenced by impurities such as the concentration of ion or organic matters,It has huge advantage to be utilized as the preconditioning process of membrane separation when treating high salinity waste water such as RO brineand Shale gas drawback water. In the case of cation analysis every cation rejection is higer than 50%.It also have more than 50% of performance in treatment efficiency of B^{3+} with the highest difficulties in treatment so they can be easily utilized in the front side of RO. Therefore, the development of HBID technology can be utilized alone in the process of seawater desalination or waste water treatment to contribute to generating pure water and decreasing the volume of waste water such as RO brine.

Contents

1.Introduction

1.1. Research background

1.1.1. Freezing desalination

When sea water freezing the pure H_2O molecules make hydrogen bonds and other impurities are excluded. That phenomenon is used in freezing method in desalination technology. First, make large quantity of ice from sea water. And,seperate pure ice with concentrated brine. We can get clean water by melting iceafter seperating. There are two different way in freezing method. First, direct contact freezing and another is indirect contact freezing. At direct contact freezing, sea water and refrigerants are mixed in the reactor. And, when refrigerants evaporating sea water temperature cooling down and finally freezing. In indirect contact freezing, sea water temperature cooled down by heat exchanger. There is a loss of heat energy because of using heat exchanger. Characteristics of an indirect contact freezing is similar to direct contact freezing.However, the heat exchange efficiency inferior to freezing is done directly through the walls of the condenser to which the refrigerant is cooled by evaporation.Figure1 shows process of freezing desalination. Figure2 and figure3 shows direct contact freezing and indirect contact freezing.

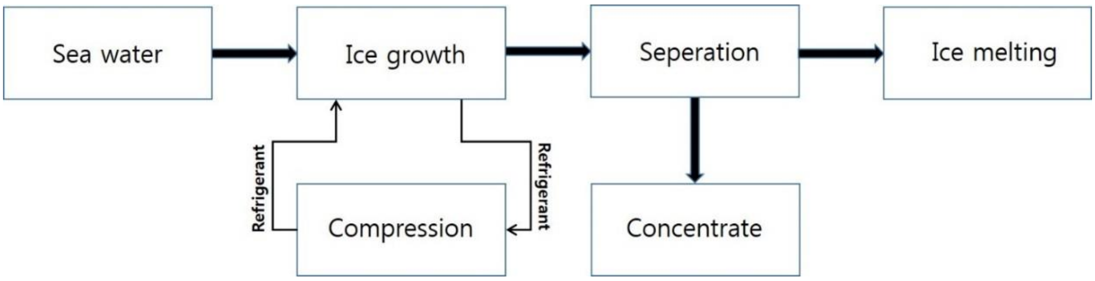


Figure 1. Process of freezing desalination

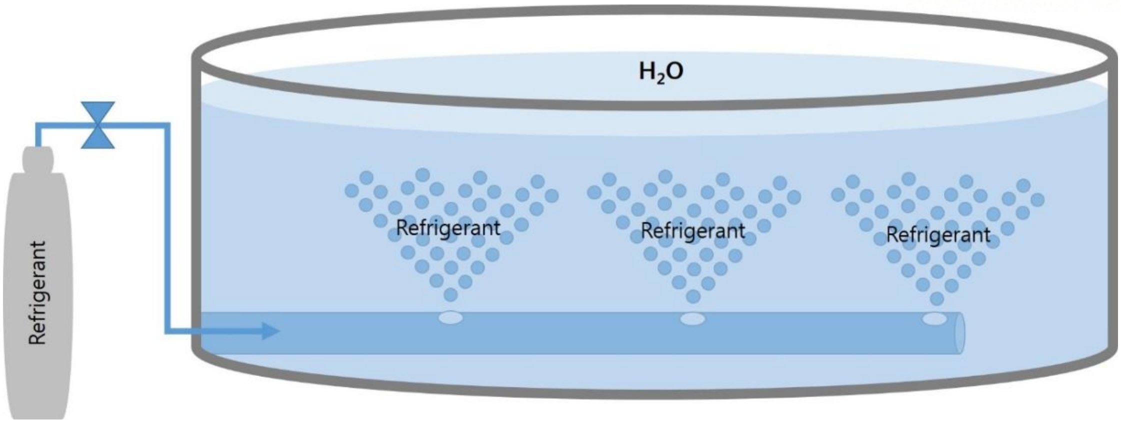


Figure 2. Direct contact freezing

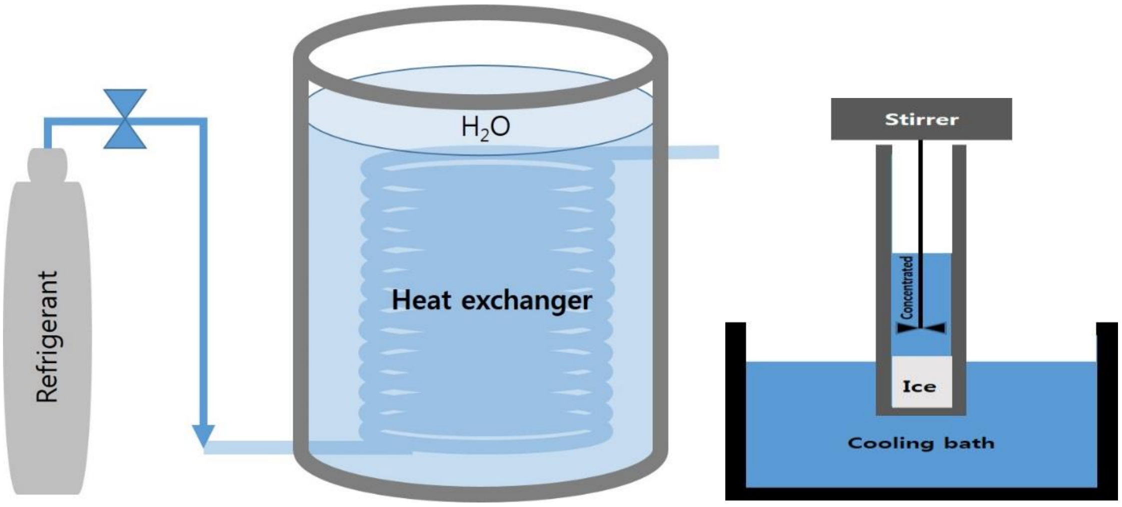


Figure 3. Indirect contact freezing

1.1.2.Hydrate and Hydrate desalination

Hydrate consists of H_2O molecules and guest molecules. Guest molecules are trapped inside cage of H_2O molecules. Hydrate is resembled with ice. But, the hydrate forming condition is different with ice. Hydrate can be formed in low temperature with high pressure. The forming condition of temperature and pressure is changing. And it is affected by guest molecules. When forming hydrate the pure H_2O molecules make hydrogen bonds and only guest gas are trapped in the cage. Then other impurities are excluded. This phenomenon is similar with ice forming. This property of hydrate is used in hydrate desalination. Hydrate desalination process consists of formation, separation and melting.

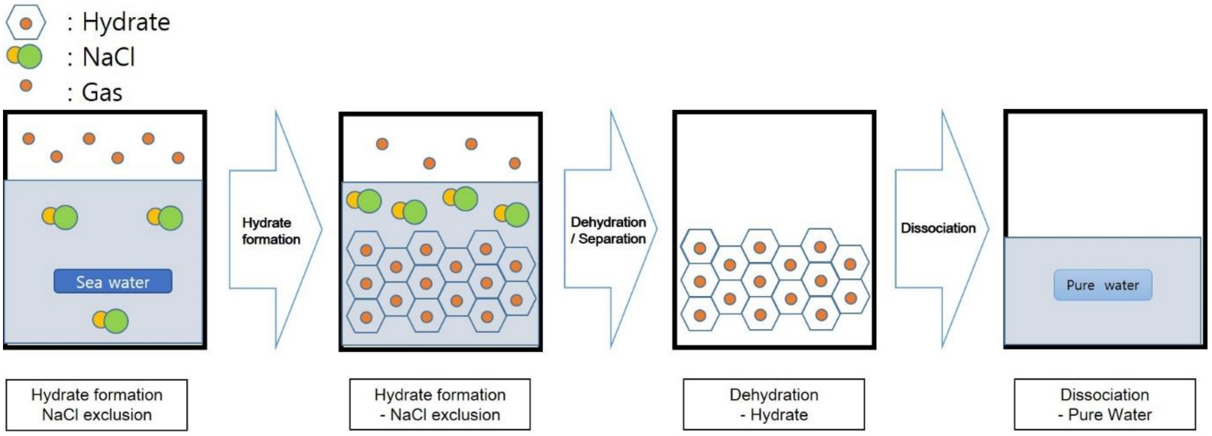


Figure 4. Process of hydrate desalination

1.1.3. HBID process

HBID (Hydrate Based Ice Desalination) process is one kind of freezing methods. The principle of HBID is the ice formation only consists of water molecules, and impurities are excluded. In HBID process, hydrate dissociation energy is used for cooling down water temperature. It means hydrate is used for refrigerant in this process.All steps of HBID process isdescribed as following. Firstly, In order to generate hydrate, the making reactor condition low temperature and high pressure. Because hydrate is generated at high pressure and low temperature. Secondly, the pressure in the reactor is reduced to dissociate hydrate. Finally, hydrate melts, and ice freezes.Figure 5 shows the process of HBID.

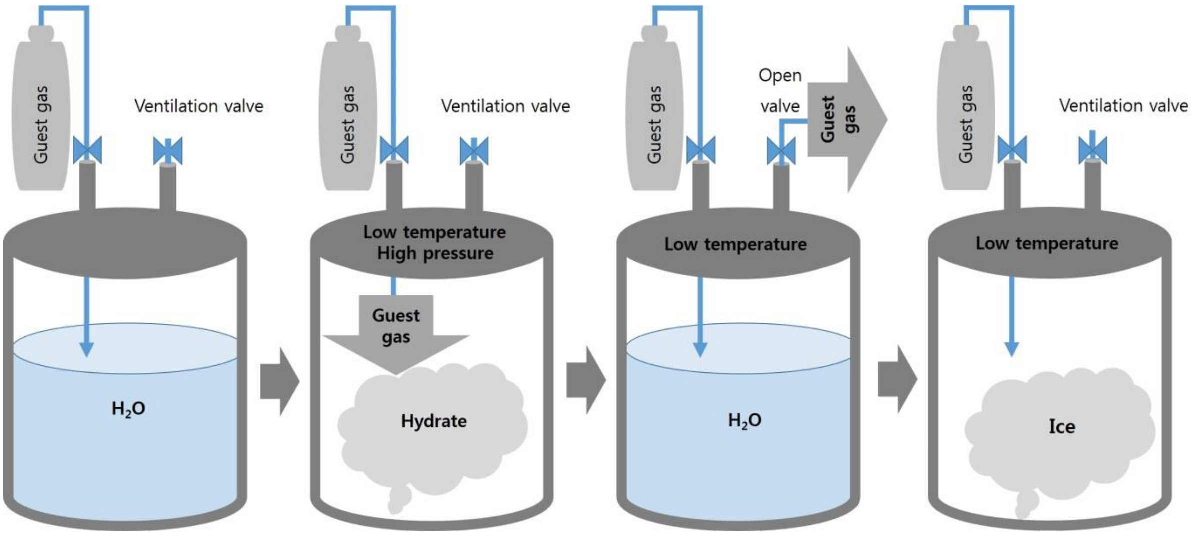


Figure 5. Process of HBID

Table 1 shows comparisonof ice desalination, hydrate desalination and HBID.Advantage of ice desalination isit usually needs no energy for forming ice because this process dissolves natural ice. However,ice desalination process needs huge area. Moreover, this method takes long time for forming ice, which makes itdifficult to be used for desalination plants. On contrary, hydrate desalination takes short time for whole process. The big advantage of hydrate desalination is it can be performed at over 0℃. However, hydrate desalination also has some disadvantages such as separating solid-liquid should be performed in high pressure, and it used harmful guest. Whereas, HBID process also can be performed in over 0℃, and CO_2 is used for guest in HBID process. Therefore,HBID has advantage in carbon dioxide reuse. But this method faces a challenge of losing of energy to change phases during forming hydrate, dissociating hydrate and forming ice.

Table 1. Comparing ice desalination, hydrate desalination and HBID

	Ice desalination	**Hydrate desalination**	**HBID**
Freezing temperature	Under -1.8℃	Over 0℃	Over 0℃
Energy of changing phase change	333KJ/kg	500.13KJ/kg	500.13KJ/kg
Speed of formation	Slow	Fast	Fast
Condition of formation	Low temperature	Low temperature and High pressure	Low temperature and High pressure
Composition	Water molecules	Water molecules Guest gas	Water molecules Guest gas
Kind of guest	-	CO_2, CH_4, C_5H_{10} and so on	CO_2
Process of phase changing	Water→Ice→Water	Water→Hydrate→Water	Water→Hydrate→Water→Ice→Water
Principle of process	Solid-Liquid separation	Solid-Liquid separation in high pressure	Solid-Liquid Separation

1.1.4. History of freezing desalination

In order to solve the problem of water shortage around the world, the development of seawater desalination to convert seawater that occupies the majority of water in the earth into drinking water or water available for many purposes has been actively conducted. From the early 1960s to the early 1970s, evaporation method was mainly used. Although it was commercially used, its price is still expensive[1]. Sea desalination method, which is commercialized and generalized at present, includes Distillation and RO. RO technology has raised occupation rate through rapid development in recent technology[2]. According to the development of technology, the cost of desalination technology gradually decreases and the capacity of seawater desalination gradually increases as well [2].

Besides, the development of Freezing technology is also actively conducted, which is not commonly utilized yet but has long history[3]. Freezing refers to the method to eliminate ion in the target water by utilizing the principle that impurities and ions are excluded from pure water molecules when generating ice. Starting from the report by Thomas Bartholinus, a Danish physician in the 1600s, the studies on this method has been undertaken for half a century[4].Utilizing this technique for generating clean water by ice has been currently funded by the Chinese government on large-scale laboratories[5]. There are also some examples of seawater desalination by freezing desalination in plant of Eliat in Israel, Florida in the United States, Wrights-ville beach in North Carolina in the United States, and so on [6]. Since ice as a major factor of freezing desalination has 333kj/kg heat of fusion which approximately corresponds with 1/7 of heat of evaporation (2500kj/kg), it uses less energy compared to distillation method [7]. In addition, freezing desalination is costly advantageous in terms of corrosion potential [8]. As the ways of freezing desalination, direct contact freezing and vacuum freezing as indirect contact freezing are investigated, and more diverse forms are also investigated including generating hydrate aside from ice[3]. More recently studies conducts freezing desalination as varying the seed ice conditions in raw water with various ion concentration and various temperature, and the corresponding rejections are measured. The results reveal that rejection is higher when the slower process of freezing in high temperature is performed, the concentration of initial raw water is lower, and seed ice exists. The experiments on freezing desalination in similar forms are still in progress[9, 10]. When seawater is frozen, the phenomenon that ions are confined within ice in the form of brine pocket occurs due to the uncompleted exclusion. Since such phenomenon operates as a factor to impede rejection, a lot of methods to eliminate the confined ions within ice are performed, for instance, using gravity, centrifuge, sweating, etc: a large-scale laboratory was established in Bohai area in China and an experiment to eliminate brine pocket within ice for seawater desalination by utilizing gravity and natural temperature change [5]. Another research group found that rejection becomes higher as the pace of sweating is slower and the loss of ice becomes higher in sweating process as the concentration of raw water is higher by varying the pace of sweating and the concentration of raw water prior to ice freezing[11]. L. xie conducted centrifugal desalination, finding that brine is more excluded from ice as the speed of centrifugal dehydrator is faster and the circulation time is longer when using a centrifugal dehydrator[12].Freezing method is also utilized in the fields of treating waste water in pulp factories, eliminating heavy metal substances with toxicity, treating RO concentration water aside from changing seawater into drinking water [13-15]. In addition to purify water, more studies on freezing method are actively undertaken in the field of concentration[16-18], because it is particularly advantageous in concentrating beverage for fresh condition, such as juice[16, 19].

On the other hand, the processing of seawater desalination by generating hydrate has been developed as a way of another freezing method. As the development technology of underground methane hydrate buried in the earth is expanded, the studies on seawater desalination by utilizing hydrate gradually become vigorous. Hydrate refers to an ice-like form of solid gas surrounded by water molecules in environment of high pressure and low temperature, for instance, deep sea. The molecule confined within water molecules is called as guest, which is classified as a variety of types including methane, carbon dioxide, cyclopentane, etc. The conditions of melting hydrate vary depending on the types of guest. Like ice, ions and impurities are excluded when hydrate is formed, thus, the studies on seawater desalination utilizing freezing method have been constantly conducted.[3] Examining the recent research trend, the studies on desalination by utilizing not only methane gas, a representative guest of generating hydrate, but also cyclopentane as guest are highly in progress. Also, the studies on desalination by utilizing CO_2 are conducted a lot. cyclopentane has the advantage of generating hydrate with higher temperature and lower pressure than utilizing guests such as methane or CO_2, which leads to more active studies nowadays. .[20-22] However, the toxicity of cyclopentane provides a limitation of not allowing people to drink safe water when included in the drinking water processing. Therefore, the processing of usingcyclopentane should be added by heating up the material over 50 degrees Celsius, which makes additional costs.[20] In comparison, CO_2 is a safe gas without toxicity, given that it is utilized in producing carbonated drink. Utilizing CO_2 gas is also valuable in terms of recycling carbon dioxide because it is regarded as a major factor of recent global warming.

In the process of hydrate desalination, solid-liquid separation is required, same as generating ice by using freezing method. However, the separation should be performed without the dissociation of hydrate structure so the solid-liquid separation is somewhat difficult than the desalination processing utilizing ice. For instance, the separation without hydrate dissociation can be performed only when the temperature and pressure is simultaneously maintained. From an experiment which utilized cyclopentane as guest to generate hydrate and then eliminated concentrated water by vacuum filtration to perform solid-liquid separation, a report found that the performance of centrifuge is superior among the differences of rejection when comparing the methods of washing, centrifuge, sweating. [21] Like the processing of water treatment by generating ice, the processing of water treatment by generating hydrate has led a variety of studies, such as treating waste water in pulp factories, treating draw back water of shale gas, concentrating juice, desalinating seawater, etc[22-25].

1.1.5. RO process

As the demand for water has increased throughout the world due to the population growth and rapid industrialization, the scale of water market tends to grow. Therefore, the plans for water production and water industry are required, and seawater desalination emerges as a technology to solve the related problems. It is an economic technology to efficiently utilize seawater which occupies 98% of water in the earth, which refers to a water treatment processing to remove solution materials including salt to produce pure water for drinking and living, and industrial water.

There are two basic techniques of seawater desalination: In the evaporation method, seawater is heated by heat source and the produced steam is condensed to produce plain water. In the reverse osmosis method, seawater is passed through semipermeable membrane by reverse osmosis phenomenon to produce plain water. Since the evaporation method has a disadvantage of consuming much energy when heated, the reverse osmosis method which requires less energy than the evaporation method is globally used in these days.

The osmosis phenomenon refers to a phenomenon in which the amount of high-concentrated solution increases over time when the same amount of low-concentrated solution (plain water) and high-concentrated solution is placed with an in-between semipermeable membrane. The phenomenon proceeds till the pressure difference between the high-concentrated solution and low-concentrated solution is in equilibrium to last. The pressure in this circumstance is called osmotic pressure. On the contrary to this, the solvent of the high-concentrated solution flows backward to the low-concentrated solution when the pressure over the osmotic pressure is exercised to the high-concentrated solution, which is called reverse osmosis. The exercised pressure is called reverse osmotic pressure.

The reverse osmosis method is the membrane separation process to separate ions and solutes with less than 10Å molecule size. It is successfully industrialized in seawater desalination and waste water treatment in the 1970s. With the materials of asymmetric cellulose acetate membrane in which separation layer is placed over bearing layer or polyamide, the composite membrane is recently developed to eliminate 99% of dissolved salt. In the case of bearing membrane, polysulfone is mainly used due to its higher mechanical strength and chemical resistance property. Celluloseacetate or crosslinked polyether is mainly used in the case of separation layer. Since the hole-diameter of such reverse osmosis membrane is approximately 10Å with rare micropores, it can be regarded as nonporous membrane. The material transmission is conducted through the intervals of micelles constructed by organic macromolecules.

In the reverse osmosis processing, the pre-treatment process to eliminate the substances that remove the substances to cause membrane pollution in advance is highly important. The reason why membrane pollution is inevitable in the reverse osmosis processing is that seawater contains a lot of floating materials, micro particles, salt, and the excluded substances sink and are attached to lead to the deterioration of transmittance and the life-shortening of separation membrane. Lots of problems, such as the decrease of productivity and the increase of operation cost, can be also caused due to the rise of operation pressure, the decline of processing flux, and the degeneration of processing water quality.

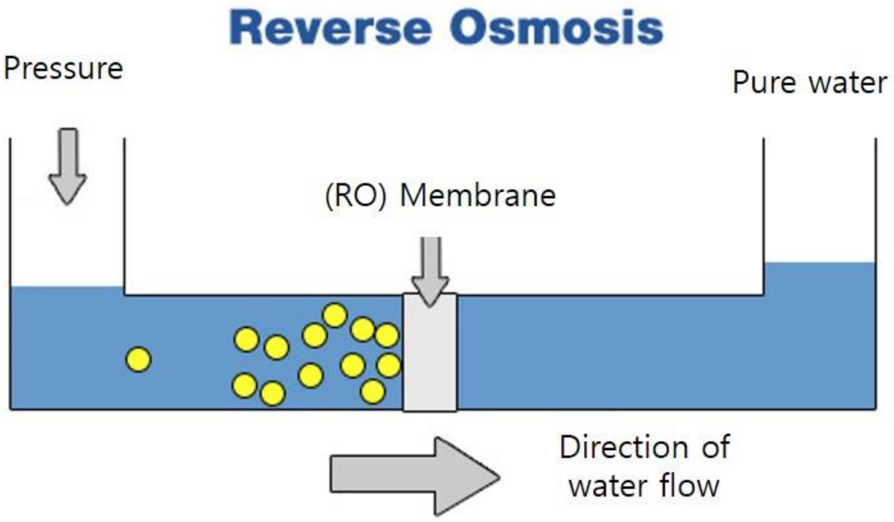


Figure 6. Reverse Osmosis (RO) desalination

1.1.6. Comparing advantage and disadvantage of desalination processes

Table 2. Comparing advantage and disadvantage of desalination processes

Freezing process	**RO process**
-It needs the transfer of little energy. -It needs almost no pretreatment. -It has minimal corrosion. -It is relatively insensitive about feedwater. -It is less commercially developed. -Final produced water quality is not good.	-The energy requirements are low. -Space requirements are less than with other desalination process, -Due to their modular design, maintenance is Easy. -It has high pressure requirement. -It has membrane fouling. -The RO process usually cannot be applied Without pretreatment.
Distillation process	**HBID process**
-There are many big commercial plants and previous study about distillation. -Final produced water purity is good. -It needs high energy consumption. -There is scaling.	-It needs only pressure in winter climate. -It needs no high pressure condition at liquid solid separation. -It has benefit in aspect of CO_2 reuse. -It needs almost no pretreatment. -It has minimal corrosion. -It is relatively insensitive about feedwater. -It is less commercially developed. -Final produced water quality is not good.

1.2. Objective of this study

This study aims to produce clean water by HBID and RO hybrid processand observe the characteristics of HBID process and performance of HBID process. HBID process is new kinds of freezing desalination. This study used guestCO_2 gas which can help HBID overcome disadvantage of hydrate desalination separation step in condition of high pressure or using harmful guest gas.

2. MATERIALS AND METHODS

2.1. Apparatus

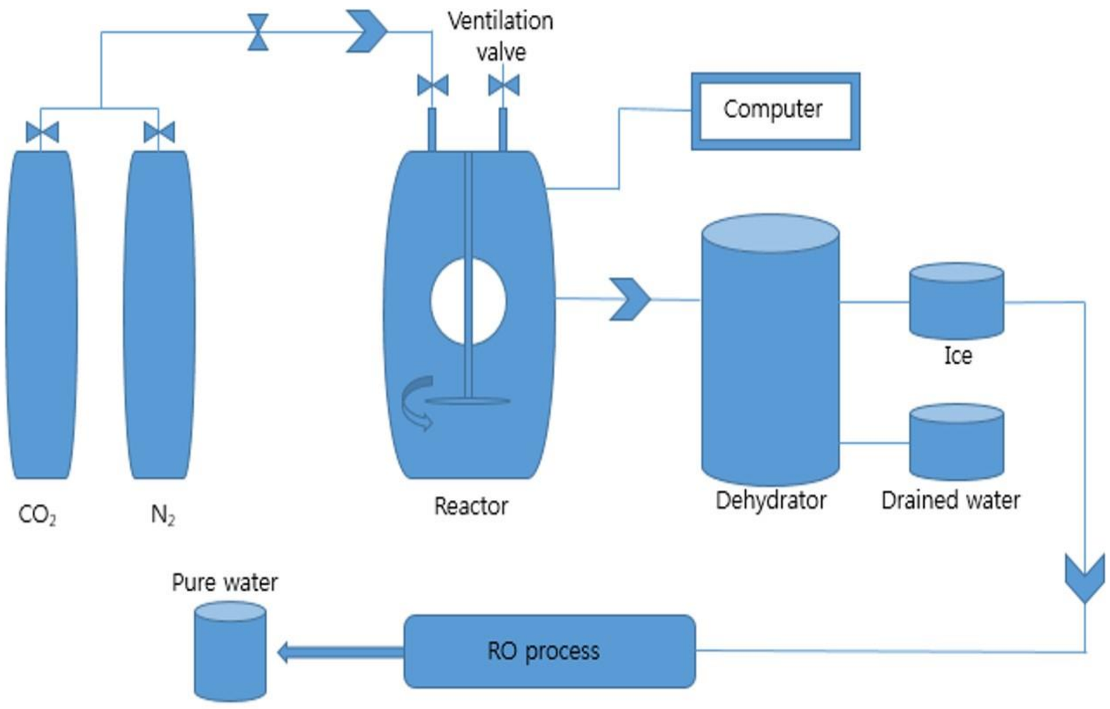


Figure 7. Apparatus of the experiment

The apparatus used to perform HBID is constructed in the following form presented in Fig7. It is largely classified into the part to provide pressure by utilizing CO2, the reactor part to generate hydrate and ice, the centrifuge dehydrator part to separate the generated ice from concentration water, the part connected with computer and program that records the temperature and pressure in real-time.

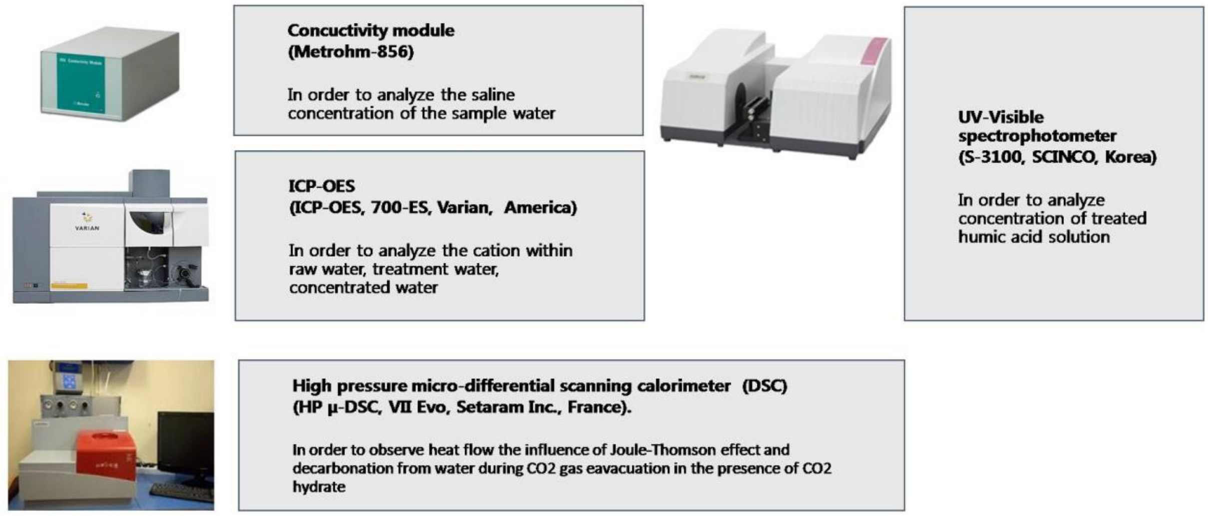
The CO_2 gas-providing part is linked to a valve and CO_2 gas cylinder to preciously provide gas with consistent pressure. The reactor is constructed in form of cylinder (100mm in diameter, 150mm in height), and its effective capacity is 1.1L. Inside the reactor, the temperature sensor (SD-560 RS485, omega, Stamford, America) and pressure sensor (General industrial pressure transmitter A-10, WIKA, Klingenberg ,Germany) are equipped in order to measure the internal temperature and pressure. An impeller is also equipped for stirring in order to cause proper hydrate reaction within the reactor. The window utilizing two polycarbonates as materials is constructed in order to allow close observation on the reaction of generating hydrate and ice. The circulator to maintain the regular temperature of the reactor is (RW-1025G, Jeio-tech, Daejeon, Korea). The capacity of the circulator is 20L. The solution injected into the circulator for freezing-prevention is made from DI and ethylene glycol in the ratio of 2:1. A computer is linked in order to check the temperature and pressure inside the reactor in real-time, and a program is set to record the real-time temperature and pressure. The part of centrifugal dehydrator has specialized-design for 1600rpm and 800g as maximum processing weight per a session

2.2. Materials

The solutions to be treated by HBID system are largely classified into the four categories: seawater, nacl solution, humic acid solution, humic acid + nacl + water solution. The seawater sampled from Ulsan coastal water (Ilsanji beach, latitude: 12904308750, longitude:35.4957346) and filtered once by glass fiber fiter. The conductivity and cation analysis is presented in the following table. Nacl solution is prepared as 0.05, 3.5, 7.0wt%. Humic acid solution is prepared as 10, 20, 50ppm concentration. Nacl 0.05wt% + humic acid 50ppm, nacl 3.5wt% + humic acid 50ppm, nacl 7.0wt% + humic acid 50ppm solution is used as Humic acid + nacl solution. The product by Bioshop is used as Nacl over 99.5% purity level. The product by Alfa aesar is used as Humic acid sodium salt 50~60%. CO2 gas and N2 gas made by Korea SEM is used with 99.999% purity level.

2.3. Analysis

The conductivity of the final treatment water and concentration water separated by centrifugal dehydrator is analyzed through ConductivityModule(Metrohm-856, Metrohm,Herisau, Switzerland), and the salinity is explored. The cation within raw water, treatment water, concentration water is analyzed through ICP-OES(700-ES, Varian, America). Regarding the concentration of treated Humic acid, rejection is measured to assess the optical density through UV-Visible spectrophotometer(S-3100, SCINCO, Seoul, Korea) in 254 nm wavelength.



Concuctivity module
(Metrohm-856)

In order to analyze the saline concentration of the sample water

ICP-OES
(ICP-OES, 700-ES, Varian, America)

In order to analyze the cation within raw water, treatment water, concentrated water

UV-Visible spectrophotometer
(S-3100, SCINCO, Korea)

In order to analyze concentration of treated humic acid solution

High pressure micro-differential scanning calorimeter (DSC)
(HP µ-DSC, VII Evo, Setaram Inc., France).

In order to observe heat flow the influence of Joule-Thomson effect and decarbonation from water during CO2 gas eavacuation in the presence of CO2 hydrate

Figure8. Analyzing equipments

In order to examine the influence of Joule–Thomson effect and decarbonation from water during CO_2 gas evacuation in the presence of CO_2 hydrates, the heat flow was monitored using a high pressure micro-differential scanning calorimeter (HP µ-DSC, VII Evo, Setaram Inc., France). The HP µ-DSC system was designed to perform up to 40 MPa and included reference and sample cells, which were surrounded by high-sensitivity Peltier elements. Both reference and sample cells were made of Hastelloy C276 to prevent corrosion and contamination and had an internal volume of 0.5 cm3. In this study, approximately 0.02 g of water was charged into the sample cell.

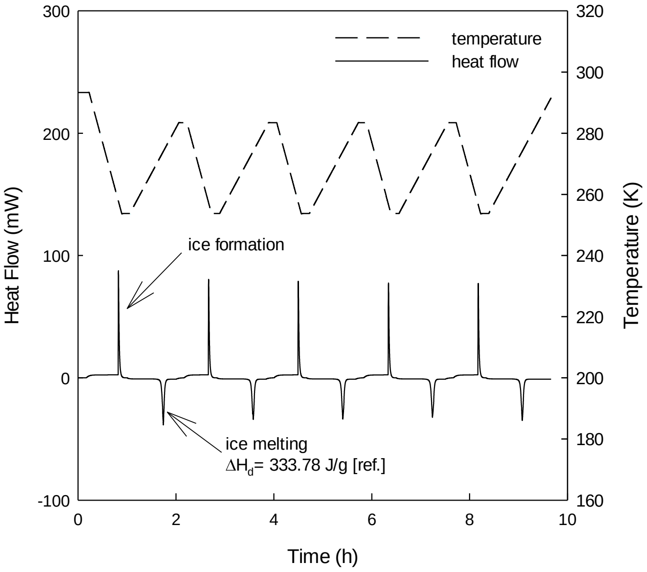


Figure 9. Changes in heat flow and temperature during cooling–heating cycles for estimation of the amount of water.

As shown in Figure 9, a multi-cycle mode of cooling-heating was repeated five times to obtain the endothermic thermogram from ice melting. The accurate amount of charged water could be calculated back from these integrated areas of the endothermic thermogram, because the dissociation heat of ice melting was well known in the literature. After the amount of water was accurately estimated, both cells were flushed three times with the CO_2 gas to eliminate any residual air. In order to monitor the heat flow changes attributed to Joule–Thomson effect or decarbonation from water, the heat flow changes from CO_2 gas injection/evacuation with and without CO_2 hydrates were measured. A more detailed description of the experimental apparatus and procedure has been provided in the previous studies.

2.4 Each step of HBID process

In order to generate CO_2 Hydrate, the temperature in the reactor is set as 0.2℃ by utilizing the circulator. The stirring within the reactor is set for 600rpm. When the temperature in the reactor is fixed as 0.2 degree, carbon dioxide is injected with constant pace of 10, 15, 20, 25, 30 bar. As pressure is injected, Joule-Thomson Effect raises the temperature. In addition, the injection of CO_2 gas makes CO_2 gas dissolve in water in high-pressure circumstance, which leads to heating reaction to raise the temperature in the reactor. Also, when the condition of generating CO_2 hydrate is satisfied, hydrate is generated to increase the internal temperature by heating reaction. The change of temperature according to each pressure is identified. Like CO_2 gas experiment, the gas is replaced by N2 to perform the experiment in the same condition of 10, 15, 20, 25, 30 bar. After advancing the reaction for 4 hours, the pressure is reduced to generate ice. When opening ventilation valve, the pressure as well as temperature become lower at the same time due to Joule-Thomson Effect. Also, CO_2 dissolved in water comes out of water with bubble as the pressure in the reactor decreases. Since such reaction is endothermic reaction, it decreases the temperature in the reactor. Moreover, when the pressure decreases under the condition of maintaining hydrate, CO_2 hydrate inside the reactor that generated CO_2 hydrate becomes to dissolve. Since the dissociation of hydrate is endothermic reaction, these three endothermic reactions are combined to make the temperature drop below the freezing point of seawater is -1.8℃. [26], which transforms raw water in the reactor to ice. When ice is formed, exothermic reaction occurs. The endothermic reaction mentioned above makes the temperature in the reactor drop to a certain level, and the temperature becomes higher by the exothermic reaction as ice is formed. When pressure is entirely reduced, the processing of eliminating ions existing within ice is undertaken by put the formed ice into the centrifugal dehydrator. At this point, the pace of the centrifugal dehydrator is set for 1600rpm, and the time is set for 5minutes. When measuring the cation concentration, mass, conductivity of the dehydrated solution, the 5-minute dehydrating process is performed. Taking the dehydrated ice by the centrifugal dehydrator and melting the ice in room temperature leads to clean water from final treatment. During the dehydrating processing, cation, PH, conductance in dehydrated water and final treatment water is analyzed and recorded through ICP-OES, PH meter, conductivity respectively.

2.5 Each step of RO performance test

The SHF membrane produced by Toray Chemical Korea was tested in RO mode using a test cell of which a similar schematic diagram has been elsewhere described [27]. Two 19.635 cm^2 effective area membrane coupons with 1 L/min flow rates were used for the RO performance test. Prior to the utilization of separation membrane, the separation membrane is soaked more than over two days for fully hydration. The feed solution was ice-desalinated seawater and raw seawater to investigate effect of HBID at room temperature. The operating pressure for stabilization was set to 225 psi during 6 h, and then measured initial water permeation and salt rejection. The water flux was calculated using as described in Eq. (1). The salt rejection is measured by ICP-OES. Then, the salt rejection, R (%), for each feed solution was calculated using as described in Eq. (2).

$$\boldsymbol{J_w = \frac{\Delta W}{\Delta t \times A \times \rho}} \tag{1}$$

where, ΔW (g) is the permeation water over a predetermined time Δt (h), A (m^2) is the effective area of FO membrane, and ρ (g/L) is the density of the feed solution.

$$\boldsymbol{R = \left(1 - \frac{C_p}{C_f}\right) \times 100}(\%) \tag{2}$$

where, C_p and C_f are concentration of permeate and feed solutions, respectively.

3. Results and discussion

3.1.Accompanying phenomenon with HBID process

3.1.1. Temperature changes with injecting gas

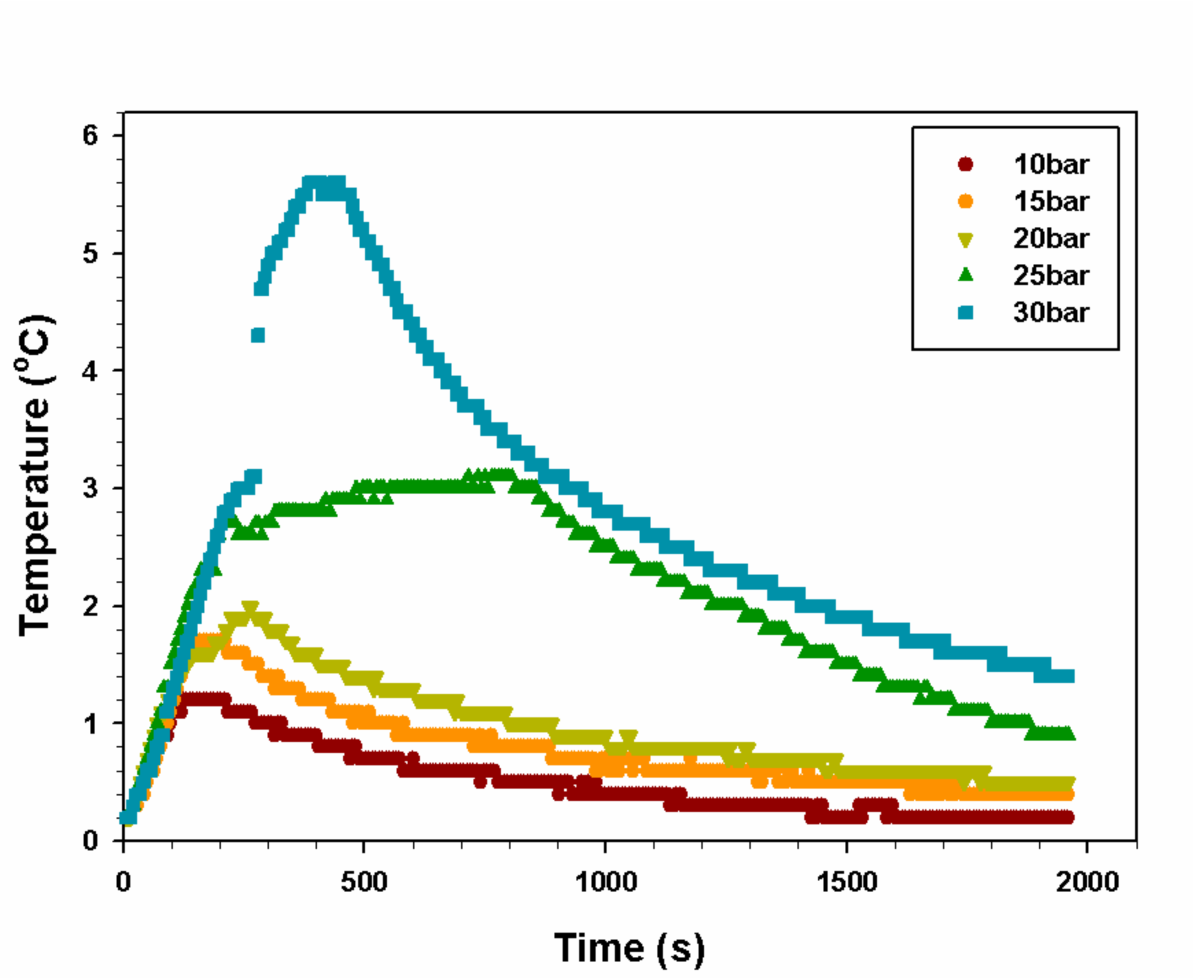


Figure 10. Increase of CO_2 temperature upon time

Table 3. Temperature changing of CO_2 injection

	10bar	15 bar	20 bar	25 bar	30 bar
Starting temperature	0.2	0.2	0.2	0.2	0.2
Highest value	1.2	1.7	2.0	3.1	5.6
Temperature changing gap	1.0	1.5	1.8	2.9	5.4

Since HBID process utilizes hydrate as refrigerant, generating hydrate is essential. In order to generate hydrate, the condition of low temperature and high pressure should be satisfied. Regarding the heating reaction of generating hydrate, the following experiment is conducted to observe the temperature change in the HBID process. As explained above, the condition of low temperature and high pressure is necessary, the reactor is stabilized in 0.2 ℃, and CO_2 gas is injected in 10, 15, 20, 25, 30 bar to meet the condition of high pressure. Then, the accompanying temperature change is identified. When providing CO_2 in 10 bar, 1.0℃ temperature raises, with the highest temperature of 1.2 ℃. After reaching the highest point as 1.2℃, the temperature lowers toward 0.2℃, which is the initial temperature, because the reactor becomes cooling due to the circulator fixed in 0.2℃. When providing CO_2 in 15 and 20 bar, the highest point of the temperature increase is 1.7℃ and 2.0℃ respectively. It is found that the temperature rises from 1.5℃ and 1.8℃ as initial temperature and becomes lower due to the circulator cooling. The temperature increase in 10, 15, 20 bar leads to the temperature-increase effect due to the Joule-Thomson effect and CO_2 makes heating reaction by generating HCo^{3-} as dissolving into water, which leads to the observation of the temperature increase.

When providing CO_2 in 25 and 30 bar, the highest point of the temperature increase reaches 3.1℃ and 5.6℃ respectively. The increase range is 2.9℃ and 5.6℃ which leads to the observation of higher increase range than injecting CO_2 in 10, 15, 20 bar. In addition, the rapid heating reaction of generating hydrate makes the slope of the temperature increase. After the temperature raises, the temperature does not easily drop in 25 and 30 bar in which hydrate is generated, and it is found that the circumstance of high temperature is maintained longer. In 25 and 30 bars, the temperature increase effect due to the adiabatic compression processing and the heating reaction as CO_2 dissolves into water and hydrate forming endothermic reaction. Since the temperature rises due to the heating reaction accompanying the creation of hydrate, higher temperature increase can be found compared to the CO_2 provision in 10, 15, and 20 bars. Then, the phenomenon of the temperature decrease occurs because of cooling as well. It is confirmed that 25 and 30 bar is a hydrate-generating condition [28], while the CO_2 hydrate forming is not found due to the lack of driving force for generating CO_2 hydrate in 10, 15and 20 bars.

The increase of temperature due to physical and chemical reaction is confirmed when injecting CO_2. Among these effects of the temperature increase in the reactor, an experiment utilizing N_2 instead of CO_2 gas is conducted to compare the size of the effects from the increasing internal pressure due to the CO_2 injection and the effects from the heating reaction due to the dissolution of CO_2 into water. N_2 gas that has significantly lower reactivity than CO_2 is utilized in the experiment in 10, 15, 20, 25, and 30 bars, the identical injection pressure of CO_2. Since providing N_2 gas allows an observer to check the size of the temperature increase due to the increasing pressure in the reactor, it can be compared to the case of providing CO_2 in 10, 15, and 20 bars. The contribution of the temperature increase effect by the heating reaction from the CO_2 dissolution into water can be identified compared to Joule-Thompson effect.

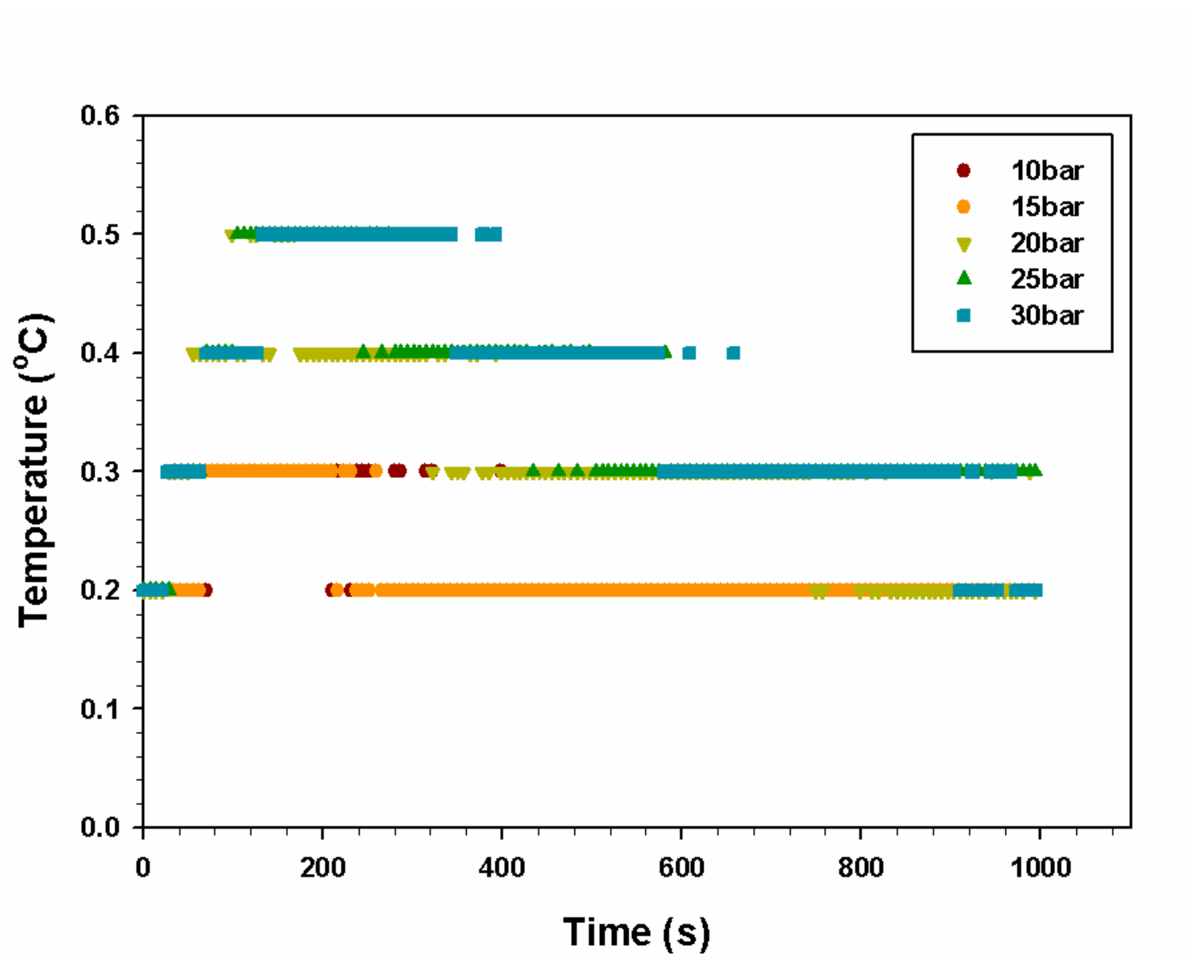


Figure 11. Increase of N_2 temperature upon time

Table 4. Temperature changing of N_2 injection

	10bar	15 bar	20 bar	25 bar	30 bar
Starting temperature	0.2	0.2	0.2	0.2	0.2
Higest value	0.3	0.3	0.5	0.5	0.5
Temperature changing gap	0.1	0.1	0.3	0.3	0.3

As explained above, the experiment is conducted to confirm which factor gives dominant effects on the temperature increase of the reactor between Joule-Thompson effect and the CO_2 dissolution reaction into water after checking the temperature change in 10, 15, 20 bar compared to the case of injecting CO_2 by utilizing N_2 gas which has lower solubility. In Figure 11 presents the temperature increase data of injecting N_2 gas in 10, 15, 20, 25, 30 bar like the CO_2 experiment. The results reveal that the increasing pressure causes the increasing temperature, and then cooling phenomenon causes the temperature decrease. In the starting temperature, 10, 15, 20, 25, 30 bar maintains 0.3, 0.3, 0.5, 0.5, 0.5℃ at its highest temperature. The range of the temperature increase is 0.1, 0.1, 0.3, 0.3, 0.3℃ which increases a little as the pressure increases. When injecting CO_2 in 10, 15, 20 bar, the temperature of the highest point is 1.2, 1.7, 2.0℃ respectively. The range of the temperature increase is 1.0, 1.5, 1.8℃ respectively, differing more than 6 times. As a result, it was confirmed that the temperature increase is much higher when injecting CO_2 than N_2. Therefore, the temperature increase by Joule-Thompson Effect has much smaller energy than the temperature increase effect by the heating reaction of the CO_2 dissolution when comparing N_2 and CO_2 in the pressure condition of 10, 15, 20 bar.

3.1.2. Temperature changes with ventilation

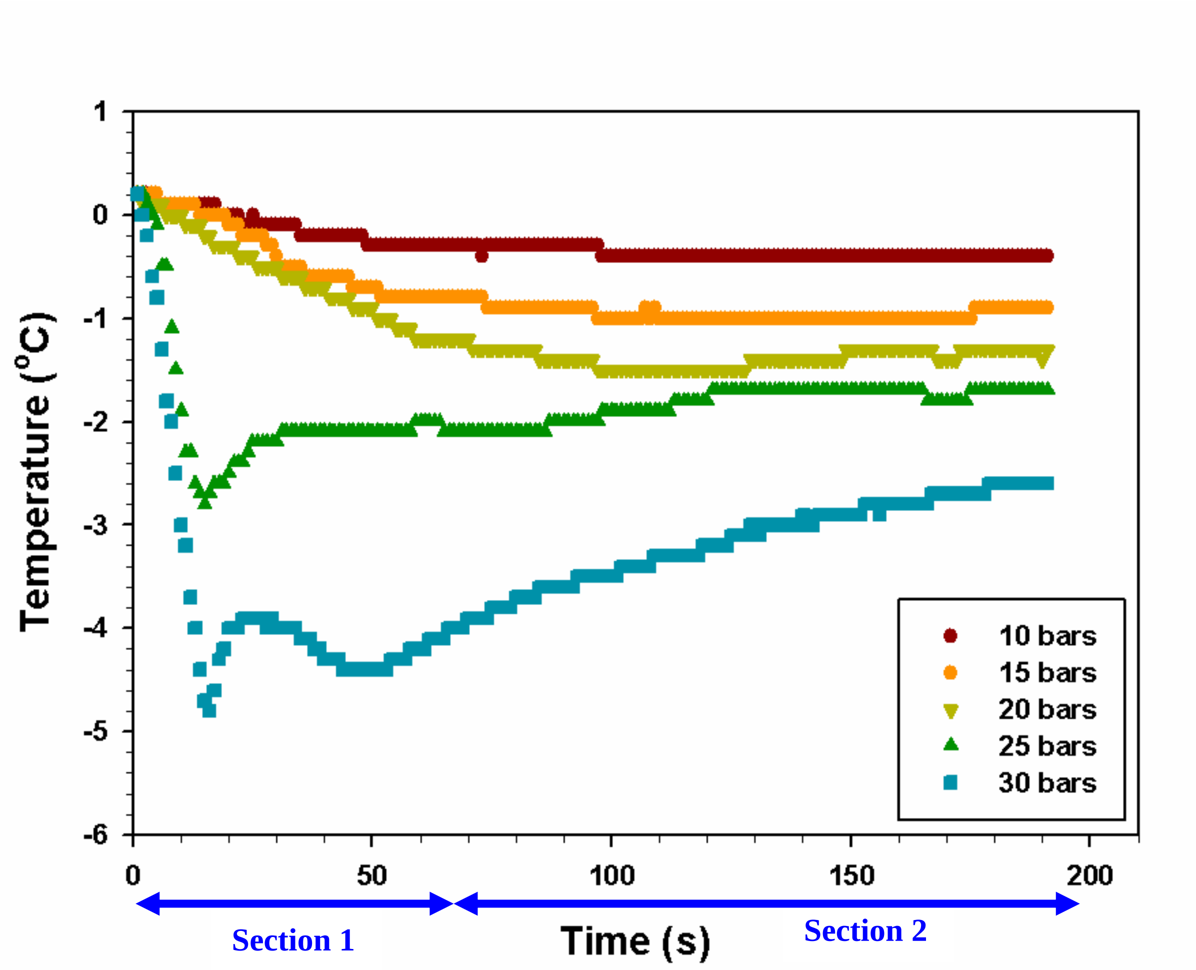


Figure 12. Decrease of CO_2temperature upon time

Table 5. Temperature changing of CO_2 ventilation

	10bar	15 bar	20 bar	25 bar	30 bar
Starting temperature	0.2	0.2	0.2	0.2	0.2
Lowest value	-0.4	-1.0	-1.8	-2.8	-4.4
Temperature changing gap	0.6	1.2	2.0	3.0	4.6

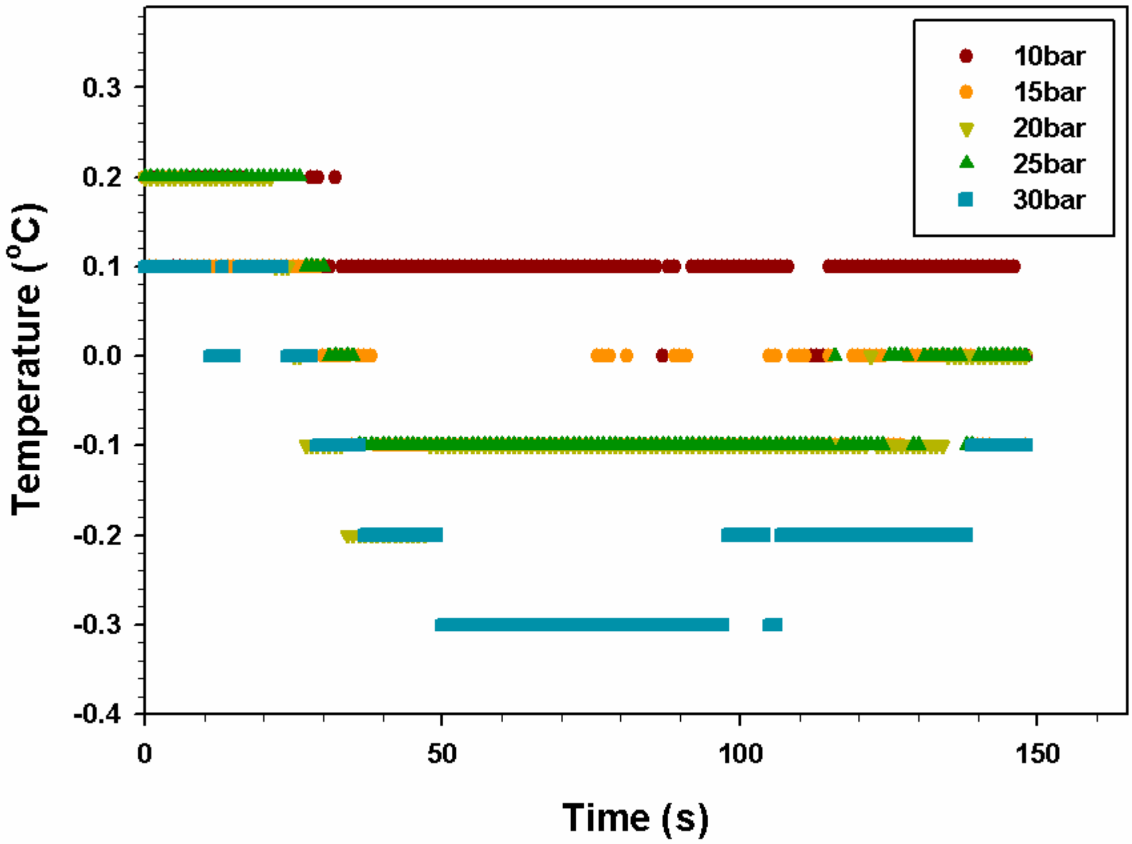


Figure 13. Decrease of N_2 temperature upon time

Table 6. Temperature changing of N_2 ventilation

	10bar	15 bar	20 bar	25 bar	30 bar
Starting temperature	0.2	0.2	0.2	0.2	0.1
Lowest value	0	-0.1	--0.1	-0.2	-0.3
Temperature changing gap	0.2	0.3	0.3	0.4	0.4

Since HBID process is a new method of freezing desalination, an experiment to check the freezing factors and compare its size and identify its principle is conducted as follows. During the freezing process, each factor to cause freezing phenomenon is compared by observing real-time temperature change.

Figure 12 and Figure13 above show the temperature change by the cooling reactor accompanying the pressure decrease when subtracting CO_2 gas and N_2 gas from the reactor. CO_2 gas and N_2 gas is injected in the pressure of 10, 15, 20, 25, 30 bars, and the reaction is proceeded in the reactor for 4 hours. After 4 hours, the pressure decreases under the same condition by opening the ventilation valve with constant intervals, and the change in the reactor is observed. The expected outcome is as follows: in the case of injecting CO_2, the pressure in the reactor decreases by ventilation so the effects of the temperature decrease can be predicted by Joule-Thompson Effect. Secondly, the emission of the dissolved CO_2 from water causes the heating reaction. Finally, CO_2 hydrate become dissociated in 25, 30 bars in which CO_2 hydrate is generated because the pressure drops below the pressure condition that maintains hydrate. At that time, the effect of the temperature decrease by hydrate dissociation occurs, since CO_2 hydrate dissociation is an endothermic reaction.

As examined in Figure12, the condition of 10, 15, 20 bar does not generate hydrate. Among the three endothermic reactions, it is confirmed that the temperature decrease by Joule-Thompson Effect and the temperature decrease effect in which the dissolved CO_2 in water is emitted to cause an endothermic reaction causes the temperature decrease in the reactor when subtracting the pressure in the reactor.

In order to explore what is more influential between the temperature decrease effect by Joule-Thompson Effect and the dissociation effect by the CO_2 emission when the temperature decreases in 10, 15, 20 bar, an identical experiment is conducted by providing N_2 gas which is not easily dissolved into water in the same pressure of CO_2 gas. It is found that the temperature in the reactor decreases into -0.4℃, -1℃, -1.8℃ after subtracting the pressure. The temperate decrease is higher when the pressure is higher. The range of temperature decrease is 0.6℃, 1.2℃, 1.9℃. To compare with the previous condition, the experiment is conducted with N_2 and the temperature change is presented in Figure 13. Examining the case of N_2 under the same condition of CO_2 in 10, 15, 20 bar, the temperature decreases into 0℃, -0.1℃, -0.2℃respectively in 10, 15, 20 bar. The range of the temperature decrease is 0.2℃, 0.3℃, 0.4℃ in10, 15, 20 bar, which has considerably trivial range than CO_2. Such result reveals that the temperature decrease in the reactor in 10, 15, 20 bar is dominantly caused by the CO_2 emission, and Joule-Thompson Effect and the CO_2 emission dissolved into the solution occupies relatively small part. The ice formation is not found when conducting the temperature decrease experiment by injecting air pressure of 10, 15, 20 bar

When observing the temperature decrease in the condition of CO2 in 25 and 30 bar, it is found that the heating reaction and ice formation occurs as the range of the temperature decrease is higher than 10, 15, 20 bar in which hydrate is not generated. The lowest point of the temperature decrease is found as -2.8℃, -4.4℃ respectively in 25, 30 bar. Although the temperature is maintained 0.2℃ the range of the temperature decrease is 3.0℃and 4.7℃, which is higher compared to 10, 15, 20 bars. The reason is that the reaction to lowering the temperature in the reaction occurs as the dissociation of hydrate makes an endothermic reaction. It is found that ice is formed in 25 and 30 bars. As mentioned above, ice formation is seawater occurs in -1.8℃. Since the temperature lowers as -2.8℃ in 25 bar and as -4.4℃in 30 bars, a lot of ice is formed. Since the reaction of H_2O changing liquid into ice is a heating reaction, the force to lowering the temperature in the reaction due to the endothermic reaction of melting hydrate and the force to rise the temperature due to the heating reaction of ice formation conflict each other and then reach an equilibrium level. The temperature gradually increases into 0.2℃ as the circulator is fixed as 0.2℃.

To examine the temperature decrease process, it is found that the temperature rapidly decreases in section 1. As the pressure decreases, the energy pressure also decreases by Joule-Thompson Effect, and the CO_2 emission causes an endothermic reaction to reduce the temperature. The phase equilibrium of CO_2 hydrate is destroyed and disassociated by pressure decrease. Its endothermic reaction accompanies the effect of lowering temperature, which leads to the rapid decrease of energy. In section 2, the temperature decrease below -1.8℃ leads to the inverse between the endothermic reaction and the exothermic reaction, and the temperature becomes swayed. After the inverse sway is completed, it is found that the temperature becomes stabilized and constantly maintained.

3.1.3. Changes in the heat flow during CO_2 injection and ventilation

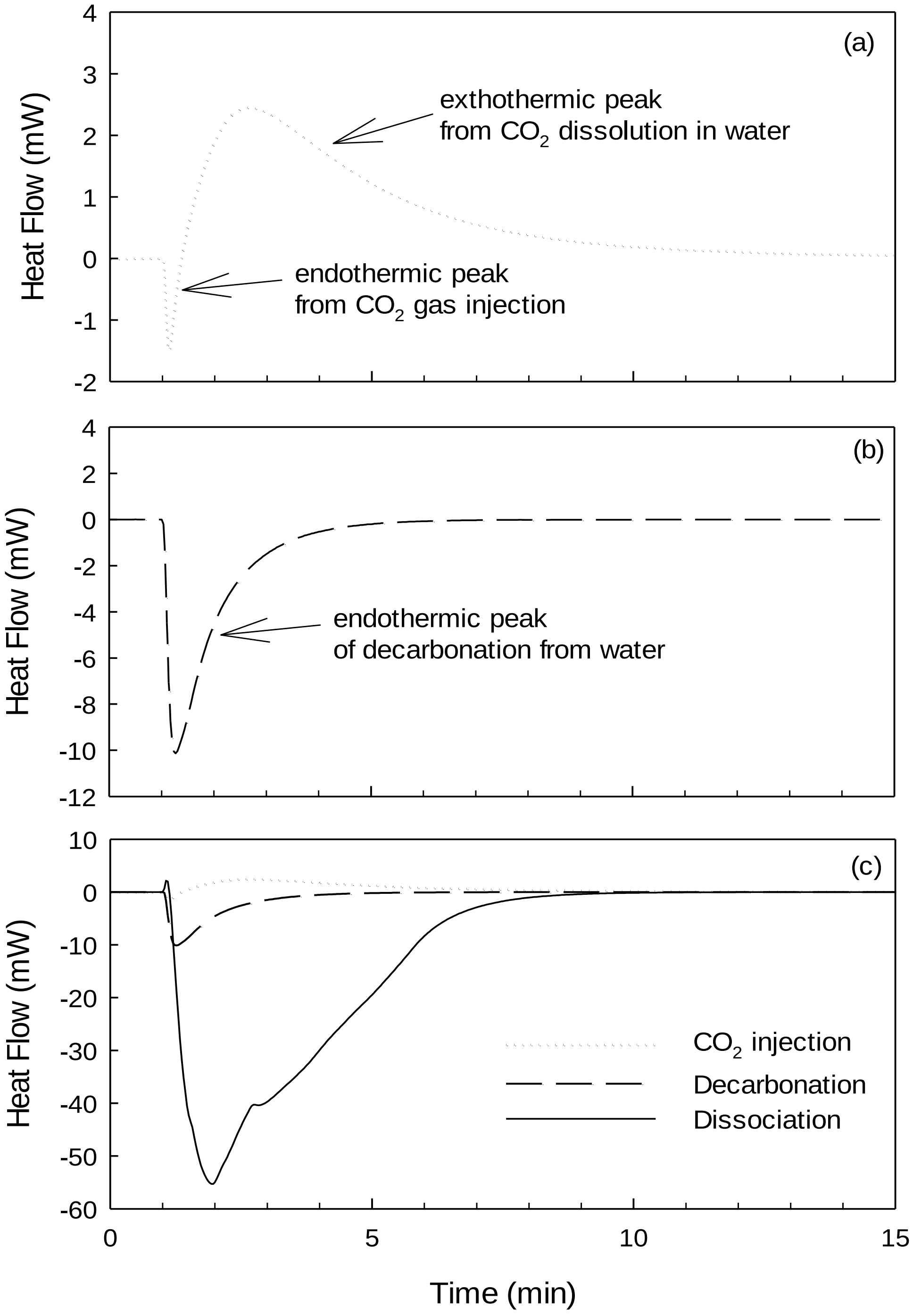


Figure 14. Changes in the heat flow during (a) CO_2 injection followed by CO_2 dissolution, (b) evacuation followed by decarbonation, and (c) comparison with evacuation followed by CO_2 hydrate dissociation at 2.0 MPa and 275.15 K.

Seeing that the endothermic reaction in the combined ice-hydrate-based desalination process was directly related to the expulsion efficiency of salts, the significant factors in the endothermic reaction should be revealed in order to optimize the efficiency of the process. In this study, the heat of dissociation of the CO_2 hydrates (ΔH_D) after evacuation were experimentally measured using a HP μ-DSC. In addition, the heat of decarbonation (ΔH_d) from water was compared with the ΔH_D values in order to estimate the significant factors in the endothermic reaction. Joule–Thomson effect could also be monitored because the occupation of water or hydrates in the sample cell made a difference in the heat capacity between cells. Figure 14 (a) indicated that the heat flow change during CO_2 gas injection and the following CO_2 dissolution thermogram. On the other hand, only endothermic peak from decabonation from water was observed; but the exothermic peak from gas evacuation did not occur in Fig. 14 (b). It was confirm that the decarbonation was relatively faster than CO_2 dissolution in water and the Joule–Thomson effect could be negligible. The heat of decarbonation was estimated as 34.48 J/g water, while that of CO_2 hydrate dissociation was estimated as 500.13 J/g water, which was good agreement in previous literature [ref]. As also shown in Figure 14 (c), the integrated area of decarbonation was less than 7 % of that of CO_2 hydrate dissociation. It should also be noted that heat of CO_2 dissociation did not include the endothermic peak from decarbonation because there is no water remained for CO_2 dissolution when the CO_2 hydrates were completely formed. Therefore, the heat of CO_2 hydrate dissociation were significantly outweigh than that of decarbonation.

3.2. Performance of HBID process

3.2.1. Rejection and mass of NaCl solution

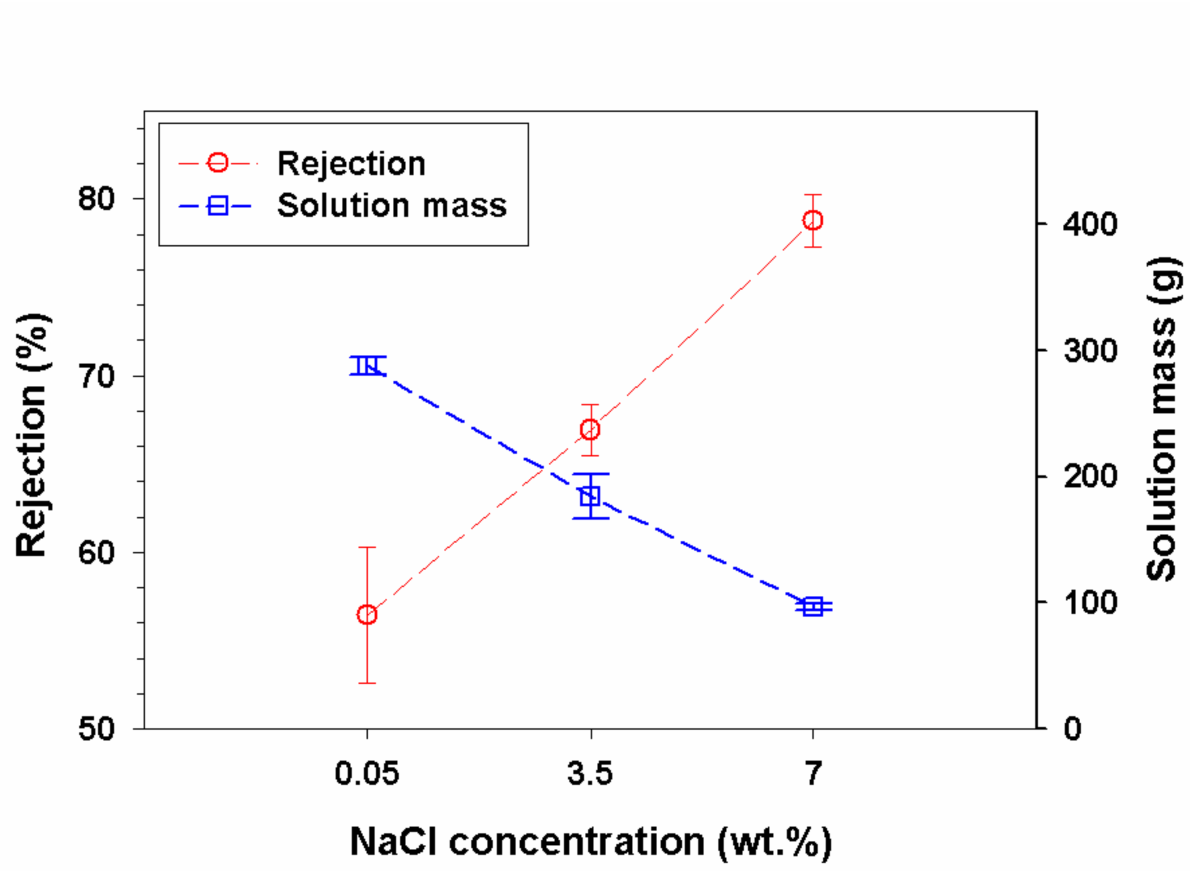


Figure 15. 0.05 3.5 and 7.0wt% NaCl solution rejection and mass data

Waste water from various industrial fields or various areas has different salt concentration. There is brackish water with low salt concentration, seawater that occupies the largest proposition of water existing in the earth, RO brine produced in the processing of seawater desalination [29], and flow back water produced in the processing of shale gas with high salt concentration[22]. The following experiment is conducted to evaluate the performance of HBID process when processing raw water in a variety of concentrations.

0.05wt% (brackish water), 3.5wt%(seawater), 7.0wt%(RO brine) solution is produced respectively by combining DI water and NaCl, and CO_2 gas is injected in 30 bars. The temperature is maintained in 0.2℃for 4 hours. Then, a centrifugal dehydrator is operated for 4 minutes and 30 seconds. The remained ice is melted in room temperature, and the NaCl rejection and mass of the final solution is measured. The values are presented in Figure 15. As a result, the rejection is 78.77% in 7.0wt% with the highest concentration, 66.93% in 3.5 wt%, 56.44% in 0.05wt%. In contrast, the mass of the final treated water has the highest value of 287.94g in 0.05wt%, followed by 184.25g in 3.5wt%, 96.75g in 0.05wt%. It is confirmed the rejection and mass according to the concentration of raw water is in inverse proportion.

Since the concentration of NaCl is higher, the phase equilibrium of hydrate moves compared to the initial condition due to the inhibiting reaction of ions, and the amount of hydrating generation becomes smaller. Ions, such as Na^+ and Cl^-, play the role to inhibit the activity of H_2O to generate pure hydrate, which makes difficulties in generating hydrate[28]. The amount of hydrate generation causes an endothermic reaction, and its energy is used as the cooling energy to form ice. In the case of 0.05wt% with smaller inhibiting effect, the hydrate generation relatively becomes higher for 4 hours, which leads to larger amount of endothermic energy and larger amount of ice formation. In contrast, the case of 7.0wt% with relatively higher inhibiting effect generates less hydrate so it has relatively small amount of endothermic energy, which eventually leads to smaller amount of ice formation. In the case of CO_2 hydrate, the inhibit level of 3.5wt% is absolute temperature with the difference of -1.1K difference.[28] In terms of rejection, the amount of hydrate generating of 7.0wt% is relatively smaller than solution with different concentration. As the size of the endothermic energy caused by melting hydrate becomes relatively smaller, the ice in the form of slush is formed. When dehydrating such lump of ice in the pace of 1600rpm, the concentrated liquid contained in the ice easily escapes. Also, its melting speed is relatively faster than the ice with low concentration, the ion solution with higher concentration can rapidly escape when melting. Inversely, the case of 0.05wt% forms solid ice with relatively high concentration than 7.0wt%. The concentrated ions does not easily escape from ice when dehydrating, which leads to relatively lower rejection.

3.2.2. Rejection of humic acid solution

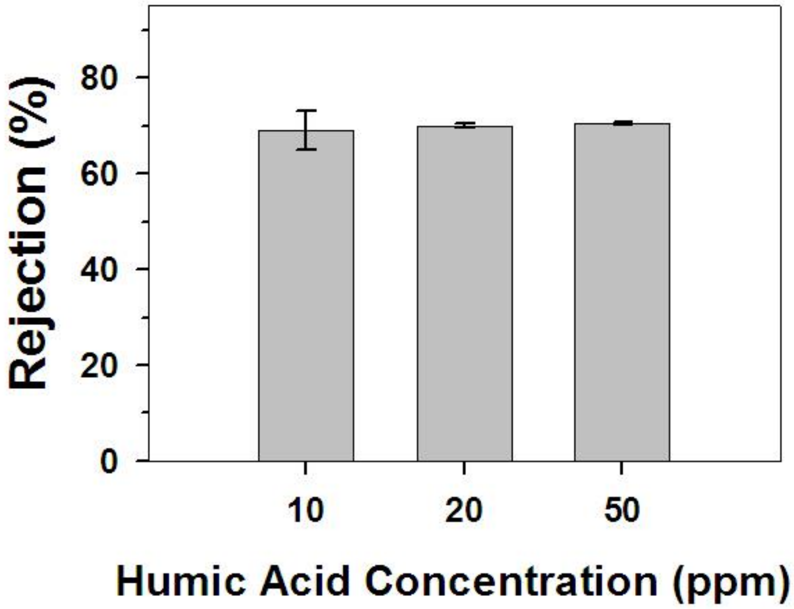


Figure 16. Rejection of 10, 20, and 50ppm Humic acid

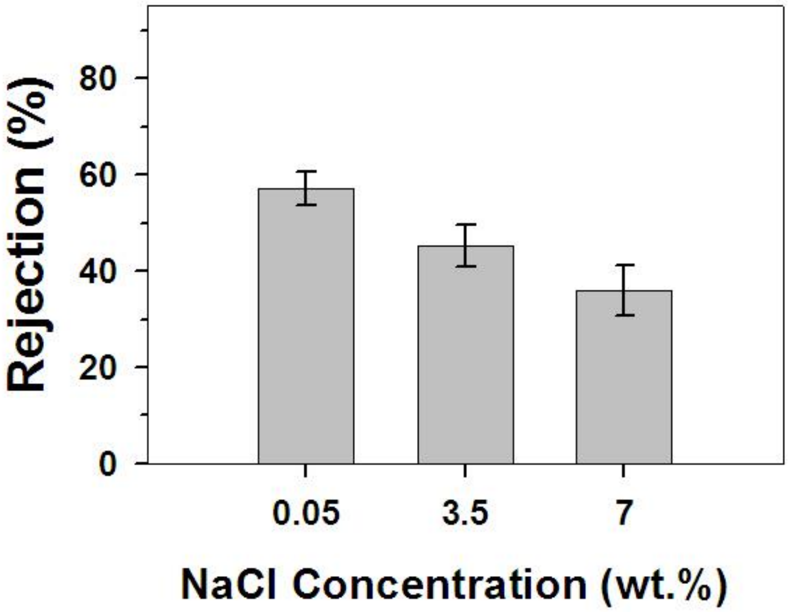


Figure 17. Rejection of 0.05, 3.5, 7.0wt% NaCl + 50ppm humic acid

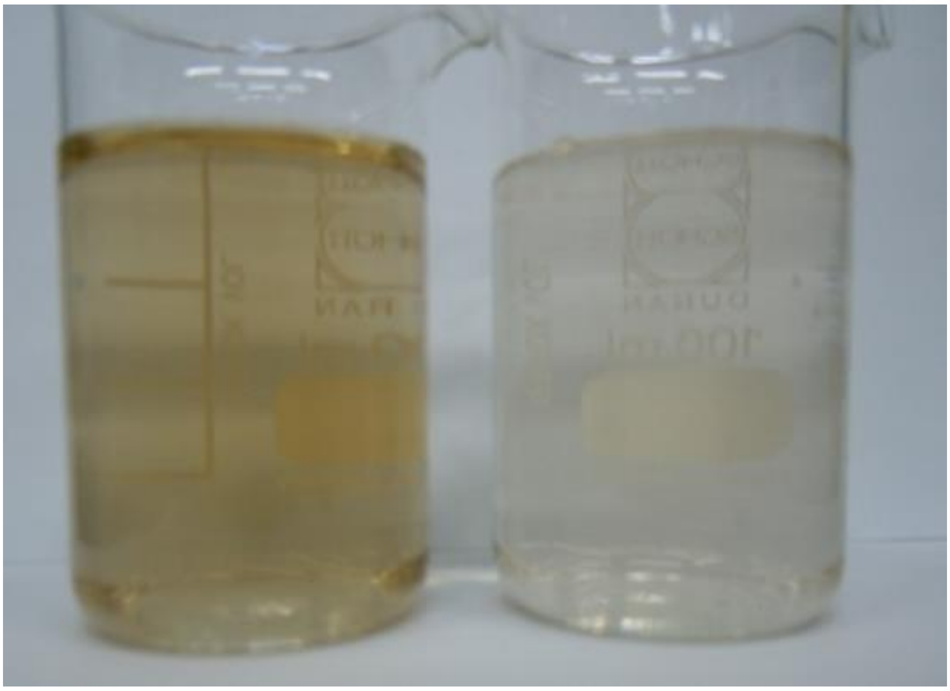


Figure 18. Photographof treated 50ppm Humic acid

Seawater has organic matters in a variety of forms. Using seawater with a large amount of organic matters as drinking water can be harmful to human bodies. In the desalination utilizing membrane, the penetration into the membrane that contains such organic matters occurs fouling phenomenon, which causes not only the performance decline of membrane in the processing but also cost problems due to cleanse or replacement[9]. To explore the efficiency of HBID process that lowers the fouling problems as the preconditioning of membrane processing, the performance evaluation of eliminating organic matter through HBID processing by producing solution with Humic acid. The concentration and elimination rate of raw water is measured by utilizing UV. It is measured in optical density of 254nm wavelength.

Figure 16 presents the results from treating Humic acid in 10, 20, 50ppm by applying solution 500ml into HBID process. The elimination rate is 68.93% in 10ppm, 69.98% in 20ppm, 70.50% in 50ppm. Such results reveal the possibility to eliminate organic matters with approximately 70% of elimination rate among three levels of concentration. They do not largely vary according to the concentration, which suggests the possibility as precondition of membrane process. The images of Figure18 compare 50ppm Humic acid solution and the treated solution through HBID process. The improvement of turbidity of the solution can be identified with the naked eye.

Figure 17 presents the treatment efficiency when humic acid and NaCl meet. After creating NaCl solution in 0.05wt%, 3.5wt%, 7.0wt% and humic acid 50ppm solution and creating NaCl+humic acid solution, 500g is treated through HBID process. The elimination rate of humic acid of the final treated water is checked. The elimination rate from each case is as follows: 56.12% in 0.05wt%, 47.7% in 3.5wt%, 35.93% in 7.0wt%. It is found that the elimination of humic acid decreases as the concentration of NaCl solution increases. This is because the structure of humic acid becomes larger when humicacid and NaCl meet to cause coagulation[30]. As these particles are larger, the molecules are locked within hydrate when ice is formed and cannot completely escape from ice when conducting dehydrating processing. Therefore, the rejection of humic acid is measured smaller as the concentration is higher.

3.2.3. Rejection of cation

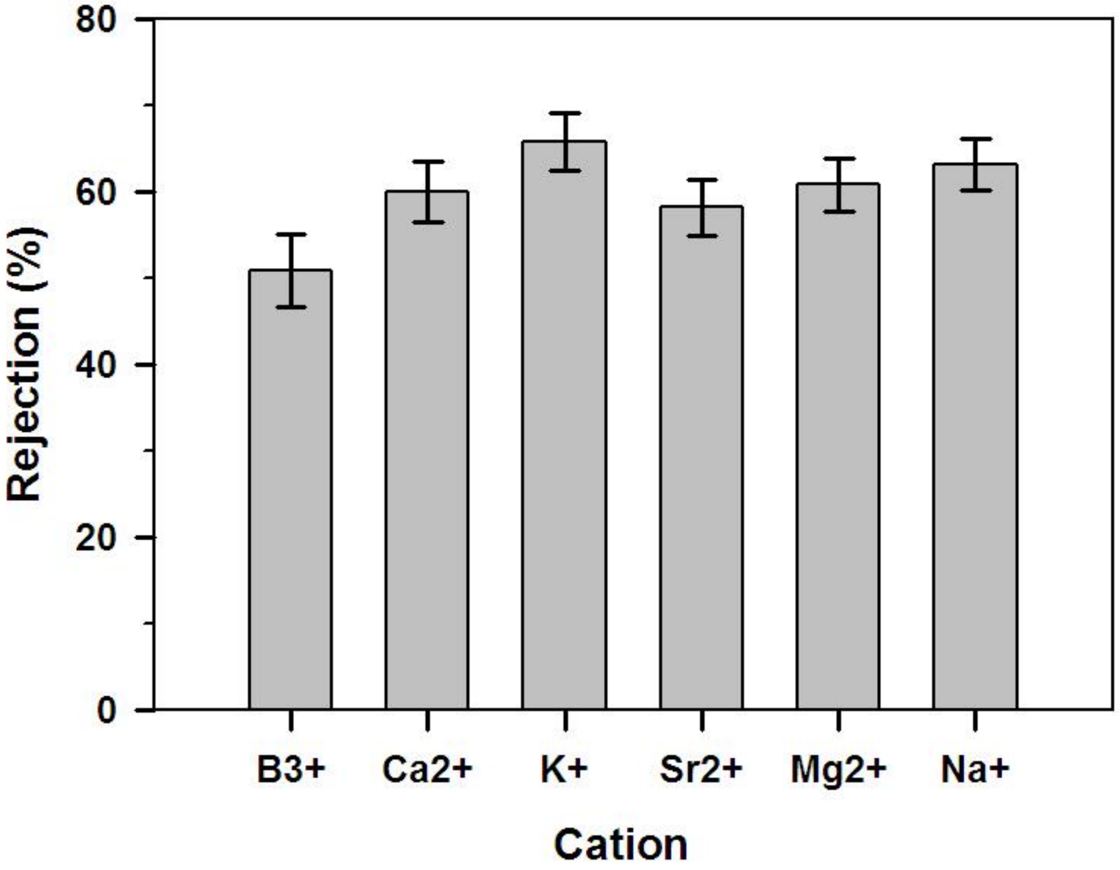


Figure 19. Rejection of Cations

Figure19 presents the results from conducting the seawater desalination experiment with seawater from Ilsanji beach in Ulsan. The experiment method is same as the experiments above. 500g of seawater is filtered by 0.45µm-filter, and HBID system is conducted. To identify the ion elimination rate of the final wasted water, the major cation (B^{3+}, Ca^{2+}, K^{+}, Sr^{2+}, Mg^{2+}, Na^{+}) of seawater are measured through ICP-OES prior to the processing. The elimination rate is as follows per each ion: B^{3+} 55.23%, Na^{+} 63.42%, Ca^{2+} 64.61%, Mg^{2+} 64.32%, K^{+} 70.53%. They form a similar level of rejection, approximately 65%, except for B3+ and K+. K+ presents higher rejection and B3+ presents lower rejection than other ions. Such result corresponds with the study by Lee[25]. in the process of seawater changing into CO_2 hydrate, the ions within the seawater is gradually excluded from hydrate, and CO_2 hydrate is generated from the combination of pure water molecule and CO_2 molecule. However, some ions are locked into CO_2 hydrate in the form of highly-concentrated hydrate solution, not being excluded from rapid hydrate generating. As hydrate is generally shifted a lot, the concentration of locked seawater solution becomes higher, and crystal is educed. The book[26] presents the educed form as crystal in highly-concentrated ion solution contained within ice as the concentration becomes high.

The part of the educed molecule in the form of salt is locked within ice without dissolution into water in the process in which hydrate is rapidly dissolved and shifted into ice. After pressure-reducing and hydrate disassociation, the endothermic reaction causes the dissolution of CO_2 hydrate in the reactor, which leads to the ice formation under the condition below 0℃. As ice is formed, the exclusion process of ion is conducted once again; the ions are partially locked into the ice in the form of the highly-concentrated seawater solution. Like the previous process, the ions in the solution in the ice are partially educed as salt when the ice formation gradually proceeds.

3.2.4. Quanta SEM image of ice sample

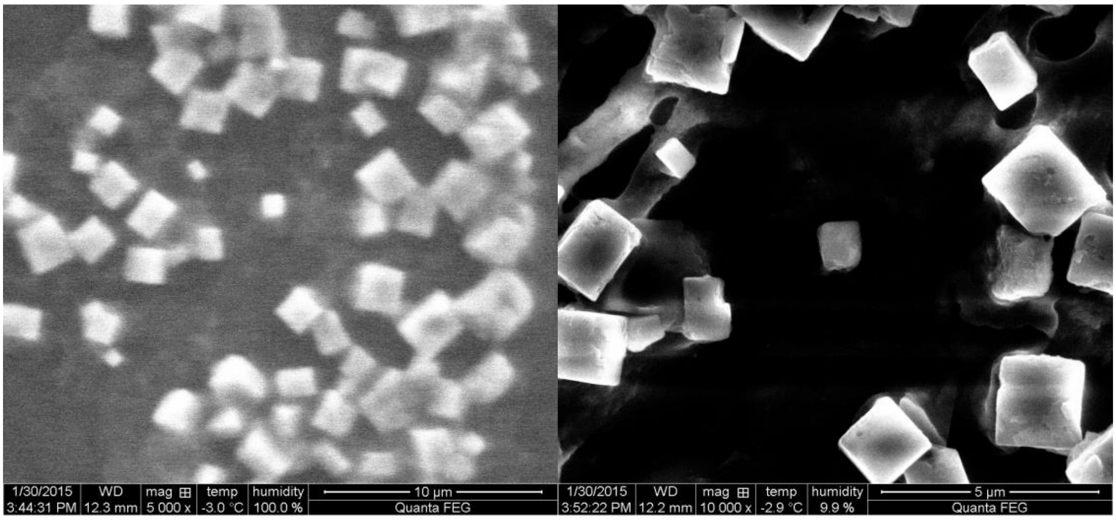


Figure 20. Quanta SEM image

In Figure 20, the pictures of ice sample formed from HBID process is taken in -2,9℃ through Quanta SEM. It is found that salt is partially formed in ice. The salt-formation reaction proceeds twice in such process, and K^+ ion, which is not easily educed as salt, exists as ion in the solution compared to other ions. When dehydrated after finishing ice formation, the ions educed as salt cannot easily escape through the path to be hydrated in ice compared to the ions dissolved in the form of solution. In contrast, K^+ can easily escape through channel in the form of solution when hydrated, because it is dissolved into the solution. As a result, the content of K^+ ion becomes smaller than other ions in the hydrated ice. The rejection of K^+ turns to be higher when finally measured after melting ice.

3.2.5 Analysis of drained water

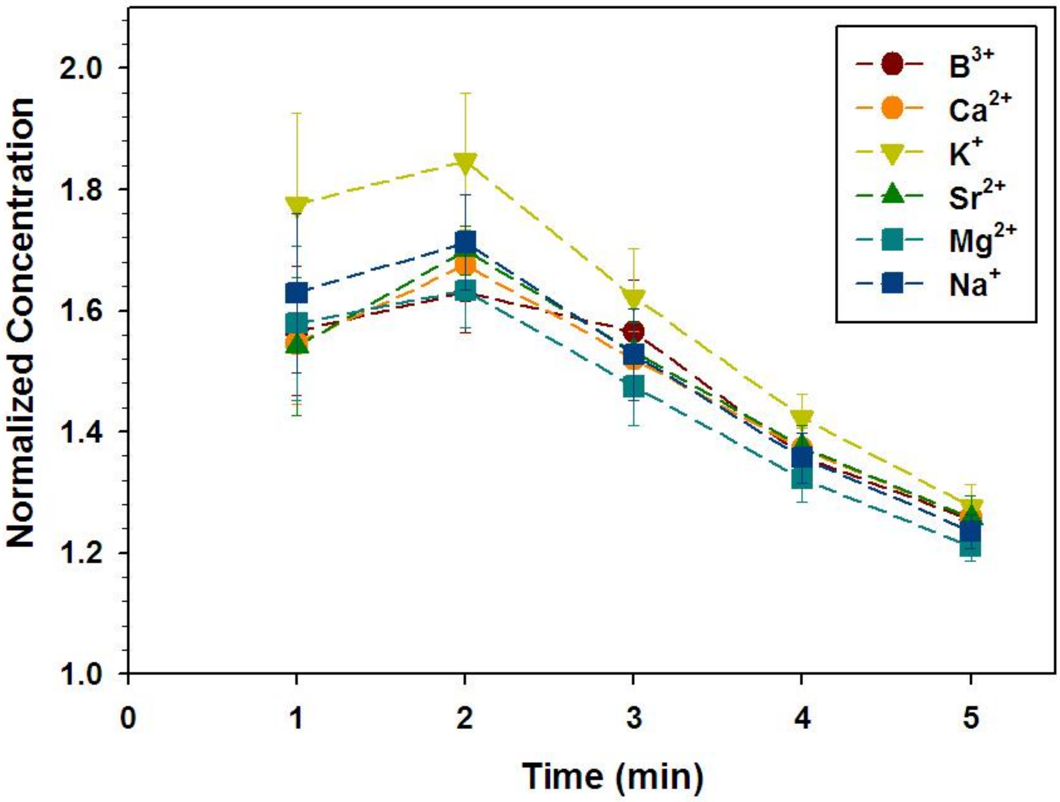


Figure 21.Drained water cation concentration

Figure 21 presents the measurement data of cation concentration contained each sample after sampling the drained solution for one session per minute. When examining each concentration after normalization, K^+ ion is much higher in the drained water. It is confirmed that K^+ ion easily escapes from the drained solution than other ions. One study shows the K^+ ion remains conformation of ion in the sea water when sea water changing ice.

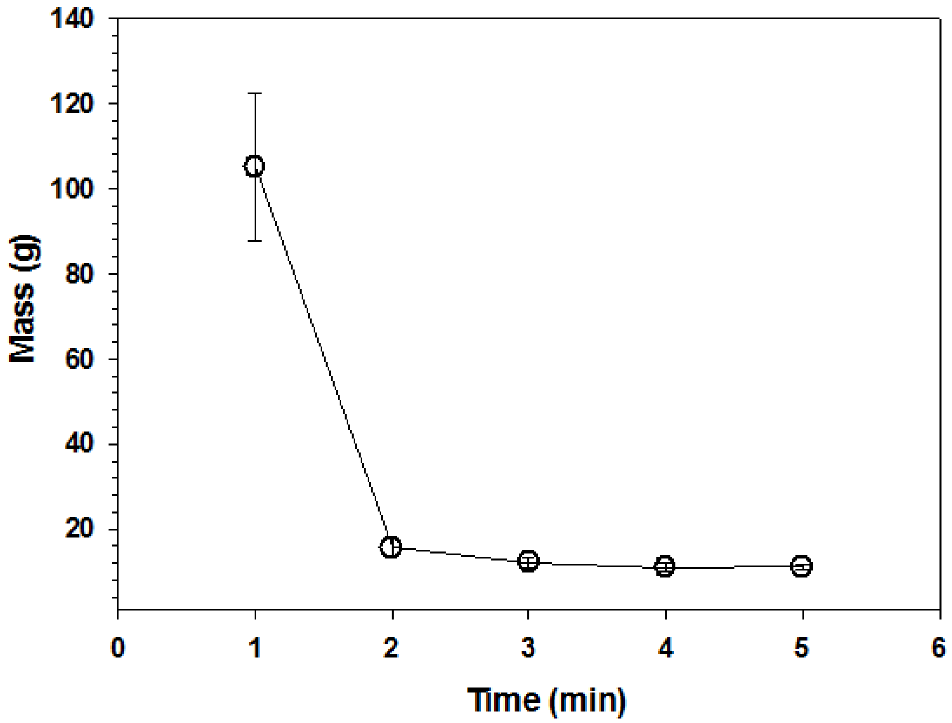


Figure 22.Drained water mass

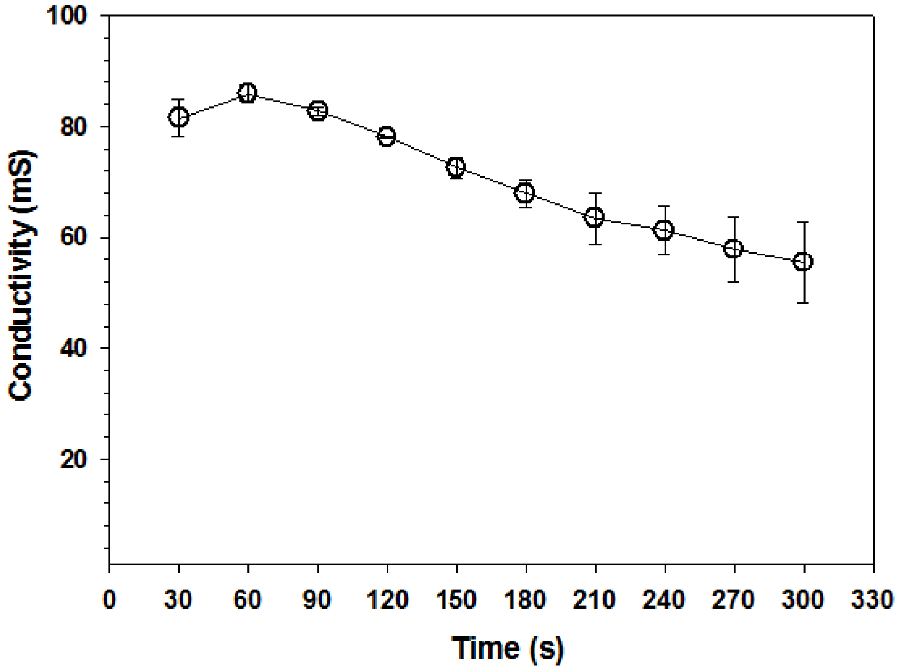


Figure 23.Drained water conductivity

The experiment above shows the results from sampling the drained water in 1-minute interval as draining the formed ice in a centrifugal dehydrator for 5 minutes after the 4-hour reaction of seawater in CO_2 30 bar. Figure 21 presents the results from analyzing the mass of samples and ion concentration. Regarding the average value of the mass of 3-time repetition, the drained mass in 1, 2, 3, 4, 5 min is 105.22g, 15.71g, 12.16g, 11.05g, and 11.11g respectively. In the initial stage, the surface of ice which contains water that cannot be fully formed as ice and highly-concentrated salt rapidly melts to produce large amount of mass. After certain period of time, the mass of drained solution maintains the level of 11g as it constantly melts. The ice in the form of slush is all dehydrated in the initial stage when melting, since the ions are mainly excluded from the solution after certain period time and the melting point becomes higher than the original ice. Figure 23 presents the data of measuring conductivity for 5 minutes as conducting HBID process and dehydration on 500ml of seawater and sampling the solution with 30-second interval. The conductivity becomes lower as time passes because the concentration of the solution becomes lower, which implicates that the ice becomes purer as the ions in the ice are largely excluded.

3.3.Performance of HBID process pretreatment RO membrane

Table 7. Final concentration of permeate ice-desalinated water rejected by RO membrane

Seawater elements	Na^+	Ca^{2+}	K^+	Mg^{2+}	B^{3+}	Sr^{2+}
Concentration (mg/L)	95.6 ± 23.2	1.2 ± 0.4	7.6 ± 1.8	3.8 ± 1.3	0.5 ± 0.02	0.03 ± 0.01

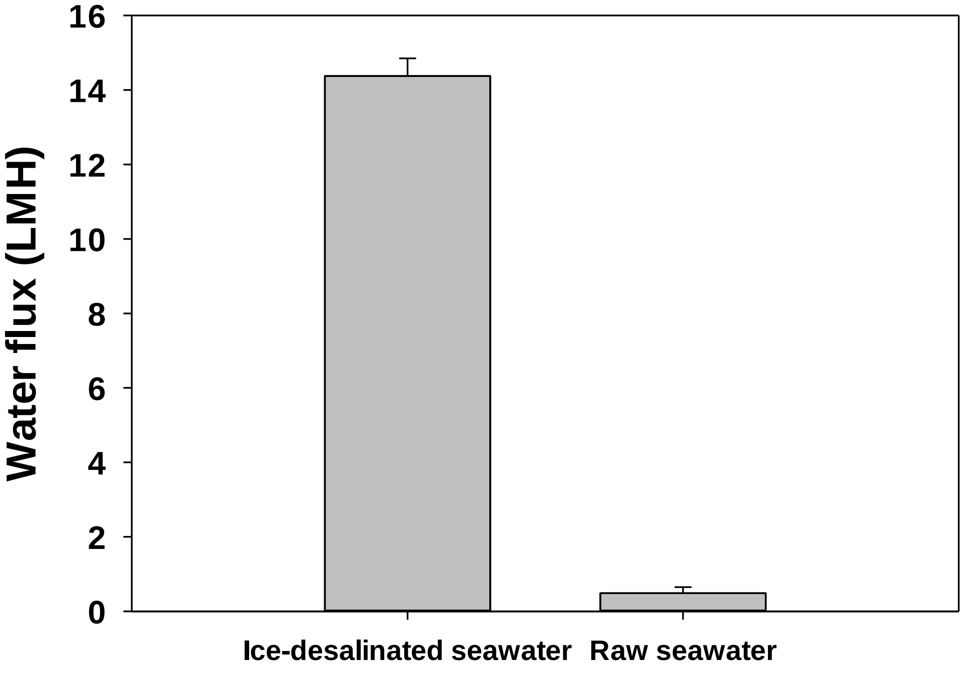


Figure 24. Comparison of water flux between ice-desalinated seawater and raw seawater.

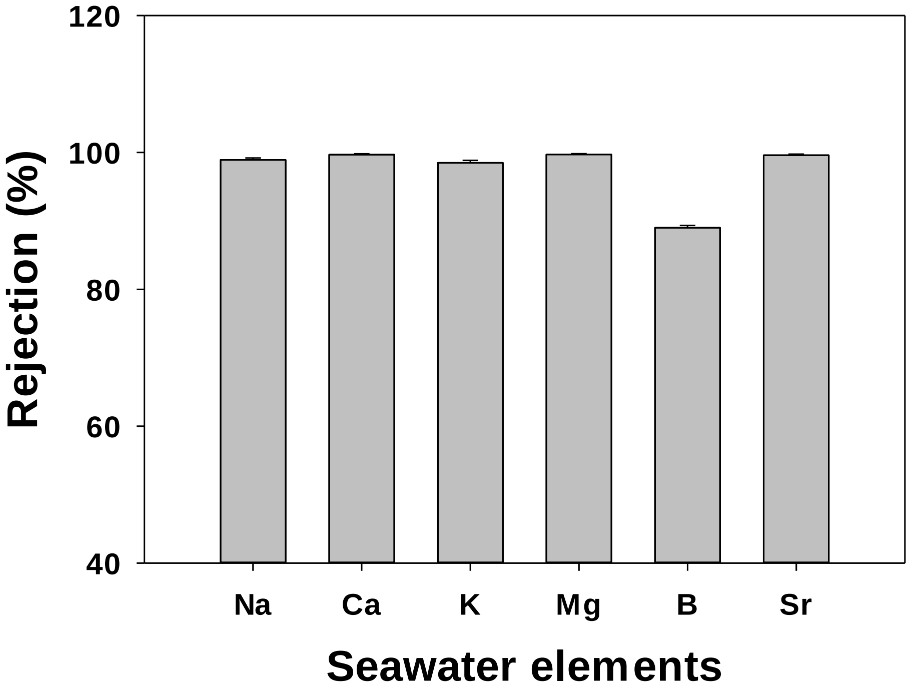


Figure 25. Rejection (%) of ice-desalinated seawater

Figure 24 presents comparison of the water flux between ice-desalinated seawater and the raw seawater by SHF membrane. The water flux of raw seawater is less than 0.5 LMH, because the operated pressure (15 bars) is smaller than the osmotic pressure of the raw seawater (~26.4 bar in 35,000ppm). However, approximately 65% of salt is primarily subtracted from the ice-desalinated seawater (9.24 bars). Thus, its osmotic pressure becomes lower than the operated pressure (15 bars) to have the water flux (~14 LMH).

Figure 25 shows the salt rejection regarding the ions contained in seawater. Na^+ and K^+, a monovalence ion, presents the salt rejection of 98.5-99.0%. Ca^{2+}, Mg^{2+}, Sr^{2+}, a divalance ion presents the salt rejection over 99.5%. However, boron presents the salt rejection of approximately 90%. Because boron exists in the form of boric acid at pH below 9, this result can be explained that boric acid is poorly hydrated and uncharged, then, it is expected to be very small in size. Therefore, boron rejection is quite low than other charged salts. Table.1 shows final concentration of permeate ice-desalinated water rejected by RO membrane. Finally, in the case of boron with 90% salt rejection, the final concentration of hydrate-treated water is 0.5 (mg/L), thus it satisfied the drinking water level by World Health Organization (WHO): 0.5 (mg/L).

4. Conclusion

- There are three factors in the contributive order of lowering temperature in HBID process: the endothermic energy of hydrate dissociation > the endothermic energy occurring in the emission of CO_2 from water > Joule-Thompson Effect. In addition, it is found that the endothermic energy of hydrate dissociation highly occupies the major part among these three factors.

- In the experiment with varying concentration of raw water, the rejection is higher as the concentration of raw water is higher when conducting the HBID processing. However, hydrate is consequentially less generated, since the generating condition of hydrate requires more temperature decrease and pressure increase as the concentration of feed water is higher. Therefore, it is confirmed that the amount of treatment water accordingly becomes lower, since the freezing energy by hydrate dissociation is relatively small and the amount of freezing ice becomes lower altogether.

- Through Humic acid experiment, the possibility of organic treatment of HBID can be verified. Regarding organic matters in brine, the efficiency of treatment becomes lower as the concentration is higher due to the effect of coagulation.

- When checking the rejection and cation rejection in the preconditioning process of seawater, the rejection of K^+ is relatively high because the formation of salt is difficult when frozen compared to other cations. The rejection of boron is low compared to other cations.

- Regarding final treatment water of membrane, the water with HBID preconditioning process has higher rejection and flux than the direct conduct with seawater.

- The study so far shows that there are some difficulties in seawater desalination only by HBID process, because the rejection is highly insufficient. However, as the pace of centrifuge is higher, more brine is excluded, which leads to the improvement of rejection when the period becomes longer. The follow-up study attempts to conduct experiments in serial processing as well as single processing and to increase rejection based on the mentioned results so that HBID process can be utilized more usefully in the field of seawater desalination.

Reference

[1] A. Subramani and J. G. Jacangelo, "Emerging desalination technologies for water treatment: A critical review," *Water Research,* vol. 75, pp. 164-187, 5/15/ 2015.

[2] N. Ghaffour, T. M. Missimer, and G. L. Amy, "Technical review and evaluation of the economics of water desalination: Current and future challenges for better water supply sustainability," *Desalination,* vol. 309, pp. 197-207, 1/15/ 2013.

[3] M. S. Rahman, M. Ahmed, and X. D. Chen, "Freezing-Melting Process and Desalination: I. Review of the State-of-the-Art," *Separation & Purification Reviews,* vol. 35, pp. 59-96, 2006.

[4] G. Nebbia and G. N. Menozzi, "Early experiments on water desalination by freezing," *Desalination,* vol. 5, pp. 49-54, // 1968.

[5] W. Gu, Y. Lin, Y. Xu, S. Yuan, J. Tao, L. Li*, et al.*, "Sea ice desalination under the force of gravity in low temperature environments," *Desalination,* vol. 295, pp. 11-15, 6/1/ 2012.

[6] A. Rich, Y. Mandri, N. Bendaoud, D. Mangin, S. Abderafi, C. Bebon*, et al.*, "Freezing desalination of sea water in a static layer crystallizer," *Desalination and Water Treatment,* vol. 13, pp. 120-127, 2010.

[7] T. Mtombeni, J. Maree, C. Zvinowanda, J. Asante, F. Oosthuizen, and W. Louw, "Evaluation of the performance of a new freeze desalination technology," *International Journal of Environmental Science and Technology,* vol. 10, pp. 545-550, 2013.

[8] W. E. Johnson, "State-of-the-art of freezing processes, their potential and future," *Desalination,* vol. 19, pp. 349-358, 1976.

[9] R. Fujioka, L. P. Wang, G. Dodbiba, and T. Fujita, "Application of progressive freeze-concentration for desalination," *Desalination,* vol. 319, pp. 33-37, 6/14/ 2013.

[10] C.-s. Luo, W.-w. Chen, and W.-f. Han, "Experimental study on factors affecting the quality of ice crystal during the freezing concentration for the brackish water," *Desalination,* vol. 260, pp. 231-238, 2010.

[11] Y. Mandri, A. Rich, D. Mangin, S. Abderafi, C. Bebon, N. Semlali*, et al.*, "Parametric study of the sweating step in the seawater desalination process by indirect freezing," *Desalination,* vol. 269, pp. 142-147, 3/15/ 2011.

[12] L. Xie, J. Ma, F. Cheng, P. Li, J. Liu, W. Chen*, et al.*, "Study on sea ice desalination technology," *Desalination,* vol. 245, pp. 146-154, 9/15/ 2009.

[13] P. M. Williams, M. Ahmad, and B. S. Connolly, "Freeze desalination: An assessment of an ice maker machine for desalting brines," *Desalination,* vol. 308, pp. 219-224, 1/2/ 2013.

[14] W. Gao, M. Habib, and D. Smith, "Removal of organic contaminants and toxiciy from industrial effluents using freezing processes," *Desalination,* vol. 245, pp. 108-119, 2009.

[15] G. Gay, O. Lorain, A. Azouni, and Y. Aurelle, "Wastewater treatment by radial freezing with stirring effects," *Water Research,* vol. 37, pp. 2520-2524, 5// 2003.

[16] M. Gunathilake, M. Dozen, K. Shimmura, and O. Miyawaki, "An apparatus for partial ice-melting to improve yield in progressive freeze-concentration," *Journal of Food Engineering,* vol. 142, pp. 64-69, 12// 2014.

[17] E. Iritani, N. Katagiri, K. Okada, D.-Q. Cao, and K. Kawasaki, "Improvement of concentration performance in shaking type of freeze concentration," *Separation and Purification Technology,* vol. 120, pp. 445-451, 12/13/ 2013.

[18] G. Petzold, K. Niranjan, and J. M. Aguilera, "Vacuum-assisted freeze concentration of sucrose solutions," *Journal of Food Engineering,* vol. 115, pp. 357-361, 4// 2013.

[19] G. Petzold, J. Moreno, P. Lastra, K. Rojas, and P. Orellana, "Block freeze concentration assisted by centrifugation applied to blueberry and pineapple juices," *Innovative Food Science & Emerging Technologies,* vol. 30, pp. 192-197, 8// 2015.

[20] D. Corak, T. Barth, S. Høiland, T. Skodvin, R. Larsen, and T. Skjetne, "Effect of subcooling and amount of hydrate former on formation of cyclopentane hydrates in brine," *Desalination,* vol. 278, pp. 268-274, 9/1/ 2011.

[21] S. Han, J.-Y. Shin, Y.-W. Rhee, and S.-P. Kang, "Enhanced efficiency of salt removal from brine for cyclopentane hydrates by washing, centrifuging, and sweating," *Desalination,* vol. 354, pp. 17-22, 12/1/ 2014.

[22] J.-H. Cha and Y. Seol, "Increasing gas hydrate formation temperature for desalination of high salinity produced water with secondary guests," *ACS Sustainable Chemistry & Engineering,* vol. 1, pp. 1218-1224, 2013.

[23] S. Li, Y. Shen, D. Liu, L. Fan, and Z. Tan, "Concentrating orange juice through CO2 clathrate hydrate technology," *Chemical Engineering Research and Design,* vol. 93, pp. 773-778, 1// 2015.

[24] Y. T. Ngan and P. Englezos, "Concentration of mechanical pulp mill effluents and NaCl solutions through propane hydrate formation," *Industrial & engineering chemistry research,* vol. 35, pp. 1894-1900, 1996.

[25] K. C. Kang, P. Linga, K.-n. Park, S.-J. Choi, and J. D. Lee, "Seawater desalination by gas hydrate process and removal characteristics of dissolved ions (Na+, K+, Mg2 +, Ca2 +, B3 +, Cl−, SO42 −)," *Desalination,* vol. 353, pp. 84-90, 11/17/ 2014.

[26] W. Weeks, *On Sea Ice*: University of Alaska Press, 2010.

[27] Y.-N. Kwon and J. O. Leckie, "Hypochlorite degradation of crosslinked polyamide membranes: II. Changes in hydrogen bonding behavior and performance," *Journal of Membrane Science,* vol. 282, pp. 456-464, 10/5/ 2006.

[28] S.-C. Sun, C.-L. Liu, and Y.-G. Ye, "Phase equilibrium condition of marine carbon dioxide hydrate," *The Journal of Chemical Thermodynamics,* vol. 57, pp. 256-260, 2// 2013.

[29] J. Arnal, M. Sancho, I. Iborra, J. Gozalvez, A. Santafe, and J. Lora, "Concentration of brines from RO desalination plants by natural evaporation," *Desalination,* vol. 182, pp. 435-439, 2005.

[30] L.-F. Wang, L.-L. Wang, X.-D. Ye, W.-W. Li, X.-M. Ren, G.-P. Sheng*, et al.*, "Coagulation kinetics of humic aggregates in mono-and di-valent electrolyte solutions," *Environmental science & technology,* vol. 47, pp. 5042-5049, 2013.

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감사의 글

2 년 이라는 길 수도 있지만 짧은 시간 동안에 아무것도 모르던 제가 환경분야의 아주_작은 부분이지만 한 분야에 전문성을 갖게 되었다는 것이 신기하고 뿌듯합니다.

저를 학문의 세계로 인도해 주신 저의 지도 교수님이신 권영남 교수님께 진심으로 감사 드립니다. 교수님의 부드러우시지만 학문에 있어서 만큼은 원칙을 지키시고 절대 포기하지 않으시는 학자이시자 연구자의 모습을 존경하며 석사 생활을 할 수 있었습니다.

저의 석사생활의 처음과 끝을 보아온 병문이, 비록 나이는 어리지만 학문적으로나 생활적으로나 많이 도움이 되어 주어서 감사합니다. 선배이자 동료로서 자신의 시간을 할애해 제가 논문작업을 진행하는데 도움을 준 속이 깊은 Nga, 그리고 마지막까지 제가 논문을 쓰는데 힘이 되어준 분위기 메이커 유경이, 연구실 생활 하는 동안 막내로써 연구실 생활을 충실히 해준 형개, 지금은 졸업하셨지만 저의 학업을 항상 신경 써 주시던 은태형, 그리고 제가 처음 들어왔을 때 저에게 다양한 연구 주제를 소개해 주며 학문의 재미를 알려주었던 은호씨, 항상 묵묵한 모습으로 후배를 지도해 주셨던 현규형, 멀리서 후배들을 응원해 주셨던 정은누나, 앞으로 제가 하던 일을 이어가 고생해 주어야 할 우정이, 모두 진심으로 감사 드립니다. 석사 생활을 마치기 까지 저에게 가장 큰 힘이 되었던 저희 연구실 사람들에게 진심으로 감사드립니다.

저의 연구에 많은 도움을 주셨던 서용원 교수님께 진심으로 감사 드립니다. 처음 연구를 시작해 Hydrate 를 전혀 몰랐던 저를 다른 연구실임에도 불구하고 친절하게 가르쳐 주었던 요한이, 후배이지만 힘들 때 힘이 되어 주었던 동영이, 너무 감사합니다.

제 논문의 부족한 부분을 신경 써 주신 이창하 교수님께 진심으로 감사드립니다. 연구가 막힐 때 새로운 돌파구를 시도할 수 있게 아이디어와 용기를 주신 홍신형, 다른 연구실이지만 같은 연구실 사람같이 친하게 지냈던 형은이, 혜진이, 민식씨, 지원이, 학현이, 민정이, 준영이, 기명이 정말 감사합니다. 고민이 있을 때 상담을 함께해 주었던 민규, 언제나 밝은 성준이, 친절하신 혜옥누나 감사합니다.

마지막으로 석사생활을 무사히 마칠 수 있도록 뒤에서 묵묵히 도와주신 부모님, 하늘에 계신 친할아버지, 외할머니, 외할아버지 그리고 친할머니 감사합니다. 정들었던 UNIST 를 졸업하고 새로운 사회에서 항상 성장하고자 노력하는 사람이 되겠습니다.