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Freeze desalination of seawater using LNG cold energy

Jian Chang^a, Jian Zuo^a, Kang-Jia Lu^a, Tai-Shung Chung^{a,b,*},

^a Department of Chemical & Biomolecular Engineering,

National University of Singapore, 4 Engineering Drive 4, Singapore 117585

^b Water Desalination & Reuse (WDR) Center, King Abdullah University of Science and
Technology, Thuwal 23955–6900, Saudi Arabia

* Corresponding author. Tel.: 65 6516 6645; fax: 65 6779 1936.

E-mail address: chencts@nus.edu.sg (T. S. Chung)

Abstract

With the aid of cold energy from regasification of liquefied natural gas (LNG), freeze desalination (FD) is an emerging technology for seawater desalination because of its low energy characteristics and insensitivities to fouling problems. This work aims to investigate the major operating parameters of FD such as coolant temperature, freezing duration, supercooling, seeding, agitation, crystallizer material and subsequent washing procedure on ice production and water quality. It was found that the optimal freezing duration per batch was 1 h for an iron crystallizer and 1.5 h for a glass crystallizer. The optimal coolant temperature should be around -8 °C. The optimal amount of washing water to clean the raw ice was about 50 wt% of the raw ice. Over 50 wt% of the feed could be recovered as raw ice within 1 h, which means an overall ice recovery rate of higher than 25% (of the original seawater), considering the consumption of washing water. Both artificial and real seawater were tested under the optimized conditions. The total dissolved solid in the product ice was around 300 ppm, which met the World Health Organization (WHO) potable water salinity standard of 500 ppm. Therefore, the process parameters optimized in this study can be directly used for the freeze desalination of seawater.

Keywords: Freeze desalination; LNG cold energy; Seawater desalination

1. Introduction

Alleviating water scarcity is one of the major challenges facing the 21st century (Gude, 2016; Subramani and Jacangelo, 2015; Roberts et al., 2010). In light of the vast amount of seawater, much research has been conducted to desalinate seawater via processes such as reverse osmosis (RO) (Fritzmann et al., 2007; Sirkar et al., 1982; Kang and Cao, 2012), multi-effect distillation (MED) (Al-Shammiri and Safar et al., 1999), membrane distillation (MD) (Khayet and Matsuura, 2011; Wang and Chung, 2015; Zuo et al., 2016) and forward osmosis (FO) (Zhao et al., 2012; Valladares et al., 2014; McGovern and Lienhard, 2014). However, these processes also face challenges of either high-energy consumption or severe membrane fouling. Freeze desalination (FD) is an emerging desalination technology because of its insensitivities to fouling problems and the provision of cold energy from processes such as regasification of liquefied natural gas (LNG) in recent years (Nebbia and Menozzi, 1968; Johnson, 1976; Shirai et al., 1999; Wang and Chung, 2012). The cold energy is the heat absorbed from ambient surrounding when converting LNG (-162 °C) back to natural gas at LNG terminals (Wang and Chung, 2012; Miyazaki et al., 2000). It is one of high quality energy sources to cool other media, but most cold energy during LNG regasification has been wasted until today. Because the latent heat of ice fusion is only 1/7 of the latent heat of water vaporization (Rahman et al., 2006), it is much easier and more cost-effective to induce and harvest ice crystals from seawater by the cold energy in FD than to produce potable water by means of evaporation in many distillation processes (Wang and Chung, 2012; Cao et al., 2015).

There are two categories of freezing processes in FD; namely, direct and indirect contact freezing (Lu and Xu, 2010). The former mixes seawater with a liquid refrigerant directly. The refrigerant vaporizes and escapes from the top of the freezer. At the same time, seawater is cooled and then freezes. This process has a high production rate, but the requirements of the refrigerant are stringent. It should be nontoxic, chemically inactive, immiscible in water, and resistant to forming hydrates (Rahman et al., 2006). In contrast, indirect freezing uses walls to isolate the refrigerant from seawater (Zvinowanda et al., 2014). Heat exchange happens through the crystallizer walls with adjustable cooling conditions (Wang and Chung, 2012; Mandri et al., 2011). An intermediate coolant may be utilized to pass the cold energy from LNG to seawater at an appropriate temperature to facilitate ice production without incurring salts. Some previous studies used -10 °C or -15 °C for simplicity (Wang and Chung, 2012; Badawy, 2015; Efrat, 2011), while this work will find the optimal coolant temperature.

Various crystallizer configurations such as static layer crystallizer (Rich et al., 2010), progressive crystallizer (Fujioka et al., 2013), dynamic layer crystallizer (Rich et al., 2012) have been employed to investigate the ice formation in FD. In a static layer growth system, the seawater stays stagnant on a surface, the driving forces for heat and mass transfers are free convection and gravity. Thus, it would take a long time, usually more than 10 h per batch, to form a reasonable amount of ice crystals. In a progressive crystallizer, only one single ice crystal is present, which is at one end of the vessel. The ice-solution interface gradually moves towards the other end. However, the speed of the freezing front is highly constrained. A fast moving freezing front would inevitably cause concentration polarization. In a dynamic growth system, seawater flows down along a cold surface and ice crystals form underneath the flowing film. One of the major obstacles in this process is the salt entrainment (Reddy et al., 2009). The brine tends to be trapped in the interstices of ice crystals due to

capillary force. Different from aforementioned approaches, the current study uses a simple batch reactor. We aim to have a deeper understanding of each basic parameter that would benefit FD development in years to come.

There are two major challenges in the FD technology. One is the amount of salts adsorbed on the ice crystals, while the other is the amount of washing water to remove these salts. Since ice crystals generated in FD have very small sizes, they have an enormous specific surface area. Their surfaces are usually covered by a slew of salts due to the strong adhesive force between ice and brine. Therefore, one must wash ice crystals to remove these salts. The amount of washing water has been overlooked in most of past studies, but this study would revisit this crucial issue and optimize the amount of washing water. Therefore, this study may provide useful insights and operational data for the entire FD process. In addition to these challenges, FD also faces the difficulties of being accepted as a new technology from industries, especially when it is perceived as costly and mechanically complex (Randall and Nathoo, 2015).

2. Background and Theory

2.1. Pivotal role of washing in FD

Freezing pure water and saline water are distinctly different. Without the disturbance of soluble ions, the ice crystals grow on top of one another. Their sizes can be very large. Visibly, the ice could form an entire chunk in the cylinder. However, water does not freeze in the same manner when many ions are present. Instead, dendritic ice crystals (Tleimat, 1980; Lorain et al., 2001) will occupy the space and form a slurry.

Brine adheres to ice crystals considerably due to the massive interfacial tension (Shwartz and Probst, 1968). A thorough separation of ice and brine require accessory procedures other than simply draining off or normal filtration. The design of washing columns has been actively investigated (Shwartz and Probst, 1968; Harriott et al., 1969) and used in pilot plants (Efrat, 2011). The ice slurry is introduced to the bottom of the washing column that is filled with clean water. Ice crystals float up by the buoyancy force and the brine trapped in interstices would be displaced. Clean ice can then be harvested at the top of the washing column. However, there exists a serious dilemma regarding whether to use agitation and pulsing. Without them, the mass transfer would be extremely slow because the buoyant movement is severely inhibited by the adherence force between ice and water. If agitation and pulsing are adopted, their contributions to longitudinal mixing would disrupt the concentration gradient distribution (Sherwood and Brian, 1966). Once the upper portion of the column contains a high amount of salts, the column is no longer able to purify ice. In contrast, washing ice crystals with the aid of vacuum filtration can drain out salty water within seconds. Not only can it lower the salt impurity on the ice crystals to be almost negligible but also significantly reduce the energy consumption for the washing procedures.

2.2. Supercooling and nucleation

Supercooling is the process where a liquid is cooled below its freezing point without crystallizing. For instance, pure water has to be cooled below 0 °C to initiate freezing. Although 0 °C is widely understood as its freezing point, it is rather an equilibrium point during the freezing process. The real temperature for water to start freezing depends on when nucleation happens. According to crystallization kinetics, a trace amount of ice lattice larger than the critical size must be generated (Tiller, 1992). In other words, there is a minimum

embryo-crystal size (i.e., the critical radius) for the embryo to grow spontaneously. In fact, for a given temperature there will be a critical radius. The relationship among them is reflected by the Kelvin equation (Tleimat, 1980):

$$r^* = \frac{2\sigma T_f}{L_f \Delta T} \quad (1)$$

where r^* is the critical radius, T_f is the freezing temperature, L_f is the latent heat of fusion, ΔT is the temperature difference departed from the freezing point, and σ is the interfacial tension between water and ice that is estimated to be 22 erg/cm². The critical radius is then plotted relative to water temperature in Fig. 1 (a).

Once ice has the critical radius, nucleation may take place by either homogeneous or heterogeneous nucleation. Theoretically, a cluster of about 25 water molecules would form ice at -41 °C via homogeneous nucleation. In reality, it is difficult to cool the water down to near this temperature without forming ice because the nucleation barrier is largely reduced by the existence of impurities that lead to heterogeneous nucleation. As depicted in Fig. 1 (b), when water molecules wet an impurity surface, a small portion can actually correspond to a much larger radius (Muldrew and McGann, 1999). As a result, this cluster of water molecules is likely to stabilize themselves at a much higher temperature and spontaneously set off the heterogeneous nucleation. The ice crystal would then grow irreversibly as long as the cooling condition is maintained.

Additionally, the supercooling condition can be interrupted when nucleation is triggered by external nucleus (Randall and Lewis, 2009). If any seed ice is added into the supercooled solution, the status of supercooling would cease immediately and a large amount of ice crystals would form shortly. This process releases so much heat that the system temperature

would rise shortly to the equilibrium point, i.e., freezing point. In the absence of a seed, the temperature at which ice crystallization will occur is highly stochastic (random). Seeding helps to overcome this variability because ice crystallization will occur at the same temperature with seeding (Randall et al., 2012).

2.3. Freezing-point depression

Freezing-point depression is a phenomenon where the freezing point of a solvent is decreased by the presence of solutes (Gooch, 2011; Halde, 1980). It is noted that the lowering of the freezing point does not depend on the nature of the solutes. Instead, it is only proportional to the number of dissolved molecules and ions. The expression of freezing-point depression is generally given as:

$$\Delta T_f = -K_{FP}m \quad (2)$$

where ΔT_f is the freezing point depression, K_{FP} is the cryoscopic constant which is 1.86 K·kg/mol for water, and m is the molality (mol solute/1000 g solvent).

Thus, for seawater with a salt concentration of 35 g/kg, the freezing point is depressed to -2.1 ~ -2.2 °C. However, once the solution starts freezing, it gets more and more concentrated. The freezing point is therefore further depressed. Fig. 2 illustrates this process on a NaCl-water phase diagram. Route 1 stands for the cooling of saline water from room temperature to its freezing point. Route 2 is the process of supercooling explained in section 2.2. The temperature quickly jumps back to the freezing point in Route 3 when nucleation takes place. Then the entire system proceeds along the equilibrium curve as shown by Route 4. If seeding is applied at the point when seawater is just cooled to the freezing point, supercooling would be forestalled and the process paths become 1 & 4 instead.

3. Experimental methods

3.1. Experimental setup and materials

To mimic the LNG regasification process in a LNG vaporizer, an environmental friendly Freon[®] gas (R23, DuPont, boiling point: -82.1 °C) was used in this experiment because it possesses the closest vaporization behaviour as LNG and its vaporization can lower the temperature of the coolant (EG, >99.5%). A customized gas compressor and condenser unit (Yohokomo, Singapore) were used to compress Freon[®] gas into a liquid form and recycle the liquid, respectively. Fig. 3 shows the setup of the ice crystallization unit (Wang and Chung, 2012). To ensure enough mixing in the cylinder, a mechanical stirrer with a 3-bladed impeller (MG-1, Li Yuan) was installed in the center with an adjustable rotation speed of 0 – 300 rpm. The cylinder wall of the crystallizer was made of either glass or iron in order to study their effects on ice formation.

Fig. 4 displays the schematic diagram and the image of the vacuum filtration unit. The vacuum pump (MAJP – 40V(L)) has a maximum vacuum of 80 torr (≈ 0.125 atm). Three types of seawater were employed in this study: (1) a NaCl (35 g/kg) solution was used to simulate seawater for most parts of the parameter studies; (2) an artificial seawater was made according to the formulation of Subow (Subow, 1931), as listed in Table 1 (a); and (3) a real seawater was obtained from the Public Utilities Board (PUB), Singapore (Qin et al., 2009) after pre-treatments to remove insoluble solids and organisms. Table 1 (b) tabulates its composition.

3.2. Experimental procedures

The cooling medium EG was firstly cooled to a desired temperature. Meanwhile, a NaCl solution (35 g/kg) or seawater of M_0 (1 kg) was pre-cooled in a freezer to around 0°C before being poured into the crystallizing cylinder. A certain amount of seed ice (M_s) was used to trigger the nucleation at its freezing point (-2.1 °C) or a certain supercooled temperature. The seed ice was weighed and grinded by a bench-top mill (Cole-Parmer, Singapore). The process was timed starting from the onset of nucleation. After a specified freezing duration, the entire ice slurry was transferred to a washing unit which is a vacuum filtration unit consisting of a metal mesh with a wire diameter of 0.12 mm and an aperture of 0.198 mm. The brine was drained off from the slurry by applying vacuum filtration for 10 s to completely remove the brine. The raw ice was weighed (M_i). Then, chilled tap water (0°C) was used to re-wash the raw ice. For each re-wash, a designated amount of tap water was used with aid of vacuum filtration for 10 - 20 s. Eventually, the product ice (M_{pi}) was transferred to a melting unit to melt naturally.

The mass of washing water was represented as a percentage (η) of the raw ice (M_i), i.e., $\eta \cdot M_i$. In this study, η was studied in the range of 0 – 60 wt%. The recovery rate of the product ice and the ice salinity were used to quantify the performance of the FD process. The ice recovery rate (φ) was defined as following:

$$\varphi = \frac{M_{pi} - M_s - \eta M_i}{M_0} \times 100\% \quad (3)$$

$\eta \cdot M_i$ is included in the numerator because it is the amount of tap water used to wash the raw ice.

For NaCl solution tests, the ice salinity was measured by a conductivity meter (Lab960, SCHOOT instrument, Germany). For artificial seawater and real seawater tests, the ion composition was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-OES, Optima 7300DV, Perkin Elmer, USA).

To achieve the highest purity and productivity, the parameters that were optimized in this process are coolant temperature, process duration, supercooling, agitation and washing design. Each of them was investigated under *ceteris paribus* conditions. (i.e., with other conditions remaining the same). For comparison, a base case was established where a NaCl solution (35 g/kg) of 1kg was cooled for 1 h without supercooling, agitated by the stirrer at 100 rpm and a coolant temperature of -8 °C.

After optimizing the operation parameters using the NaCl solution, both artificial and real seawater were tested respectively under the optimal conditions. The artificial seawater contained all the major ions of seawater, so it served as a better simulation than the NaCl solution. After understanding the roles of Mg^+ , Ca^{2+} and K^+ , real seawater that has a much more complicated composition was finally tested.

Each test was repeated at least 3 times to check reliability and the average values were reported.

4. Results and discussion

4.1. Determination of major parameters

The major process parameters that greatly affect the FD unit performance are washing procedure, coolant temperature, process duration, supercooling and agitation (Rahman et al., 2006). Among them, washing procedure outweighs other parameters because the product water must contain minimal impurities and the salts adhered onto the ice crystals' surfaces actually account for most of the impurities (Kobayashi et al., 1996).

4.2. Washing procedures

4.2.1. The amount of washing water without recycling

Fig. 5(a) shows the salinity of the product ice as a function of η (i.e., the mass ratio of chilled tap water to raw ice) with a stepwise increment of 10%. The salinity decreases after each step of washing. After six steps, the ice salinity meets the WHO potable water standard (<0.5 g/kg). In other words, to meet this standard, the amount of washing water should be about 60 wt% of the raw ice. This translates to that about 40% of the raw ice can be delivered as the product ice, considering a portion of the clean ice will be consumed as washing water. To simplify the washing procedure, the η value is increased in each step and the effects are depicted in Figs. 5(b)-(d). Two conclusions may be drawn from these results. Firstly, the required washing steps can be reduced with an increase in stepwise η value and produce ice that meets the WHO standard. Secondly, regardless of the η value, the total amount of washing water is all the same, which is 60 wt% of the raw ice. This proves the proposition that the total η value has to be about 60 wt%. It may be noted that the simplest case of one-step washing with an η value of 60 wt% is not included in the figure. That is because the resultant ice has a salinity of 1.101 g/kg. Therefore, at least a two-step washing should be applied.

It is worth noting that during washing, all measures were taken to minimize agglomeration of ice crystals. For instance, any compression or other external forces should be avoided on the ice bed. This is also part of the reasons why centrifugal separation is not chosen in this study to separate wastewater from the ice in the washing step.

4.2.2. The amount of washing water with recycling

To reduce the amount of tap water for ice washing, the used washing water is recycled to wash ice. A simple two-step washing is investigated. As illustrated in Fig. 6, the wastewater from the 1st step of ice washing has a high salinity close to the concentrated feed left in the reactor, whereas the one from the 2nd step of ice washing has a salinity of about 11.47 g/kg. The latter is about 80% lower in salinity than the former. It is because the porous ice bed exposes most of the crystal surfaces. After a full contact, the first stream of tap water is able to dissolve most of the surface impurities by the time when it flows away from the bed. Since there is a small amount of residues left, the wastewater from the second step is much less concentrated. Therefore, the wastewater from the 2nd step of ice washing (i.e., referred to as the wastewater 2) could be reused to wash the raw ice. To demonstrate the feasibility, experiments were conducted as presented in Fig. 7. The wastewater from the 2nd step of ice washing (i.e., wastewater 2) in batch A is reused to wash the raw ice in batch B. As a result, the tap water needed in batch B is only 40 wt% of the raw ice, which is a reduction of 20%. When combining these two batches together, one can expect that the total amount of tap water for ice washing is reduced to about 50 wt% of the raw ice.

If the wastewater from the 3rd step of ice washing in batch B (i.e., referred to as the wastewater 3 in Fig. 7) is reused, then the amount of washing water may be further reduced

to below 50 wt% of the raw ice. The reuse of washing water from more than two batches of ice washing will be studied in the future. In addition, the concentrated wastewater left from FD may be recyclable using membrane (MD) because it is less sensitive to the feed concentration (Khayet and Matsuura, 2011; Wang and Chung, 2015; Wang and Chung, 2012).

4.3. Effects of coolant temperature

As illustrated in Sections 2.3 and 2.4, the feed solution undergoes freezing process at equilibrium point (i.e., freezing point). Therefore, the driving force for freezing is the temperature difference between the feed solution and the circulating coolant. A large temperature difference would facilitate a higher ice production rate. However, an excessive driving force would distort the freezing process. When coolant temperature is lower than -10 °C, a thick ice layer would quickly form on the cylinder wall within minutes. The fast agglomeration of ice may trap salts inside, which are difficult to be washed away. In addition, the dense ice layer is difficult to be peeled off from the cylinder wall. Thus, a very large temperature difference is not desirable. On the contrary, a very small temperature difference would prolong the ice production process. Hence, an optimal coolant temperature should be identified.

Fig. 8 shows the ice recovery rate and salinity as a function of coolant temperature. The experiments were conducted using seed ice of 1g at -2.1 °C with an agitation speed of 100 rpm for 1 h and then washed optimally using chilled tap water equal to 50 wt% of the raw ice with recycling. A sufficiently high coolant flow rate was used throughout the study so that the coolant temperature increased a negligible amount after passing the cooling jacket. The resultant ice salinity varies in the range of 0.3-0.4 g/kg when the coolant temperature is

higher than or equal to -8°C . However, the ice salinity increases to 0.81 g/kg at -9°C , which is higher than the WHO purity standard, because the ice layer is formed on the cylinder wall. The trapped concentrated salt solution between the ice crystals cannot be easily removed.

Fig. 8 also shows that the ice recovery rate increases from 8.1% to 23% when the coolant temperature drops from -5°C to -9°C . However, the ice recovery rate only increases 1.9% from -8°C to -9°C , whereas it increases around 4.3% per degree of temperature drop in the range of -5°C to -8°C . The former is due to the fact that the ice layer on the cylinder wall impairs the heat exchange between the brine and the coolant, while the latter arises from the fact that ice crystals can hardly form a layer on the wall when the coolant temperature is at -8°C or above. The incorporation of a scraper to constantly remove the ice layer will be investigated in future studies. Thus, to maximize the ice production whilst maintaining high purity water, -8°C should be the best coolant temperature.

4.4. Effects of freezing duration

Apart from coolant temperature, freezing duration also determines the amount of ice produced. Generally, a longer duration would yield a higher ice production, but the purity of product ice may be sacrificed at a very high yield. There is an optimal duration to achieve both high recovery and purity.

Fig. 9 shows the effect of freezing duration on ice recovery and salinity under the same condition as Fig. 8 except the coolant temperature was set at -8°C for various durations. When the duration is shorter than 1.75 h , the ice recovery increases with time and the salinity

remains in the acceptable range. Results of very long durations are not presented here because the resultant ice is very impure with a salinity higher than 1 g/kg.

When increasing the freezing duration, the ice appearance in the reactor changes sharply. When about 20 - 30% of the seawater freezes to ice, an ice bed can be easily seen floating on top of the brine. Unlike an iceberg that rises above the sea, the ice bed remains below the brine surface due to the strong capillary effect. When the ice amount increases to roughly 40 wt% of the feed, it fully occupies the brine volume and therefore only a uniform ice slurry can be observed. Based on experimental results, converting 55% of the seawater to ice would be close to its limit and any further cooling would increase the recovery in a much slower manner. Furthermore, when it is higher than 55%, all the remaining brine would be absorbed into the voids of the porous ice bed due to the strong capillary effect. As a result, the entire system loses its fluidity and causes severe difficulties in subsequent transferring steps. In other words, it is suggested to convert only up to 50 - 55% of the seawater to ice in a single stage FD, which corresponds to an ice recovery rate of 25 - 27.5% after considering the amount of washing water. Therefore, the optimal freezing duration is around 1.5 h.

4.5. Effects of seeding at different temperatures

Without seeding, the feed NaCl solution starts homogeneous nucleation at -9.8 °C. The metastable zone (Myerson and Ginde, 2002) is therefore between -9.8 °C and -2.1 °C. The seed could be introduced at any solution temperature in the metastable zone. Fig. 10 shows the effect of seeding temperature on ice recovery and salinity. A low seeding temperature increases the ice production almost linearly while maintaining a reasonable purity. When homogeneous nucleation happens at -9.8 °C, ice crystals form rapidly in a short time. Thus,

the exclusion of salts from ice is compromised. The ice formed at this temperature has a salinity above the acceptable range.

Although a higher recovery rate can be achieved by seeding at a lower temperature, it is actually at the cost of more energy consumption. For instance, it took 42 min to cool the solution from -2.1°C to -9.8°C . Since the freezing duration lasted another 1 h, the entire duration was actually extended to nearly 1.75 h. However, its ice recovery rate of 27.2% is very comparable to that of 28.1% in Fig. 9, which was conducted at -8°C for 1.75 h. In addition, the former has an ice salinity much higher than the latter (0.6 vs. 0.31 g/Kg) and the WHO standard (0.5 g/Kg). Therefore, the degree of supercooling should be smaller than 7°C . In addition, cooling the solution below its freezing point becomes harder and harder because its heat capacity also increases simultaneously (Holten et al., 2012). One should not keep lowering the solution temperature when it is already able to produce ice. With a small amount of seed ice, it can easily eliminate the waiting period towards lower temperatures and induce a smooth transit between phase changes.

4.6. Effects of seeding amount

Fig. 11 shows the amount of ice production and its salinity as a function of the amount of seed ice (M_s) added into the feed at -2.1°C . The more the seeds result in the more the ice (M_{pi}). Surprisingly, after subtracting the mass of the seed ice, the net ice production decreases with an increase in the amount of seed ice because of the redundancy of excessive seeding.

To understand why more seeding results in a lower net ice production, the role of seeding needs to be elaborated. Essentially, it is to trigger the onset of nucleation, so a fraction of seed

ice is enough to serve the purpose. Assuming the minimum amount is M_{s-min} , then the extra portion of the seed ice (i.e., $M_s - M_{s-min}$) is redundant to activate the nucleation. In addition, it occupies the space for the ice formation from the feed. Therefore, as shown in Fig. 11, 1 g of seed ice is enough in the current case. This amount can be further reduced. Nonetheless, it is needless in this study because 1 g is already reasonably minuscule. The ice-seeding amount is thus recommended to be 0.1 wt% of the feed solution, which should be practical and economical.

4.7. Effects of agitation

Freezing is a highly heat sensitive process where a large amount of heat has to be exchanged between the cylinder and the seawater crystallizer instantaneously. Apart from the thermal conductivity of the cylinder wall, mixing in the system also plays a crucial role.

As shown in Fig. 12, the ice recovery rate improves from 18.7% to 21.4% when speeding up the stirrer from 50 rpm to 100 rpm. This is because a better agitation increases the heat transfer rate and reduces the concentration polarization. When a freezing process starts, water molecules are integrated into ice crystal lattices and the adjacent salt concentration rises (Gay et al., 2003). Without enough mixing, concentration polarization takes place and makes the crystal growth difficult. Therefore, increasing agitation improves the ice recovery. Meanwhile, the ice salinity drops from 0.52 g/kg to 0.33 g/kg because the crystal surfaces are no longer contiguous with locally concentrated brine. However, the ice recovery rate remains nearly the same (21.4%) if a further increase in agitation to 150 rpm. This indicates that 100 rpm is sufficient to mitigate the localized concentration polarization. Hence, a moderate amount of agitation, such as 100 rpm, would be feasible and advisable.

4.8. Morphology of ice crystals

Fig. 13 shows that ice crystals obtained from various conditions appear in clusters of amorphous shapes. Their sizes vary widely, but most of them are in the range of 0.3 – 1 mm. The formation of amorphous ice crystals can be comprehended according to the Kossel (1934) model of crystal growth (Mullin, 2001), as illustrated in Fig. 14. Crystals grow the fastest at kinks and gradually complete the surface. A fresh crystal could commence on the surface or at the corners, but its growth rate is much slower than those at kinks. Therefore, the maximum growth rate takes place theoretically when the surface is full of kinks. Since collisions among crystals in turbulent freezing conditions keep generating numerous kinks, it produces the ice crystals with irregular surfaces and amorphous morphologies very fast in this study.

Many studies in literatures preferred a much slower ice production because they aimed to form larger ice crystals with an easier washing step. As a result, their ice crystals must grow very slowly in static environments (Rahman et al., 2006; Williams et al., 2015) and took hours or even days for freezing duration (Williams et al., 2015; Mahdavi, 2011; Badawy, 2015). The speedy ice growth in this study comes partially from the smaller crystal sizes. It might appear harder to be washed, but the dilemma is alleviated since the proposed vacuum-filtration washing is highly efficacious. Besides, small ice crystals add a bonus to the melting step as they melt faster.

4.9. Iron crystallizer

The aforementioned studies were conducted using a crystallizer consisting of a glass cylinder wall. A metal one with the same dimension was also studied for comparison. Since the thermal conductivity of iron is around 50 - 80 times of glass (Tritt, 2004), it was expected to expedite the freezing process. As shown in Table 2, the iron cylinder generally raises the ice recovery rate by 1.2 – 1.8 times. Surprisingly, the lowest possible coolant temperature ensuring an acceptable purity is found to be around -8 °C, which is the same as that for the glass crystallizer. Similarly, a thick ice layer with a higher salinity was formed at -9 °C or below. Even though the iron cylinder facilitates heat transfer towards the seawater, it does not exacerbate the formation of a thick ice layer on its wall. This suggests temperature difference plays a more important role than cylinder material on the formation of the thick ice layer. Since a metal cylinder wall is a more practical choice than a glass one when scaling up the FD process, the above finding is encouraging because the formation of a thick ice layer on the iron cylinder is just as manageable as on a glass one.

4.10. Artificial seawater and real seawater tests

After understanding the key operating parameters for the freeze desalination of the 3.5wt% NaCl solution, both artificial and real seawater were tested under the optimum conditions using an iron cylinder. 520 ~ 525 g of raw ice was formed from a 1 kg feed solution within 1 h. After deducting the mass of seed and washing water, it translates to a recovery rate of about 26%. This value agrees with the result of 26.7% obtained from the NaCl solution. Table 3 lists the compositions of the melted ice. They have the total dissolved solid (TDS) of 310 ppm to 320 ppm, these values are very close to the ice made from the NaCl solution (i.e., 0.33 g/kg or 330 ppm). Thus, it affirms that FD technology is promising to desalinate real seawater.

Fig. 15 compares the relative percentages of major ions Mg^{+} , Ca^{2+} and K^{+} in feeds and product ice in details. Interestingly, the relative percentage of each ion is similar in both the feed and product ice. This suggests that none of these ions preferentially remains in the product ice because salt ions in the solution mainly adhere onto the ice surfaces and they are not trapped in the ice lattices. The non-trapping behaviors are important and desirable for freeze desalination of real seawater, especially in the washing process. Therefore, the process parameters optimized in this study provide good guidelines for the further development of the FD process.

5. Conclusion

In this work, the operating parameters and washing procedure of indirect contact FD using LNG were systematically investigated and optimized. The following conclusions can be drawn:

- 1) The importance of an effective washing procedure outweighs many other operating parameters. Vacuum filtration was found to effectively separate ice from the washing water. The amount of washing water needed was optimized to be 50 wt% of the raw ice.
- 2) While LNG is the source of cold energy, an intermediate coolant would be used to cool the seawater. The optimal coolant temperature should be around $-8^{\circ}C$. When using a colder coolant, a thick ice layer would likely form on the cylinder wall and thus reduce the purity of the product ice.

3) The optimal freezing duration was found to be 1 h for an iron crystallizer and 1.5 h for a glass crystallizer. With a longer duration, the amount of ice would significantly reduce the solution's fluidity. Heat and mass transfer would then be greatly impaired.

4) Seed ice should be added to the feed seawater when it reaches freezing the point. It would trigger nucleation and ensure a smooth transit to freezing. The amount of seed ice was optimized to be 0.1 wt% of the feed solution. An excess amount of seed ice would actually decrease the net ice production.

5) Homogeneous mixing was also indispensable in this process. A moderate stirrer speed of 100 rpm was found to be practical and economical. Insufficient agitation would impede heat and mass transfer, while excessive agitation would waste energy.

6) Both artificial seawater and real seawater were tested under the optimized conditions. The product ice's amount and salinity were both very close to those obtained from the 3.5 wt% NaCl solution. Raw ice of 520 ~ 525 g was formed from a 1 kg feed solution within 1 h, which corresponds to a recovery rate of about 26%. Thus, the process parameters optimized in this study can be directly used for the freeze desalination of seawater.

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References

- Al-Shammiri, M. and Safar, M. (1999) Multi-effect distillation plants: state of the art. *Desalination* 126(1–3), 45-59.
- Badawy, S.M. (2015) Laboratory freezing desalination of seawater. *Desalination and Water Treatment*, 1-8.
- Cao, W., Beggs, C. and Mujtaba, I.M. (2015) Theoretical approach of freeze seawater desalination on flake ice maker utilizing LNG cold energy. *Desalination* 355(0), 22-32.
- Efrat, T. (2011) Utilizing available “coldness” from Liquefied Natural Gas (LNG) regasification process for seawater desalination, IDA World Congress.
- Fritzmann, C., Löwenberg, J., Wintgens, T. and Melin, T. (2007) State-of-the-art of reverse osmosis desalination. *Desalination* 216(1–3), 1-76.
- Fujioka, R., Wang, L.P., Dodbiba, G. and Fujita, T. (2013) Application of progressive freeze-concentration for desalination. *Desalination* 319(0), 33-37.
- Gay, G., Lorain, O., Azouni, A., Aurelle, Y. (2003) Wastewater treatment by radial freezing with stirring effects. *Water Research* 37(10), 2520-2524.
- Gooch, J.W. (2011) *Encyclopedic Dictionary of Polymers*. Gooch, J.W. (ed), pp. 326-326, Springer New York, New York, NY.

Gude, V.G. (2016) Desalination and sustainability – An appraisal and current perspective. Water Research 89, 87-106.

Halde, R. (1980) Concentration of impurities by progressive freezing. Water Research 14(6), 575-580.

Harriott, P., Leinroth Jr, J.P., Von Berg, R.L. and Wiegandt, H.F. (1969) Comments on “an analysis of counterwashers for freeze-distillation desalination” by Schwartz and Probststein. Desalination 6(1), 117-119.

Holten, V., Bertrand, C.E., Anisimov, M.A. and Sengers, J.V. (2012) Thermodynamics of supercooled water. The Journal of Chemical Physics 136(9), 094507.

Johnson, W.E. (1976) State-of-the-art of freezing processes, their potential and future. Desalination 19(1–3), 349-358.

Kang, G.D. and Cao, Y.M. (2012) Development of antifouling reverse osmosis membranes for water treatment: A review. Water Research 46(3), 584-600.

Khayet, M. and Matsuura, T. (2011) Membrane Distillation: Principles and Applications, Elsevier, Amsterdam.

Kobayashi, A., Shirai, Y., Nakanishi, K. and Matsuno, R. (1996) A method for making large agglomerated ice crystals for freeze concentration. Journal of Food Engineering 27(1), 1-15.

Lorain, O., Thiebaud, P., Badorc, E. and Aurelle, Y. (2001) Potential of freezing in wastewater treatment: soluble pollutant applications. *Water Research* 35(2), 541-547.

Lu, Z., Xu, L. (2010) Freezing desalination process. *Encyclopedia of Desalination and Water Resources Thermal Desalination Processes*.

Mahdavi, M., Mahvi, A.H., Nasser, S. and Yunesian, M. (2011) Application of Freezing to the Desalination of Saline Water. *Arabian Journal for Science and Engineering* 36(7), 1171-1177.

Mandri, Y., Rich, A., Mangin, D., Abderafi, S., Bebon, C., Semlali, N., Klein, J.P., Bounahmidi, T. and Bouhaouss, A. (2011) Parametric study of the sweating step in the seawater desalination process by indirect freezing. *Desalination* 269(1-3), 142-147.

McGovern, R.K. and Lienhard V, J.H. (2014) On the potential of forward osmosis to energetically outperform reverse osmosis desalination. *Journal of Membrane Science* 469, 245-250.

Miyazaki, T., Kang, Y.T., Akisawa, A. and Kashiwagi, T. (2000) A combined power cycle using refuse incineration and LNG cold energy. *Energy* 25(7), 639-655.

Muldrew, K., McGann, L.E. (1999) *Physical Aspects of Freezing*, University of Alberta, Cryobiology - A Short Course. Available from: http://people.ucalgary.ca/~kmuldrew/cryo_course/course_outline.html, (accessed 16.04.23).

Mullin, J.W. (2001) *Crystallization* (Fourth Edition). Mullin, J.W. (ed), pp. 216-288, Butterworth-Heinemann, Oxford.

Myerson, A.S. and Ginde, R. (2002) *Handbook of Industrial Crystallization* (Second Edition), Butterworth-Heinemann, Woburn.

Nebbia, G. and Menozzi, G.N. (1968) Early experiments on water desalination by freezing. *Desalination* 5(1), 49-54.

Qin, J.J., Wai, M.N., Oo, M.H., Kekre, K.A. and Seah, H. (2009) Impact of anti-scalant on fouling of reverse osmosis membranes in reclamation of secondary effluent. *Water Science & Technology* 60(11), 2767-2774.

Rahman, M.S., Ahmed, M. and Chen, X.D. (2006) Freezing-melting process and desalination: I. Review of the state-of-the-art. *Separation and Purification Reviews* 35(2), 59-96.

Randall, D.G. and Lewis, A.E. (2009) Seeding for selective salt recovery during Eutectic Freeze Crystallization. *International Mine Water Conference*, 19–22 October, Pretoria, South Africa, 639–646.

Randall, D.G. and Nathoo, J. (2015) A succinct review of the treatment of Reverse Osmosis brines using Freeze Crystallization. *Journal of Water Process Engineering* 8, 186-194.

Randall, D.G., Nathoo, J., Genceli-Güner, F.E., Kramer, H.J.M., Witkamp, G.J. and Lewis, A.E. (2012) Determination of the metastable ice zone for a sodium sulphate system. *Chemical Engineering Science* 77, 184-188.

Reddy, S.T., Kramer, H.J.M., Lewis, A.E and Nathoo, J. (2009) Investigating factors that affect separation in a eutectic freeze crystallisation process. Abstracts of the International Mine Water Conference, Document Transformation Technologies, 649–655.

Rich, A., Mandri, Y., Bendaoud, N., Mangin, D., Abderafi, S., Bebon, C., Semlali, N., Klein, J.P., Bounahmidi, T., Bouhaouss, A. and Vessler, S. (2010) Freezing desalination of sea water in a static layer crystallizer. *Desalination and Water Treatment* 13(1-3), 120-127.

Rich, A., Mandri, Y., Mangin, D., Rivoire, A., Abderafi, S., Bebon, C., Semlali, N., Klein, J.-P., Bounahmidi, T., Bouhaouss, A. and Vessler, S. (2012) Sea water desalination by dynamic layer melt crystallization: Parametric study of the freezing and sweating steps. *Journal of Crystal Growth* 342(1), 110-116.

Roberts, D.A., Johnston, E.L. and Knott, N.A. (2010) Impacts of desalination plant discharges on the marine environment: A critical review of published studies. *Water Research* 44(18), 5117-5128.

Sherwood, T.K., Brian, P.L.T. (1966) Research on saline water conversion by freezing, pp. 29-43, U.S. Govt. Print. Off., Washington

Shirai, Y., Wakisaka, M., Miyawaki, O. and Sakashita, S. (1999) Effect of seed ice on formation of tube ice with high purity for a freeze wastewater treatment system with a bubble-flow circulator. *Water Research* 33(5), 1325-1329.

Shwartz, J. and Probstein, R.F. (1968) An analysis of counterwashers for freeze-distillation desalination. *Desalination* 4(1), 5-29.

Sirkar, K.K., Dang, P.T. and Rao, G.H. (1982) Approximate design equations for reverse osmosis desalination by spiral-wound modules. *Industrial & Engineering Chemistry Process Design and Development* 21(3), 517-527.

Subow, N. N. (1931) Oceanographical tables. U.S.S.R., pp. 208-208, Oceanogr. Institute, Hydro-meteorol. Com., Moscow.

Subramani, A. and Jacangelo, J.G. (2015) Emerging desalination technologies for water treatment: A critical review. *Water Research* 75, 164-187.

Tiller, W.A. (1992) *The Science of Crystallization: Macroscopic Phenomena and Defect Generation*, Cambridge University Press.

Tleimat, B.W. (1980) *Principles of Desalination (Second Edition)*. Laird, K.S.S.D.K. (ed), pp. 359-400, Academic Press.

Tritt, T.M. (2004) *Thermal conductivity: theory, properties, and applications*, Springer, New York.

- Valladares Linares, R., Li, Z., Sarp, S., Bucs, S.S., Amy, G. and Vrouwenvelder, J.S. (2014) Forward osmosis niches in seawater desalination and wastewater reuse. *Water Research* 66, 122-139.
- Wang, P. and Chung, T.S. (2012) A conceptual demonstration of freeze desalination-membrane distillation (FD-MD) hybrid desalination process utilizing liquefied natural gas (LNG) cold energy. *Water Res* 46(13), 4037-4052.
- Wang, P. and Chung, T.S. (2015) Recent advances in membrane distillation processes: Membrane development, configuration design and application exploring. *Journal of Membrane Science* 474, 39-56.
- Williams, P.M., Ahmad, M., Connolly, B.S. and Oatley-Radcliffe, D.L. (2015) Technology for freeze concentration in the desalination industry. *Desalination* 356(0), 314-327.
- Zhao, S., Zou, L., Tang, C.Y. and Mulcahy, D. (2012) Recent developments in forward osmosis: Opportunities and challenges. *Journal of Membrane Science* 396, 1-21.
- Zuo, J., Bonyadi, S. and Chung, T.S. (2016) Exploring the potential of commercial polyethylene membranes for desalination by membrane distillation. *Journal of Membrane Science* 497, 239-247.

Zvinowanda, C.M., Zikalala, N.N., Mtombeni, T., Maree, J.P., Louw, W.J. and Oosthuizen, F. (2014) Process optimization of freeze desalination of brine using HybridICE(TM) pilot plant. *Desalination and Water Treatment* 52(34-36), 6315-6324.

Nomenclature

K_{FP} = cryoscopic constant

L_f = latent heat of fusion

m = molality (mol solute/1000 g solvent)

M_0 = mass of feed solution

M_i = mass of raw ice

M_{pi} = mass of product ice

M_s = mass of seed ice

r^* = critical radius

T_f = freezing temperature

ΔT = temperature difference departed from freezing point

ΔT_f = freezing point depression

Greek symbols

σ = interfacial tension between water and ice

η = percentage of washing water's mass relative to raw ice

ϕ = ice recovery rate

List of Abbreviation

FD: freeze desalination

740 LNG: liquefied natural gas

741 MED: multi-effect distillation

742 RO: reverse osmosis

743 TDS: total dissolved solid

744 WHO: world health organization

745

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Fig. 13 – The morphologies of ice crystals. (Feed: 35 g/kg NaCl solution; Coolant temperature: $-8\text{ }^{\circ}\text{C}$; freezing duration: 1 h; agitation: 100 rpm; seed ice: 1 g at $-2.1\text{ }^{\circ}\text{C}$; optimized washing: chilled tap water = 50 wt% of the raw ice)

Fig. 14 – Kossel's model of a growing crystal surface, (A) flat surfaces, (B) steps, (C) kinks, (D) surface-adsorbed growth units, (E) edge vacancies, and (F) surface vacancies (Mullin, 2001).

Fig. 15 – Compositions of (a) artificial seawater, (b) ice produced from artificial seawater, (c) real seawater, (d) ice produced from real seawater.

Table 1: The compositions of artificial seawater & real seawater

(a)

Artificial seawater composition (Subow, 1931)								
Salt	NaCl	MgCl ₂	MgSO ₄	CaCl ₂	KCl	NaHCO ₃	NaBr	Total
g/kg	26.518	2.447	3.305	1.141	0.725	0.202	0.083	34.421

(b)

Real seawater composition								
Component	Ca	Mg	Na	K	Ba	Sr	CO ₃	HCO ₃
mg/kg	396.15	1485.45	9895.1	791.35	0.099	7.9225	24.1	107.4

Component	SO ₄	Cl	F	NO ₃	B	SiO ₂	CO ₂	TDS
mg/kg	2872.25	19793.5	2	1	4.79	4.95	0	35386.05

Table 2: A comparison of the effects of cylinder materials on ice recovery and salinity*

Run	Cylinder material	Coolant temperature (°C)	Process duration (h)	Ice recovery rate (%)	Ice salinity (after washing) (g/kg)
1	Glass	-8	0.5	11	0.32
2	Iron	-8	0.5	20	0.39
3	Glass	-8	1	21	0.33
4	Iron	-8	1	27	0.32
5	Glass	-9	1	23	0.81
6	Iron	-9	1	30	0.65

*Feeds: 1 kg NaCl solution (35 g/kg); seed ice: 1 g at -2.1 °C; agitation: 100rpm; optimized washing: chilled tap water = 50 wt% of the raw ice.

Table 3: Ice compositions, after washing ice made from artificial seawater & real seawater*

(a) Ice salinity of artificial seawater tests					
Component	Na ⁺	Mg ²⁺	Ca ²⁺	K ⁺	TDS
ppm	92.96 ±7.92	11.8 ±0.99	5.56 ±0.45	5.6 ±1.1	315.52 ±23.86

(b) Ice salinity of real seawater tests					
Component	Na ⁺	Mg ²⁺	Ca ²⁺	K ⁺	TDS
ppm	94.57 ±15.74	12.2 ±1.94	6.99 ±0.80	3.58 ±2.11	321.45 ±52.74

*Feeds: 1 kg artificial seawater or real seawater; freeze duration: 1 h using an iron cylinder; coolant temperature: -8 °C; seed ice: 1 g at -2.1 °C; optimized washing: chilled tap water = 50 wt% of the raw ice.

Fig. 1: (a) The critical radius relative to temperature (b) A water cluster's radius when it wets a surface (Muldrew and McGann, 1999).

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Fig. 6: Salinities of brine and wastewater after the 1st and 2nd step washing from FD.

Batch A **Batch B**

Fig. 7: Flowchart of the FD operation with the recycling of low concentrated wastewater.

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Fig. 15: Compositions of (a) artificial seawater, (b) ice produced from artificial seawater, (c) real seawater, (d) ice produced from real seawater.

- The major operating parameters of freeze desalination were investigated in depth.
- We studied the washing step in detail, while most previous researches did not.
- The optimization results can be directly used for the freeze desalination of real seawater