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Desalination by Freeze Crystallization: An Overview

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Abstract

Desalination by freeze crystallization is a freezing-melting process in which water is crystallized to ice and separated from saline solution. This area is observing a renascence to mitigate the staggering and sea rejected brine that has a negative environmental impact. Phase diagram of NaCl-H_2O is the key point of designing freeze desalination systems. All freeze crystallization methods follow the same process, starting from nucleation, crystal growth, separation, and finally melting. Direct contact, indirect contact, vacuum, and eutectic point are the basic methods of crystallization. Furthermore, suspension freezing and freezing on a cold plate by indirect contact with refrigerant are the found to be the most suitable methods for desalination. Initial concentration, refrigerant temperature, growth rate, and flow rate are the main operating parameters that determine the final product properties and desalination efficiency. In this work, a quick review on the subject is brought up as the area is regaining renascence this followed with simulation of an indirect freeze crystallization process in a rectangular enclosure using computational fluid dynamics (CFD) modelling. These modeling are paradigm shift to gain more insight to the complex crystallization process being based on multiple species non-isothermal flow in a two phase flow representing the liquid and the ice formation. Results show that by combined CFD in multiple species modelling much insight into freeze crystallization can be revealed, optimized and re-designed.

Keywords: *freeze desalination, crystallization, crystal growth, binary phase diagram, CFD modelling*

1. Introduction

Ice crystallization is exceedingly complex coupled fluid and two phase flow with heat transfer that trigger the ice nucleation and crystal growth. There is much interest in understanding of this process and parametrical influence such as the temperature, saturation level and other process conditions on the kinetics of ice crystal nucleation and growth [1]. This is due to the vast application of this process in food preservation, ice and frozen dessert making, and fruit juice concentration as well as renascence interest in freeze desalination [2-5]. Freeze desalination (FD) is used for water treatment by separating fresh water from saline solution in the form of ice crystals then followed with melting. Was pioneered by Thomas Bartholinus (1680) who stated that fresh water can be obtained by the melting of ice formed from seawater [6]. Freeze desalination were first used commercially in the 1950s [7]. In 1950, Karnofsky and Steinhoff [8], and Weigandt [9] were the first to proposed direct freezing process with butane as a refrigerant for saline water desalination.

In physical chemistry, ice crystals formed are made up of essentially pure water when heat is removed from saline water and thus lowering its temperature to its freezing point, since a crystal excludes impurities from its structure as they grow. Contrary to distillation being multistage flashing or Direct contact Membrane [10-12], the freezing method utilizes the phase change of water from liquid to solid. Further to crystallization, it involves the separation of the ice crystals from the brine, cleaning to remove any salts on the crystals surface, and ice melting to get lastly fresh water [13].

The general interest in desalination by freezing opposite to other desalination technologies such as thermally driven distillation and evaporation ponds, comes from the much lower heat of fusion of ice compared to the heat of evaporation of water. Energy requirement can be reduced by 75 to 90% as the latent heat of fusion of ice is 333 kJ/kg and that of evaporation of water is 2,500 kJ/kg [14]. Less fouling and corrosion problems, as well as the capability of using low-cost materials and no required pretreatment are also advantages of desalination by freeze crystallization [15].

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As depicted in Fig.1, all freeze desalination methods involve two main stages [6,16]. First Stage is the crystallization of ice by heat removal of saline water, where nucleation and growth of ice takes place in the freezing chamber (or crystallizer) at a certain supercooling temperature. The second stage is separation and melting. In this latter stage, the produced ice crystals are separated from the final concentrated brine, and then melted to produce fresh water as a final product of the process [6].

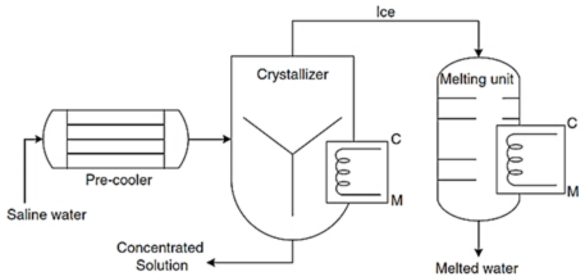

Figure 1. Freeze crystallization process [6], pre-cooler to remove the heat, crystallizer to obtain and separate ice crystal, melting to obtain desalinated water

Recently, Rahman et. al [15], and Chen [17] have stated that the cost of water desalination by thermal processes is $1.85 per 1000 kg (1m^3) of water, whereas the cost of water desalination by freezing is $0.93 per m^3 of water. However, in modern water desalination plants in UAE, thermal desalination cost is only $0.84 per m^3 of water. Himawan [18] found that a saving of 60 % of energy costs can be achieved if eutectic freezing crystallization is used for recovering both ice and magnesium sulphate from an industrial waste stream compared to evaporative crystallization.

Williams et al. [5] has proposed a hybridization of Al Khadimah reverse osmosis plant using a falling film crystallization for waste brine treatment. They found that if freeze crystallization (FC) plant is integrated, the estimated annual rate of reverse osmosis (RO) waste brine from the RO plant can be significantly reduced from 191.84 t/year to 23.39 t/year. Wang et al. [19] have also performed a feasibility study of freeze desalination with direct contact membrane distillation (FD-DCMD) hybrid desalination process utilizing the waste cold energy released from the re-gasification of liquefied natural gas. Progressive freeze crystallization method was used first followed by DCMD, total water recovery of 71.5 % with high quality drinkable water (salinity ~0.144 g/L) was achieved. Moreover, Randall et. al [20] has also conducted a case study on treating RO waste brine using the eutectic freeze crystallization. They approached zero-waste process with 99.9% overall water recovery. However, higher capital cost is needed for such desalination process, as with all new technologies [20].In this work, a quicke review of the crystallization concept and different freezing methods are presented and compared. Illustration of the crystal properties represented by crystal size, effective partition constant, and solute yield. Additionally, the effect of different performance parameters (e.g. intial concentration, freezing temperature, growth rate, etc.) on the previously mentioned crystal properties is also detailed in this work. Moreover, numerical simulation of a batch freeze desalination process in a rectangular enclosure is carried out using a multispecies non-isothermal computational fluid dynamic (CFD) model of two-phase flow in an attempt to bring more insight to the freez desalination process and its parameters.

2. Overview of Freeze Crystallization System

2.1. Concept and methods

The principle of desalination by freeze crystallization can be described by the typical phase diagram of binary solution which represents the equilibrium lines between sold and liquid states of materials. Phase change diagram of Saline water (NaCl-H_2O) is depicted in Fig 2. Line 1 defines the freezing point of water at different sodium chloride mass content, whereas line 2 represents the solubility curve of NaCl in water. The starting point is on the left side of the eutectic point where ice crystallizes first. The unsaturated saline solution is cooled until reaching the supercooling temperature; at which first ice crystal forms in binary solution and it is mainly reduced linearly at higher solute weight percentage. Further cooling will take the solution along the curve defined by line 1 until the eutectic point is reaches at -21.2˚C (for NaCl-H_2O mixture). At this point, the unfrozen portion of the mixture is saturated with NaCl; any further cooling will cause solid salt formation and no more brine is present.

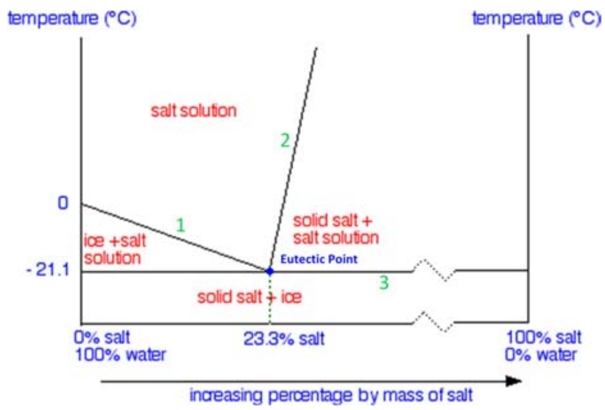

Figure 2. Phase diagram of NaCl-H_2O solution [21], showing the reduction in freezing temperature with increase of salt concentration line1, eutectic point below which solid salts and ice formed, and the solubility curve of NaCl in water line 2.

For instance, seawater at typical salinity of 35 ppt (3.5%) has a freezing point at -2 ˚C [22], and thus, ice crystals consist of pure water starts to nucleate at this temperature and continue growing by further temperature reduction. Whereas for high concentrated brine solutions, nucleation of ice crystals happens at lower freezing points as illustrated in Fig.2.
The questions of interest are how to precipitate the crystals and how to make them grow to suitable sizes and size distributions to ensure successive recovery of water in pure form and ease of handling. This can be accomplished by a suitable design of the crystallization system. The main flow of any separation by crystallization method involves sequentially: the crystallization, the separation, the washing and finally the melting. Fig.3 depicts the flow of general crystallization system. These steps can be done in single enclosed system such as a low temperature rotating drum immersed in the brine solution. It should also be noted that crystallization is a stochastic process and with either electrical stimulation or ultrasound additional to surface or heterogeneous seeding can render the process more control and productivity.

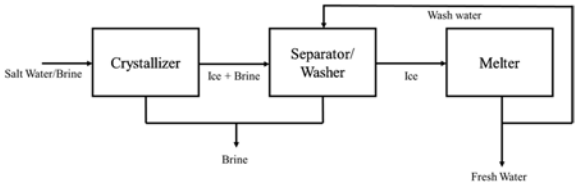

Figure 3. Flow diagram of a basic freeze crystallization system

Different methods of freeze crystallization were mentioned in literature with direct contact, indirect contact, vacuum, and eutectic freeze crystallization are the basic four methods [6,23]. Though, recent developments in freeze crystallization introduced two new methods for ice crystal formation which fall within the indirect contact crystallization: Crystallization by suspension, and crystallization on a cold surface [5,6,19-20,23]. Fig. 4 summarizes the various methods of crystallization as they described next.

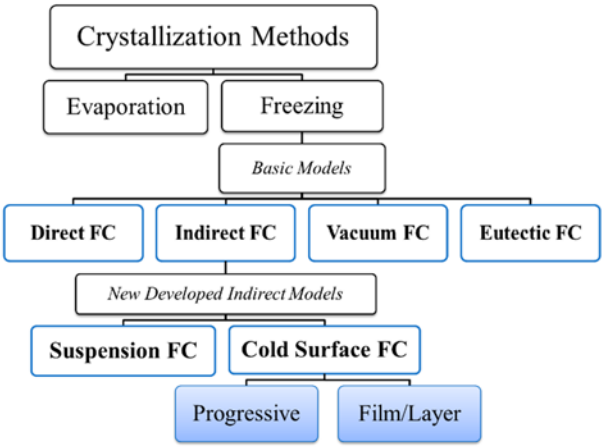

Figure 4. Hierarchical diagram of different crystallization methods

Direct contact freezing crystallization uses refrigerant in direct contact with the solution to be frozen. Mainly, this method has operating temperature of -5 ˚C characterizing it as low power consumption process [6]. High production rate at low driving force, the compactness and efficient design are the main advantages of this method. On the other hand, freeze desalination requires precise refrigerant. A suitable refrigerant should have normal boiling temperature of -4 ˚C or less, water immiscible, non-toxic, nonflammable, chemically stable, as well as inexpensive and commercially available [6]. Beside all these requirements, a good mixing of refrigerant with the solution is essential for production of ice crystals with least impurities. Fig. 5 represents a schematic diagram of a direct contact freezing crystallizer where liquid refrigerant is injected from the bottom and released finally as vapor.

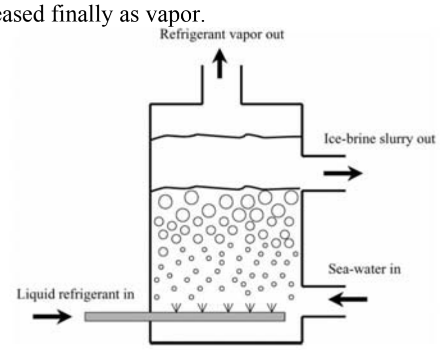

Figure 5. Direct contact freezing unit [15]

Indirect contact freezing crystallization uses refrigerant without a direct contact with the solution to be crystallized, in other words, the energy of the refrigerant will pass through the walls of heat exchanger [6,15]. Generally, indirect freezing can be classified into two main classes: i) suspension freezing and ii) freezing on a cold plate [19,23]. In suspension crystallization (see Fig.6) many small ice particles are produced in the suspension of the mother liquor in two stages where first crystals are produced in the ice nucleator then transferred to the re-crystallizer where the small crystals are grown larger through Ostwald ripening mechanism [23]. However, suspension crystallization is commonly used in food concentration industry [15], and has many cons such as cost, complicity, difficult nucleation and crystal growth control [24-26]. Alternatively, freezing on a cold surface forms a single crystal layer on a cooled surface. The operation of this process is either through progressive method (see Fig.7a) or falling film method (see Fig.7b). The most important advantage of freezing on a cold plate is that ice crystals formation happens in one dimensional direction which causes a layer by layer crystallization. In this way, impurities are prevented to be trapped in-between ice crystals.

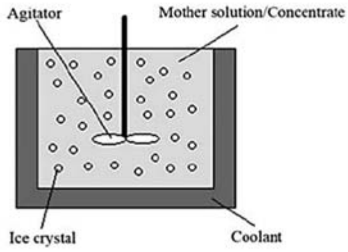

Figure 6. Illustration of suspension freeze crystallization [23]

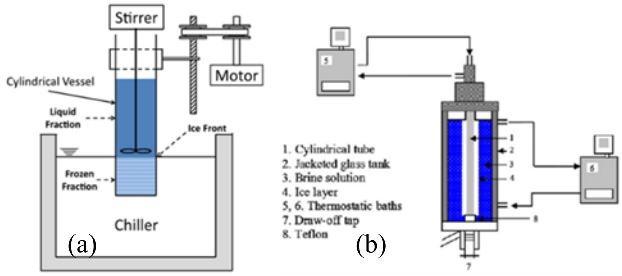

Figure 7. Freezing on a cold plate methods: (a) Progressive freezing [27] and (b) Falling film freezing [5]

Progressive freezing involves a solution filled tube to be concentrated and is progressively immersed in a cold refrigerant path as illustrated in Fig.7a. A stirrer is used at the solution tube to lower the impurity content near the ice growth layer. Alternately, the falling film freezing which is a dynamic crystallization method where the solution to be concentrated is in direct contact with a cooled vertical surface. The flow of the solution induces a shear at the crystal-solution interface which, thus, increases the mass transfer coefficient at interface and enhance the transport of impurities from the surface of growth leading to reduction in trapped impurities [5,15]. Easy to scale-up of the falling film freezing in addition to the one-dimensional growth direction are some of the pros of this process.

V***acuum freezing crystallization*** employs a high vacuum to vaporize a portion of water, which then provides the refrigeration effect by reducing the temperature of the solution causing ice crystallization [6].

Eutectic freezing crystallization operates at the eutectic temperature/point of the binary solution (NaCl-H_2O) as presented in the phase diagram in Fig. 2. In this method, salts

Table 1. Summary of freeze crystallization methods

Technology	Primary Mechanism		Pros	Cons
Direct FC [6] [15]	Crystallization of solution by direct contact with a refrigerant		-low operating temperatures -high production rate at low driving force -compact design	-limitation of refrigerant: (non-toxic, non-flammable, chemically stable, suitable boiling temp.) - poor mixing of refrigerant with solution leads to large impurities
Suspension indirect FC [15] [23-26]	Crystallization of solution by indirect contact with a refrigerant	-small ice crystals are firstly produced in the nucleator then introduced to the crystallizer to obtain crystal growth	-indirect contact allows to choose diversity of refrigerants	-cost -complicity and difficult nucleation and crystal growth
Progressive indirect FC [19] [23] [27]		-a tube filled with the solution is progressively immersed in a cold refrigerant path	- lower impurities due to 1-D crystal growth - stirrer lowers the impurity content near the ice growth surface	-bath size limit leads to difficulty in scaling-up
Falling film indirect FC [5] [15] [19] [23] [28]		-dynamic method where solution flows over a cold vertical surface	-1-D crystal growth - shear induced by the flow increase the mass transfer coefficient thus enhance impurity transfer from the growth surface -easy to scale-up -higher Reynolds number leads to lower COD	-difficult ice separation
Vacuum FC [6]	High vacuum is employed to vaporize portion of water and reduce temperature, thus causes crystallization		-complexity and expense of volatile refrigerant recovery can be prevented when atmospheric operating conditions is used	-compressor must handle large volume and low pressure of water vapor -needs more efficient design of the melting unit
Eutectic FC [6] [20]	Operates at the eutectic point temperature of the solution, therefore causing the crystallization of both ice and salts		-ease of separation due to density difference between ice and solid salts -high water recovery leading to ZLD	-very low operating temperature is needed and thus additional cost is required

separate as solids and fresh water separates as ice from brine simultaneously. Both salt and ice nucleates and grow independently. This gives the advantage of easy separation process since ice floats and the salt sinks by density difference. Though, very low operating temperature (-20 to -25 ˚C) and thus additional cost of eutectic freezing is required compared to other freezing methods [6]. Table 1 summarizes the most prominent specifications of each of the mentioned freeze crystallization methods.

Following any of the mentioned methods separation and melting comes at the end. The formed ice block is collected in the ice crystal separator where they are washed with water to purify blocks' surfaces and recover the solutes involved [23]. However, the main disadvantages of freeze desalination process compared with evaporation and RO is the incurred operational costs during the ice separation process [6]. Separation is usually done by washing the surface of the produced ice blocks with pure fresh water. Wash columns are most commonly used device for separation [6]. Melting of pure ice blocks finally takes place either directly or indirectly contact. However, energy recovery is one of the important aspects of this process and needs to be taken in highly consideration.

2.2. System metrics

Several parameters have been used through literature to evaluate the level of effectiveness of any freeze crystallization method. This include crystal size, concentration of salt in the final produced ice, effective partition constant, ice crystal front growth rate etc. Their definitions and relationships are described next.
Larger *crystal size* is desired for better desalination result as small crystal size result in entrapment of impurities and salts onto the ice phase [23]. Thus, as presented in Fig. 8, low saturation of salts in solution is required for large crystal size and thus better desalination effect.

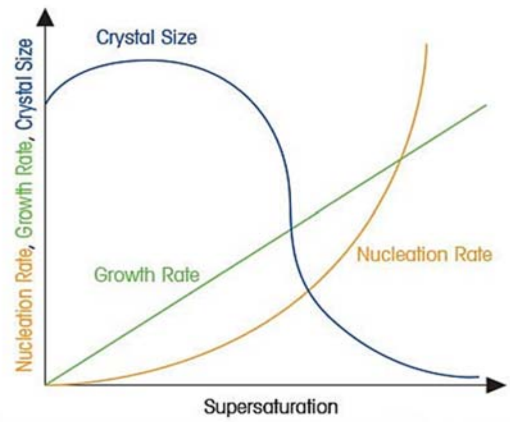

Figure 8. Effect of saturation of solute on crystal size, growth rate, and nucleation rate

Additionally, the *concentration of salt in the final produced* ice (C_i) can be calculated by measuring both the initial (C_0) and final (C_L) concentrations of the solution [24]:

$$C_i = \frac{\rho_L(C_0V_0 - C_LV_L)}{\rho_iV_i} \quad (1)$$

To evaluate the desalination effect of a series of experiments, *effective partition constant (K)* is introduced and defined as follows [23, 27]:

$$K = \frac{C_i}{C_L} \quad (2)$$

Where C_i and C_L are the concentration of solute in ice and in liquid phase, respectively. Thus, lower partition constant indicates better desalination efficiency. The effectiveness of freezing desalination process can also be defined by the *solute yield (Y)* which is a mass basis ratio that evaluate the amount of solute recovered in the concentrated final solution [23]. The following equation defines the solute yield, where (M_{sL}) is the mass of salt (solute) in the final concentrated solution, whereas (M_{s0}) is the mass of salt (solute) in the initial solution [23].

$$Y = \frac{M_{sL}}{M_{s0}} \quad (3)$$

2.3. Operational parameters

The effectiveness of freezing desalination process is highly influenced by the operating conditions of the crystallizer. Though, the most dominant parameters that highly affect ice properties are the initial concentration, refrigerant temperature, front growth rate, solution flow rate, and finally the introduction of seed crystals. From literature, lowest *initial concentration* gives the lowest partition constant (K), therefore higher desalination effect. On the other hand, high initial concentration causes higher solution viscosity and thus lower diffusion coefficient [19,23,29]. Moreover, it is obvious from the principle of freeze concentration that growth of ice crystals is highly dependent on the *refrigerant temperature* [30]. Jusoh et al. [29] and Luo et al. [31] have concluded that the freezing temperature is in linear relationship with the freezing rate (mL/h). Though, they found that desalination efficiency decreases at lower freezing temperature. This can be explained by the freezing rate. At higher freezing rate of ice crystals, more amorphous structure of ice is formed, and this causes large amount of impurities and salt entrapment.
Additionally, it is very important to track both the *ice crystal front growth rate* and *solution flow rate* (i.e. in the case of dynamic freeze crystallization) as it is highly related to amount of impurity trapped into the crystallized ice. Crystal growth rate can be calculated using the following equation [23]:

$$V_{ice} = \frac{m}{At\rho_{ice}}(1 - \omega_{s,ice}) \qquad (4)$$

Where V_{ice} is the ice growth rate (m/s), m is mass of melted ice (kg), ρ_{ice} is density of pure ice (kg/m^3), $\omega_{s,ice}$ is mass fraction of solute in the ice (w/w), t is freezing time (s), and A is heat transfer surface area (m^2). Higher growth rate leads to larger partition constant (K) and thus reduces the desalination efficiency. Furthermore, In the case of dynamic freeze crystallization such as the falling film crystallization, solution flow rate highly impacts the produced ice purity. Higher Reynolds number leads to lower chemical oxygen demand (COD) [28], lower partition constant, higher shear stress at interface which all lead to lower entrapment of salt in ice structure [23,30,32].

3. Modeling and Simulation

Simple approach to model crystallization is a batch process in a reservoir filled with brine solution of a given concentration is considered. The reservoir is subjected to cooling at one portion of the reservoir while maintain the other portions adiabatic. The brine solution can be considered as incompressible while the Boussinesq approximation is used to compensate for density temperature gradient. Further simplification is the consideration of laminar and two-dimensional flow. The system of equations can be summarized as those presented in Table 2. In which single domain is considered instead of two phase flow. It consists of liquid, solid and mushy zone that represented by the liquid fraction variable. Considering abounded rectangular domain Φ (L x h), the flow can be pursued from a resting condition at t = 0 that is patched with $\vec{V} = 0$ at given low temperature and brine concentration values, i.e. T=298 K and C_0= seawater (35 g/L). Furthermore, a prescribed cold surface, i.e. T=260 K while adiabatic and constant concentration the far boundaries i.e. $\partial T/\partial n|_{far} = 0$ and $\partial C/\partial n|_{far} = 0$, respectively as illustrated in Fig. 9. The solution is pursued using finite difference based approach in which the domain is finely discretized and the derivatives form of these equations (of an integral form of them) are resolved simultaneously leading to algebraic system. Higher order discretization schemes are pursued for the 1st and 2nd order spatial derivatives in space and the centralized temporal scheme used to for the time derivatives to achieve reasonable solution accuracy.

Figs. 10 to 12 shows the CFD model results of the freezing process. Temperature and liquid fraction are decreasing gradually with respect to the time which found to be strongly agreed with Abid and Safi [33], and Jayakody [34]. Moreover, velocity vectors shown in Fig. 12 assures the occurrence of the onset of fluid movements and mixing that propel the growth of crystal. This confirms that larger mixing appears with time. The model can be used to keep track with the removal of heat bulk with respect to time, influence of cooling direction, (i.e. top, bottom or side) as well as heat transfer coefficients to name a few. Table 2 list the decrease in heat rejection due to cooling with respect to time. This decrease is due to lower average temperature attainment of the domain with respect to time.

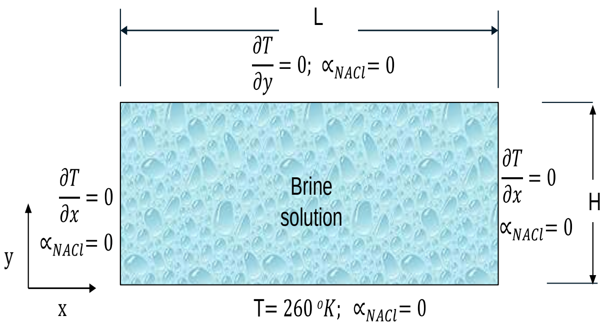

Figure 9. Simplified crystallization domain and assigned boundary conditions

Table 2. Governing equations of the freeze crystallizer model

Equation	Mathematical Representation	Equation No.
Mass (liquid)	$\frac{\partial \rho_l}{\partial t} + \vec{\nabla} \cdot (\rho_l \vec{V}_l) = 0$	(5)
Momentum (liquid)	$\frac{\partial}{\partial t}(\rho_l \vec{V}_l) + \vec{\nabla} \cdot (\rho_l \vec{V}_l \vec{V}_l) = \vec{\nabla} p_l + \mu_l \nabla^2 \vec{V}_l + \rho_l \vec{g}$	(6)
Species (liquid)	$\frac{\partial}{\partial t}(\rho_l C_{i,l}) + \vec{\nabla} \cdot (\rho_l C_{i,l} \vec{V}_l) = \vec{\nabla} J_{i,l}$	(7)
Energy (liquid)	$\frac{\partial}{\partial t}(\rho_l H_l) + \nabla \left[(\rho_l H_l \vec{V}_l) + \sum_{i-1}^{b} H_l J_{i,l} \right] = \vec{\nabla} q_l + \rho_l Q_l$	(8)
Mass (solid)	$\frac{\partial \rho_s}{\partial t} = 0$	(9)
Momentum (solid)	$\frac{\partial}{\partial t}(\rho_s C_{i,s}) = -\nabla J_{i,s} + \mu_l \nabla^2 \vec{V}_l + \rho_s \vec{g}$	(10)
Species (solid)	$\frac{\partial}{\partial t}(\rho_s H_s) + \nabla \left[\sum_{i-1}^{b} H_l J_{i,s} \right] = \vec{\nabla} q_s + \rho_s Q_s$	(11)

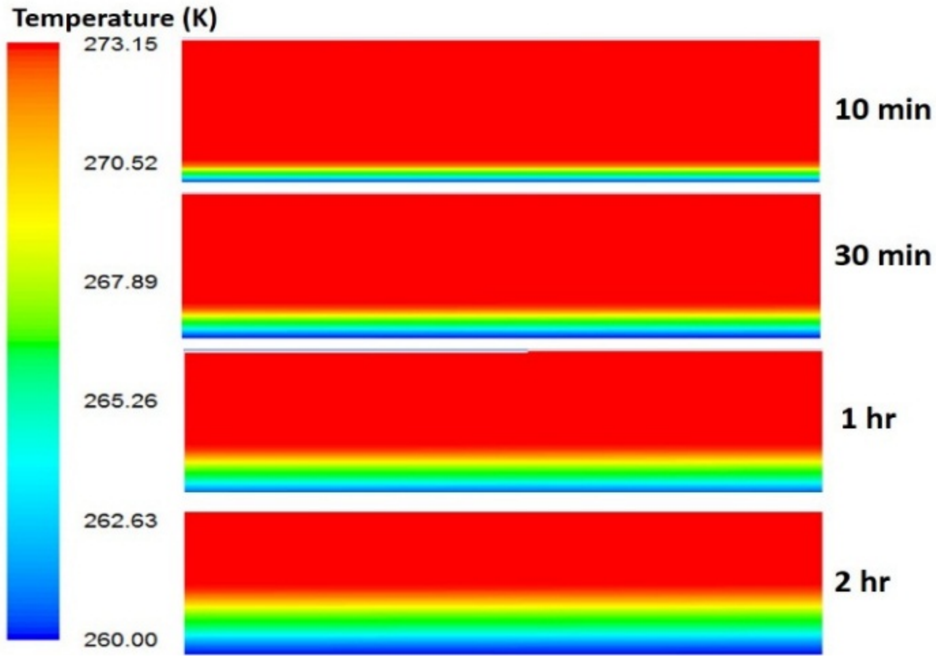

Figure 10. Temperature contours of the freeze crystallizer CFD model at different flow times

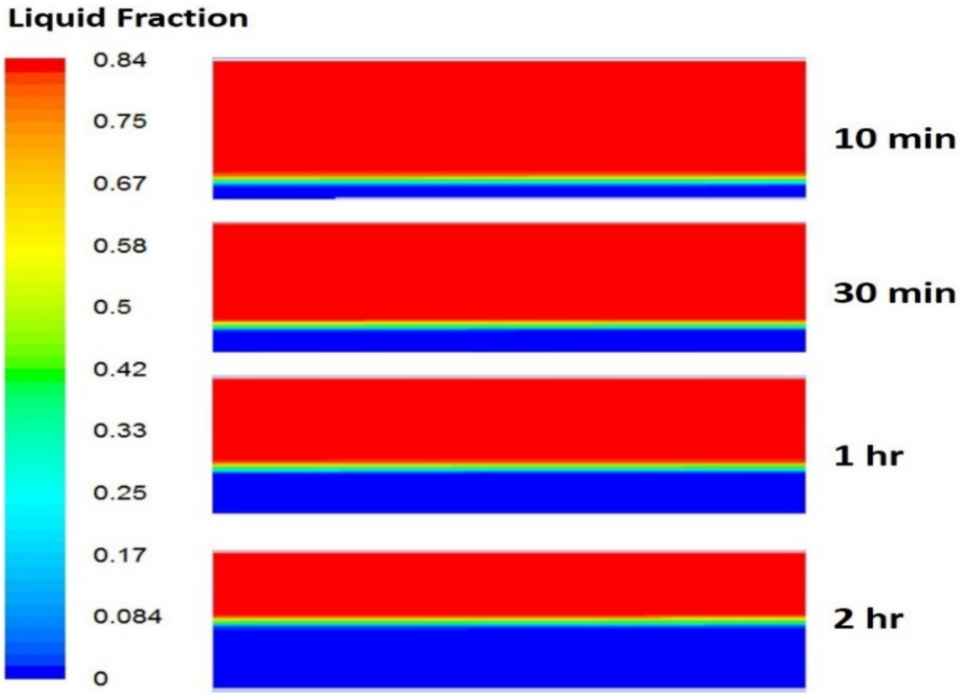

Figure 11. Contours of liquid fraction of the freeze crystallizer CFD model at different flow times.

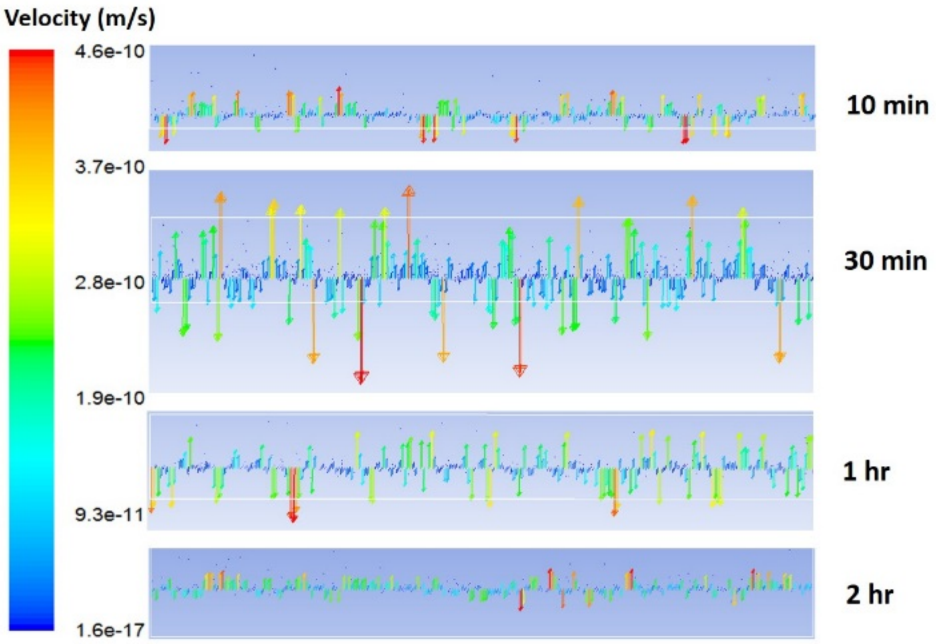

Figure 12. Velocity vectors of the freeze crystallizer CFD model at different flow times

Table 2. Total heat transfer rejection with respect to time

Flow time (min)	**10**	**30**	**60**	**120**
Heat rate (W)	-542.70	-344.32	-230.59	-165.56

4. Conclusion

Freeze desalination by crystallization seems to be successful mainly due to its ability of producing high quality product with much lower energy requirement as compared to other available technologies. This area is observing a renascence to mitigate the staggering landfill and sea rejected brine that have a negative environmental impact. This technology it comes at different configuration and setups from direct crystallization to indirect and at promising cost reduction compared to conventional thermal and RO processes. The process involves nucleation, crystal growth washing and melting. There is still much to learn on the nucleation and crystallization aspects of the process.

Recent CFD development enable to shed more light on the overall crystallization. Results shows that 2 hours of continuous freezing is eligible to reduce the liquid fraction to the half.

At present, no commercial plant is available for desalination of seawater by freeze crystallization. High capital and operational costs are the main obstacles that faces this technology. However, hybrid approach of freeze desalination with any other conventional evaporation processes could be an effective support to the desalination process.

References

[1] Lian G, Moore S, Heeney L. Population balance and computational fluid dynamics modelling of ice crystallization in a scraped-surface freezer. Chemical Engineering Science; 61:7819-26.

[2] Hartel, RW. Ice crystallization during the manufacture of ice cream. Trends in Food Science & Technology 1996; 7: 315–321.

[3] Braddock RJ, Marcy JE. Freeze concentration of pineapple juice. Journal of Food Science 1985; 50: 1636–1639.

[4] Bayindirli L, Ozilgen M, Ungan S. Mathematical-analysis of freeze concentration of apple juice. Journal of Food Engineering 1993; 19: 95–107.

[5] Williams P, Ahmad M, Connolly B, Radcliffe D. Technology for freeze concentration in the desalination industry. Desalination 2015; 356: 314–327.

[6] Kucera J. Desalination: Water from water. Scrivener Publishing, 2014

[7] Hendrickson HM, Moulton RW. Research and development of processes for desalting water by freezing. R&D Report 10, US Dept. of Commerce: Office of Saline Water, 1956.

[8] Karnofsky G, Steinhoff PF. Saline water conversion by direct freezing with butane. R&D Report 40, US Dept. of Commerce: Office of Saline Water, 1960.

[9] Wiegandt HF, Harriott P, Leinroth JP. Desalting of seawater by freezing. R&D Report 376, US Dept. Of Commerce: Office of Saline Water, p.51, 1968.

[10] Janajreh I, Hasania A, Fath H. Numerical simulation of vapor flow and pressure drop across the demister of MSF desalination plant. Energy Conv. & Manag. 2013; 65: 793-800.

[11] Janajreh I, Suwwan D, Fath H. Numerical Simulation of Low Energy Direct Contact Membrane Distillation. Int. J. of Thermal & Environmental Engineering 2014; 7(2): 133-138.

[12] Janajreh I, Suwwan D, Hashaikeh R. Assessment of direct contact membrane distillation under different configurations, velocities, and membrane properties. Applied Energy 2017; 185: 2058-2073.

[13] Lu Z, Xu L. Freezing Desalination Process. Thermal desalination process ;2.

[14] Heist JA. Freeze crystallization. Chem. Engr 1979; 86 (10): 72–82.

[15] Rahman M, Ahmed M, Chen. Freezing-Melting Process and Desalination: I. Review of the State-of-the-Art. Separation & Purification Reviews 2006; 35: 59–96.

[16] Mtombeni T, Maree JP, Zvinowanda CM, Asante JK, Oosthuizen FS, and Louw JW. Evaluation of the performance of a new freeze desalination technology. Int. J. Environ. Sci. Technol 2013; 10:545–550 DOI 10.1007/s13762-013-0182-7

[17] Chen P. Freeze concentration of food liquids using layer crystallizers. Ph. D thesis. University of Auckland: Auckland, New Zealand, 1999.

[18] Himawan C. Characterization and population balance modelling of Eutectic Freeze Crystallization. PhD Thesis. Technical University of Delft, The Netherlands, 2005.

[19] Wang P, Chung T. A conceptual demonstration of freeze desalination-membrane distillation (FD-MD) hybrid desalination process utilizing liquefied natural gas (LNG) cold energy, water research 2012; 46: 4037-4052.

[20] Randall DG, Nathoo J, Lewis AE. A case study for treating a reverse osmosis brine using Eutectic Freeze Crystallization—Approaching a zero waste. Desalination 2011; 266: 256–262.

[21] Clark J. Solid-Liquid Phase Diagrams: Salt Solution, http://www.chemguide.co.uk/physical/phaseeqia/saltsoln. html, 2005

[22] Web. "U.S. Office of Naval Research Ocean, Water: Temperature".

[23] Amran N, Samsuri S, Safiei N, Yamani Z, Zakaria, Jusoh M. Review: Parametric Study on the Performance of Progressive Cryoconcentration System. Chemical EngineeringCommunications; 2014 ,http://dx.doi.org/10.1080/00986445.2015.1075982

[24] Miyawaki, O, Kato S, Watabe K. Yield improvement in progressive freeze-concentration by partial melting of ice. J. Food Eng. 2012; 108(3): 377–382.

[25] Gunathilake M, Dozen M, Shimmura K, and Miyawaki, O. An apparatus for partial ice-melting to improve yield in progressive freeze-concentration. J. Food Eng. 2014;142: 64–69.

[26] Liu L, Miyawaki O, and Nakamura K. Progressive freeze concentration of model liquid food, Food Sci. Technol. Int. 1997; 3; 348–352.

[27] Fujioka R, Wang L, Dodbiba G, Fujita T. Application of progressive freeze-concentration for desalination. Desalination 2013; 319: 33–37.

[28] Shirai, Y, Wakisaka M, Miyawaki, O, Sakashita S. Conditions of producing an ice layer with high purity for freeze wastewater treatment, J. Food Eng. 1998; 38(3): 297–30.

[29] Jusoh M, Mohd Yunus R, Abu Hassan MA. Effect of initial concentration of solution and coolant temperature on a new progressive freeze concentration system. J. Chem. Nat. Resour. Eng. 2008b; Special Ed.: 122–129.

[30] Miyawaki O, Liu L, Shirai Y, Sakashita S, and Kagitani K. Tubular ice system for scale-up of progressive freeze-concentration. J. Food Eng. 2005; 69(1); 107–113.

[31] Luo CS, Chen WW, and Han WF. Experimental study on factors affecting the quality of ice crystal during the freezing concentration for the brackish water. Desalination 2010; 260(1–3): 231–238.

[32] Williams PM, Ahmad M, and Connolly BS. Freeze desalination: An assessment of an ice maker machine for desalting brines. Desalination 2013; 308: 219–224.

[33] Abid AJ, Safi MJ, Simulation of Binary Mixture Freezing: Application to Seawater Desalination, Int. J. of Eng. Sci. and Inn. Tech. 2015; 4(6): 158-163.

[34] Jayakody H, Al-Dadah R, Mahmoud S, Computational fluid dynamics investigation on indirect contact freeze desalination. Desalination 2017;420: 21-33.