Indirection Freeze Desalination: Towards Zero Liquid Discharge (#11)

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1. Introduction

Freeze desalination (FD) is a promising nonconventional method with numerous advantages compared to current commercial desalination technologies. In FD, the brine is cooled until crystallization occurs and the formed ice crystals reject the salts automatically achieving a low salinity in the early formed ice and progressively increasing until the latest formed ice. Latter, the ice is melted to obtain fresher water from earlier crystals or concentrated brine from the latest crystals. Compared to commercial distillation methods and membrane technologies, FD has low energy consumption, enduring less corrosion, and is suitable for high brine concentration while operating at atmospheric pressure [1]. The extracted brine can reach higher concentration than the brine reject of the common reverse osimose technology. FD hence can be integrated to commercial desalination plants to further increase the concentration of the waste brine to near saturation and thereby reducing the energy needed for zero liquid discharge [2,3]. Compared with the current thermally-driven evaporation-based zero liquid discharge (ZLD) process, ZLD driven by freeze crystallization can dispose brine at higher overall energy efficiency (around six times less than the energy required for vaporization of water [4]) and can also recover single salts from the brine by utilizing different eutectic temperatures of these salts [5]. ZLD has been the focus of numerous government to adhere to brine reject regulations, achieve higher water recovery, and to recover valuable materials from the seawater and wastewater including potassium sulfate, caustic soda, sodium salts and sulfate, lithium and gypsum. Conventionally, achieving ZLD requires the deployment of thermal/evaporation technologies, (e.g. multi stage flash (MSF), multi effect distillation (MED), or mechanical vapor compression (MCV)) additional to crystallizers and recover their condensate. This makes ZLD plants are sources of solid waste. Generally, ZLD integrate pre-treatment and evaporation of the industrial effluent aiming at precipitating the dissolved solids as crystals. These crystals are removed and are decanted using filter press or a centrifuge. Meanwhile, The evaporated water is condensed and returned to the process. In the last decades though, there has been an effort from the water treatment industry to revolutionize the high water recovery and ZLD technologies.[2] This has led to processes like electrodialysis (ED/EDR), forward osmosis (FO) and membrane distillation (MD). In this work, freezing experiments with NaCl solution are conducted to obtain the salinity gradient and concertation in the formed ice during the freezing. The salinity gradient and freezing time are used to develop and verify a freezing model based on heat-balance which is used to evaluate the freezing time and the energy analysis for the freezing process.

3. Results & Discussion

A. Attained Salinity vs freezing temperatures

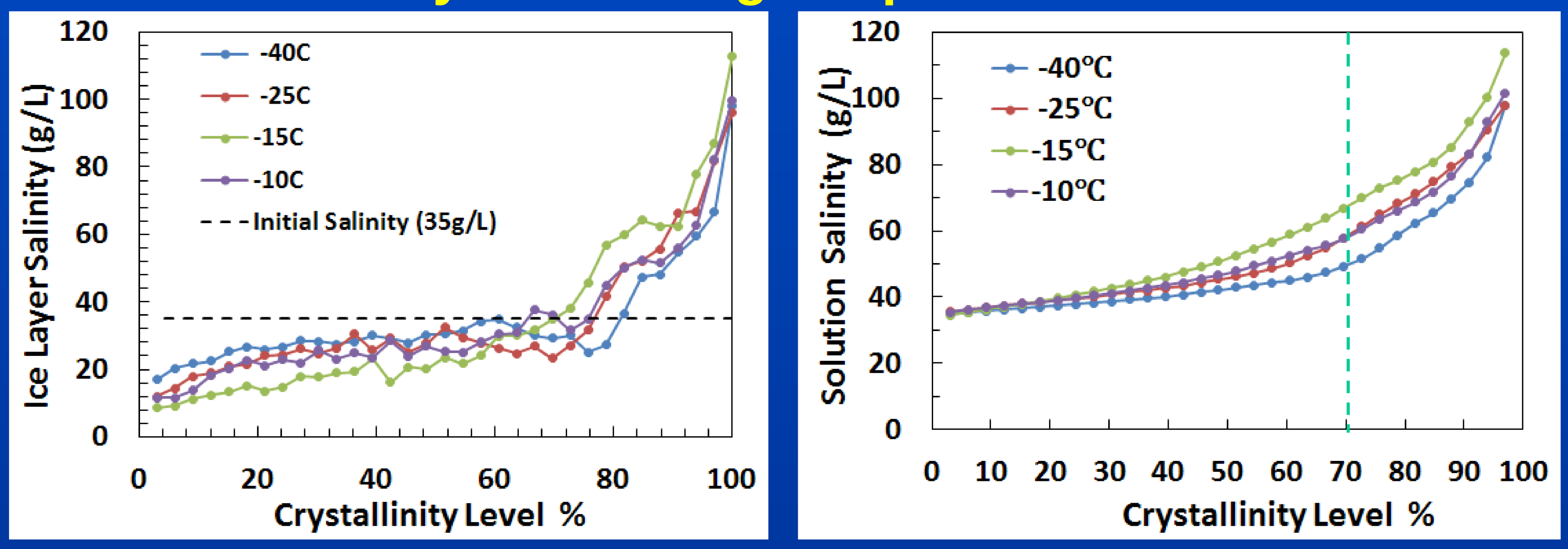

Fig. 2: Salinity gradient in the ice (left) and salinity of the remaining solution (right) during freezing under different freezing temperature (brine salinity: 35g/L)

- Early formed ice crystals (until ~70%) salinity is below, (while latter ice is above) the initial 35g/litter level at all attempted temperatures (-40, -25, -15, -10 °C)
- Solution salinity increases with crystallinity reaching above 100g/l or 10% salinity that nearly double the value of the brine reject concentration of the RO
- Higher freezing temperature results in a higher concentration. Around 45%, 52.1%, 61% and 52.2% of the salt are concentrated in the last 30% brine for -40, -25, -15 and -10 ℃, respectively.
- There is an optimal freezing temperature to reach the maximum 35g/l NaCl concentration was near -15℃.

B. Attained Salinity vs initial salinity

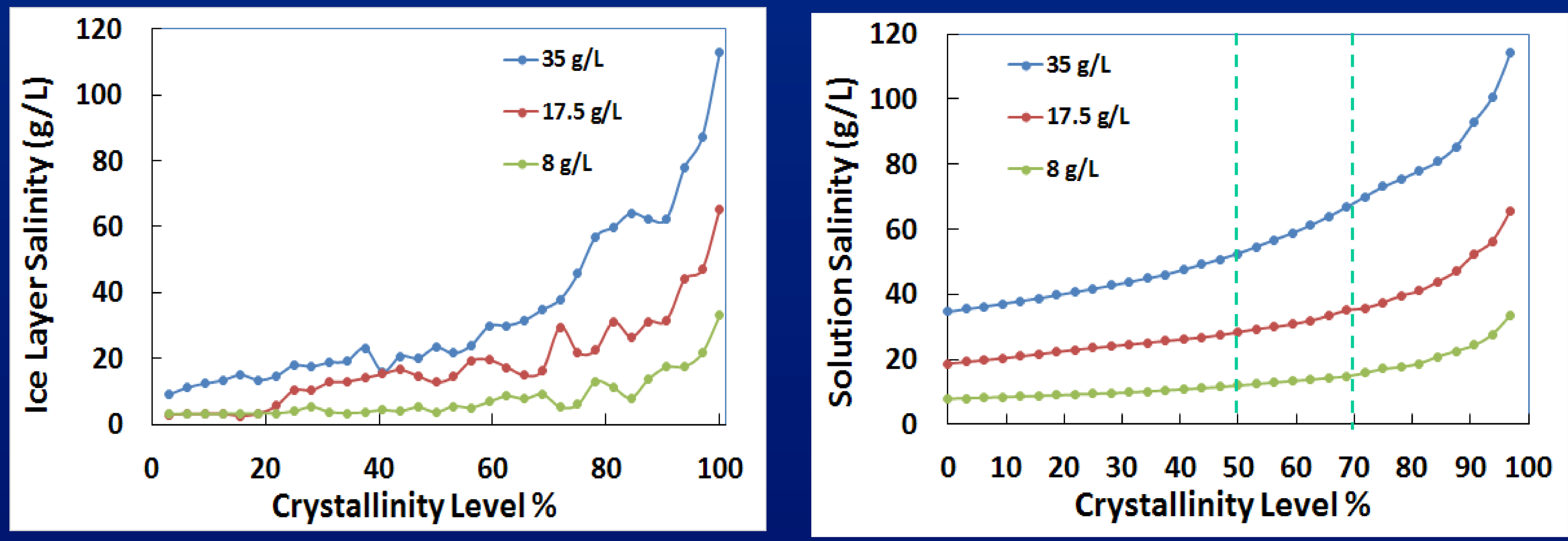

Fig. 3: Salinity gradient in ice (left) and salinity of remaining solution (right) during freezing experiment under -15 ℃ at different initial solution salinities

- Ice layer salinity and solution salinity both are increasing with freezing at all attempted salinities (35, 17 and 8 g/l)
- Concentrating efficiency for the three solutions under same freezing temperature is nearly similar.
- At 50% crystallization, the three brine solutions attained neat 1.5 times of the initial concertation and at 70% crystallization all the brine solutions doubled their initial concentration.

2. Methodology

Freezing experiments for 35g/L brine in different freezing temperatures (-10, -15, -25, -40 ℃) and for different initial salinity (8, 17.5, 35g/L) brine under same freezing temperature (-15 ℃) are conducted. The objective is to study these conditions' effects on the salt concentration. Temperature of the brine is also recorded to assess the onset of freezing. Experimental setup is depicted in Fig. 1, where brine at the three different concentrations is poured in an insulated tray and placed on the cold shelf inside the freeze dryer (Virtis/Advantage Apparatus) for freezing at also different shelf temperature (-40, -25, -15, -10 °C). Upon freezing, the frozen brine contained tray is removed from the freeze dryer chamber, and subjected to melting using hating plate and collected layer by layer by mean of syringe of 30ml capacity. Each 30ml where stoed in an equivalent size cylindrical vials, stabilized at room temperature and their salinity is measurements using conductivity meter (HQ40D Portable Multi Meter, HACH. The temperature of the top brine layer is also recorded during freezing by calibrated T-type thermocouples. The cylindrical tray is neatly 20cm dia by 5cm depth with all-sides insulated except the bottom.

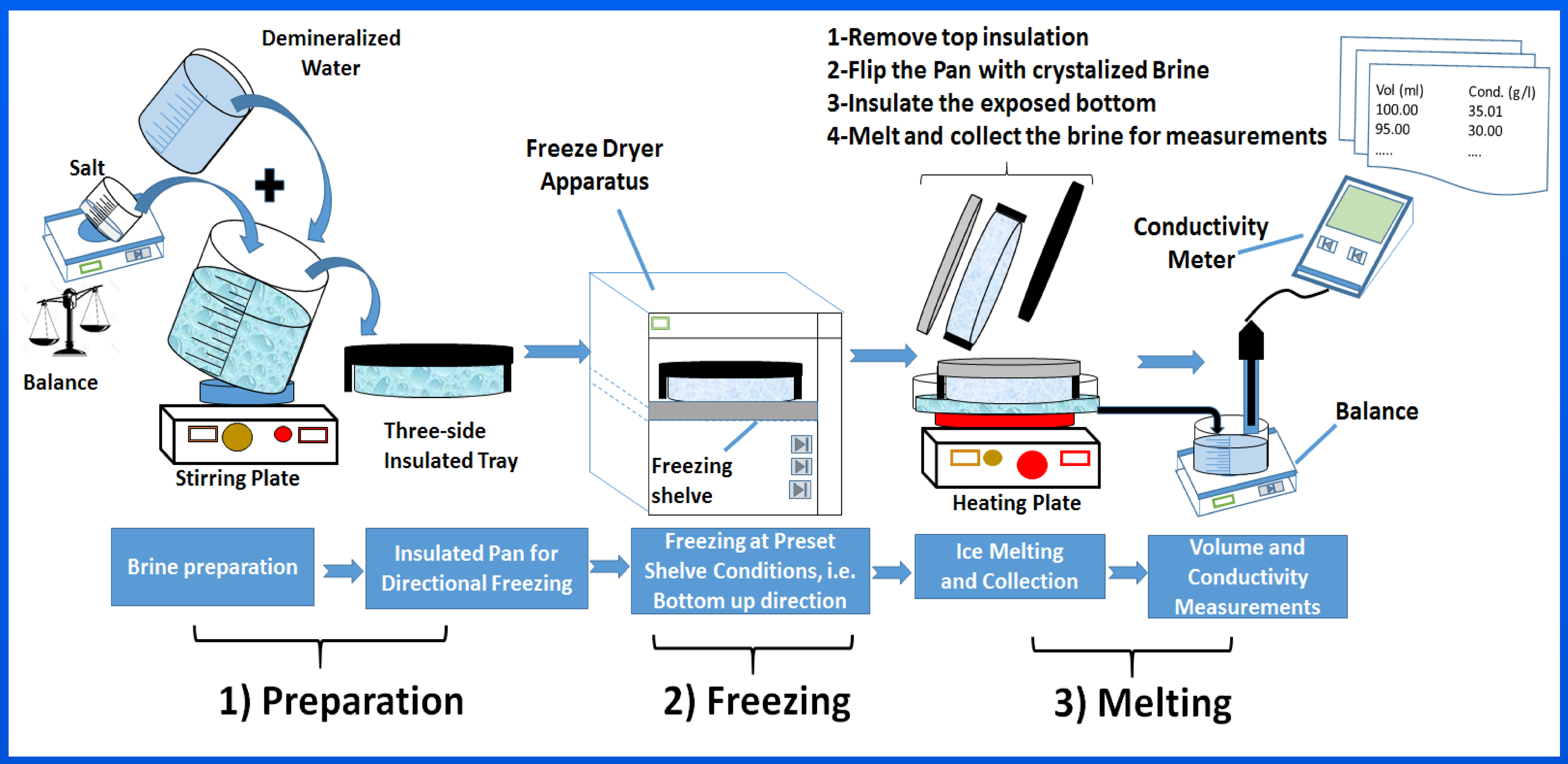

Fig.1: Brine freezing-melting process

C. Evaluation of Freezing Time

Freezing time is an important parameter revealing the freezing process as well as evaluating the freezing rate. Temperature of the brine is measured by the thermocouple and the results are shown in Fig. 4 (left). Freezing time is obtained as the temperature reached the freezing point of the top layer as shown in Fig. 4 (left). The freezing time is evaluated by energy balance model that mainly uses the two equations below that also evaluates the total heat transfer rate during the process. The predicted freezing time is compared with the experimental data in Figure 4 (right).

$$t = \left(\frac{d\delta}{k_{st}} + \frac{1}{2}\frac{d^2}{k_f}\right)\left(\frac{\Delta H_1}{\Delta T_1} + \frac{\Delta H_2}{\Delta T_2}\right)$$

$$E_{total} = Q_1 + Q_2$$

d is total depth of brine; δ is the tray wall thickness; k_f is the thermal conductivity of the frozen brine; k_{st} is the thermal conductivity of the tray wall; ΔT_1 and ΔT_2, ΔH_1 and ΔH_2 as well as Q_1 and Q_2 are are temperature gradient, volumetric enthalpy change, and the heat transferred for precooling and freezing, respectively.

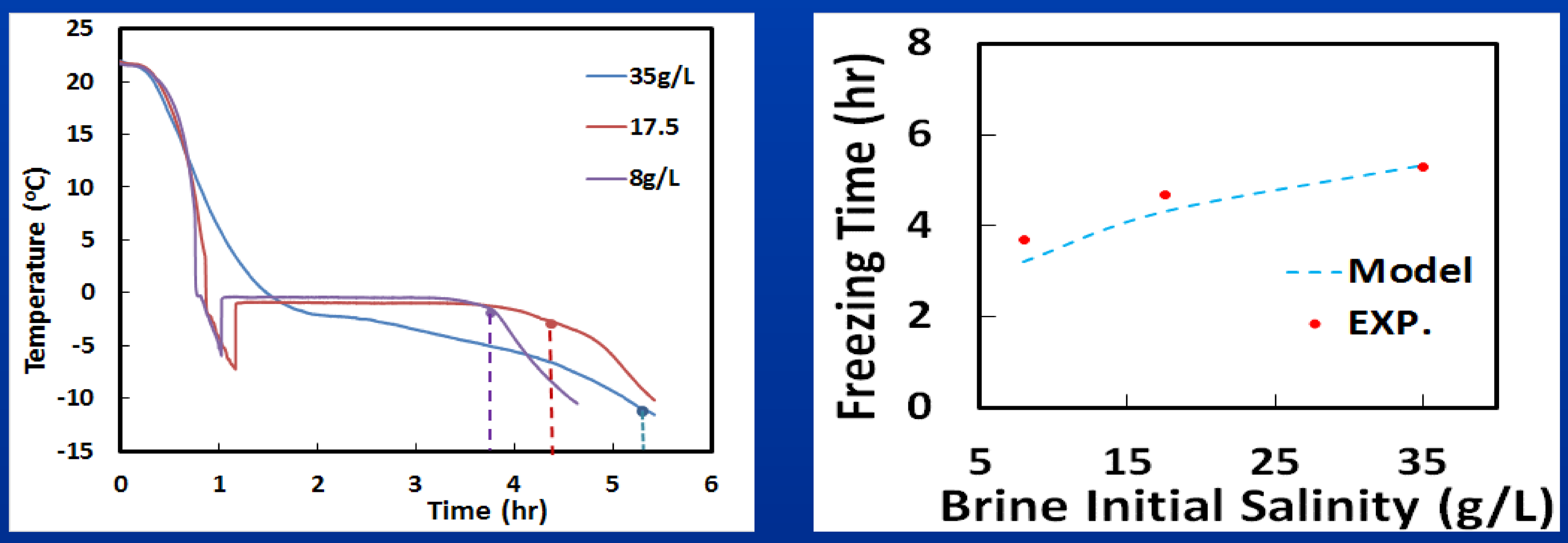

Fig. 4: Brine temperature with time (left) and freezing time comparison between experimental and model results for various initial salinity (right)

- The model predicted freezing time and within 15% accuracy
- The heat transfer is evaluated, and it was found that 4.31E5,4.18E5,4.10E5 kJ/m³ are needed to fully freeze the 35, 17.5, and 8 g/L brine, respectively.
- Heat transfer were 3.15E5, 3.08E5, and 3.05E5 kJ/m³ when 70% of brine is frozen and the remaining solution is doubled its concentration

4. Conclusions

We have investigated the brine concentration by freezing. It is found that freezing temperature has a significant effect on the attained concentration and there is an optimal freezing temperature for the brine (near -15 ℃ for 35g/L NaCl solution). The initial salinity has lesser effect on the concentration efficiency. A freezing model based on the heat-balance and experimental salinity gradient is developed that resulted within 15% experimental discrepancy. The model is used to predict the heat removed during the freezing under different initial salinity. This provides desalination engineers with an evaluation tool that estimates the freezing time and energy consumption for future deployment of FD and for NZL discharge technologies.

References

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