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Impact of Supercooling on Saltwater Freeze Desalination Efficiency: A Thermodynamic Analysis

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Abstract –This study explores the impact of supercooling on saltwater freeze desalination, a method garnering attention for its potential to address challenges encountered by traditional desalination technologies. The research traces the evolution of brine temperature over time, uncovering that supercooling hinders heat transfer during freezing, leading to prolonged freezing times. Additionally, higher degrees of supercooling correlate with increased ice salinity and reduced desalination efficiency. Consequently, this study underscores the significance of minimizing or avoiding supercooling in saltwater freeze desalination processes to improve overall efficiency and address existing limitations in the desalination industry.

***Keywords*:** Freeze desalination; Supercooling; Desalination efficiency; Ice quality

1. Introduction

In recent years, Freeze Desalination (FD) has garnered increasing attention from researchers worldwide due to its potential to address challenges in the current desalination industry[1]. Thermal distillation plants face issues of substantial energy consumption and incuring corrosion in their setup [2], while membrane desalination plants contend with membrane fouling, requiring pretreatment for intake brine, and imposed low tolerance to high-salinity brine[3]. FD freezes seawater at low temperatures, effectively avoiding fouling and the driving high temperature corrosion[4]. The latent heat of fusion during water crystallization is only one-sixth of otherwise required as latent heat of evaporation; Therefore, with the additional lower sensible cooling heat, FD has much potential to consume lower energy than the evaporation route [5]. However, supercooling cannot be avoided to trigger nucleation and ice crystallization. The lowest reported nucleation temperature can reach as low as -41℃ [6]. Luckily, brine never been very pure to crystalize down to this temperature, and nucleation occurs in the vicinity of the melting temperature as adjected/lowered according to the binary phase diagram of brine of $NaCL.xH_2O$. Nevertheless, water supercooling has been investigated since 1916 [7], and a considerable amount of research on water freezing has been published to reveal the fundamental mechanism of water supercooling. It has been established that water supercooling is affected by multiple factors such as water volume, impurity concentration, and the cooling rate[8]. However, research on supercooling in brine freezing is still limited. The author's previous work [9] discusses brine droplets' supercooling and stated supercooling of brine is less than that of pure water, also the supercooling degree of brine droplets increases by lowering the cooling source temperature. The low production rates as well as low desalination efficiency are the current shortcoming of FD despite its lower energy promise. The goal of this work is to explore the impact of supercooling on freezing time and the salinity of the formed ice. Firstly, the evolution of brine temperature during freezing is investigated to understand the brine freezing process. Secondly, a thermodynamic analysis of heat transfer during freezing, with and without supercooling, is conducted. The effect of supercooling on the time required for complete freezing is assessed. Finally, the impact of supercooling on ice salinity is experimentally examined. This work contributes to understanding the effect of supercooling on brine freeze desalination.

2. Methodology

The process of the brine freezing experiment is illustrated in Fig.1. A NaCl solution with a specified concentration is prepared and frozen in a cylindrical tray using a freeze dryer (Virtis/Advantage Apparatus) with a controlled freezing shelf ranging from -50 to 50 ℃. Subsequently, the formed ice then subjected to layer-by-layer melting, and the salinity of the melted liquid is measured using a conductivity meter (HQ40D Portable Multi Meter, HACH). The temperature evolution of the brine is also recorded by three calibrated K-type thermocouples (TC1, TC2 and TC3) during freezing at a sampling rate of 1Hz. Freezing experiments are conducted using brine with salinities of 8 g/L ,17.5 g/L and 35 g/L under a freezing temperature of -15 ℃.

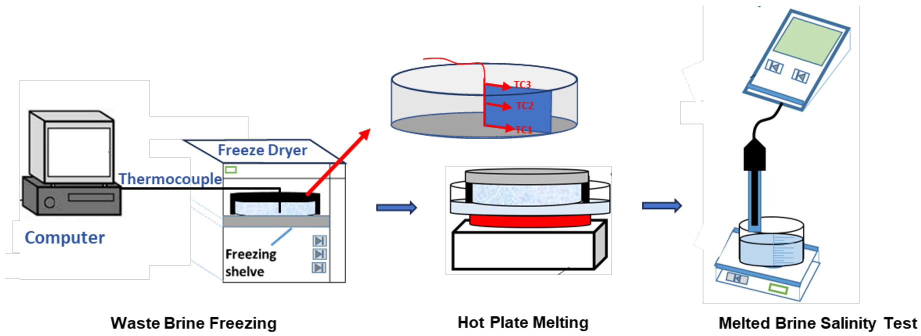

Fig. 1: Experimental setup for brine freezing process

3. Results Discussion

3.1 Temperature evolution during the brine freezing

The temperature evolution of the brine is shown in Fig. 2. Initially, the brine at room temperature (22℃) undergoes gradual and sensible cooling. The thermocouple near the bottom (T1, near cooling source) experiences a faster reduction in temperature compared to those at middle (TC2) and top depths (TC3), where the temperature decreases more slowly. As the brine continues to cool gradually, the rate of temperature decrease slows, and the temperatures of the three thermocouples converge around 0 degrees. This intriguing phenomenon may be attributed to the well-organized water molecules at this temperature, promoting efficient heat transfer, especially in the top portion, which rapidly cools.

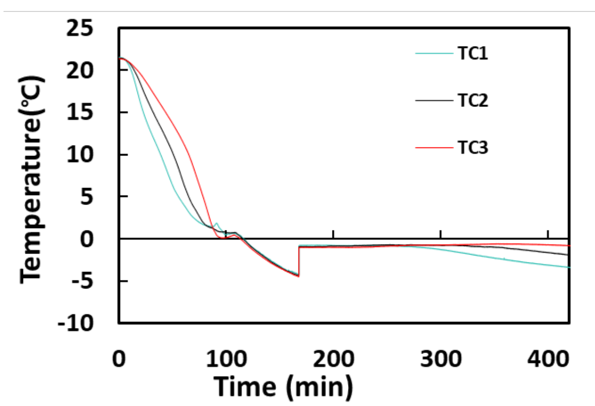

Fig. 2: Temperature evolution of brine freezing experiments (8g/L, -15°C)

Subsequently, the entire brine cools together to -4.2°C at 167 min, at a metastable supercooling state. The supercooling state is disrupted by nucleation, leading to the ice crystallization. The release of a substantial latent heat of fusion into the surroundings causes a quick temperature jump and increase as far as the sampling rate 1Hz. During this stage, crystallization proceeds rapidly until the supercooling degree is exhausted. Following this, the brine continues crystallization at a lower rate, and the temperature remains at the melting point of the brine until TC 1 is completely frozen. At this point, the thermocouple is covered by ice, which further cools down at an accelerated rate due to ice's thermal conductivity being approximately three times that of water.

It is crucial to note that nucleation occurs randomly after the brine enters the supercooling state, making it challenging to predict the exact nucleation temperature or time. The impact of supercooling on freezing time and freezing desalination efficiency is investigated below.

3.2. Supercoiling's effect on freezing time

Supercooling does not consistently occur, as nucleation is influenced by various factors. In the freezing experiments involving a 17.5 g/L NaCl solution, multiple tests are conducted under identical conditions. Among these experiments, one instance of freezing without supercooling is observed as it has been captured in Fig.3. It is also compared to/overlaid on that that exhibited supercooling. In Test 1, supercooling occurs as the cooling/energy level barrier needed to trigger the nucleation. In Test 2, however, that supercooling did not take place. The temperatures presented are recorded by thermocouple TC 2.

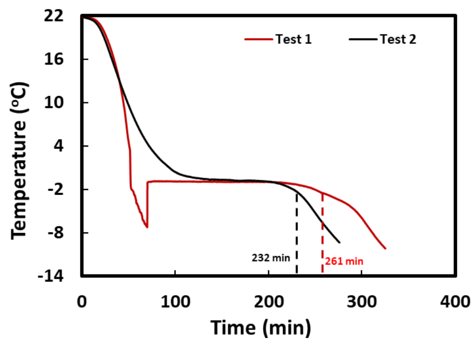

Fig. 3: Temperature evolution of brine (17.5 g/L) in freezing experiments with and without supercooling

In the early sensible cooling stage (0-40 min), the temperatures of the brine in both tests decrease at a similar rate. Subsequently, in Test 1, the temperature decreases faster than that in Test 2, entering the supercooling stage at 52.5 min. At 70 mins, the brine in Test 1 reaches the maximum supercooling degree, leading to nucleation followed by the fast recalescence stage, where the temperature rapidly bounces up to the melting point of the brine (around -1 ℃) at 71 mins. In Test 2, the brine is cooled down, and crystallization begins directly at around 110 mins with no sign of supercooling. However, Test 2 completes the crystallization stage early at around 232 mins, whereas Test 1 completes crystallization at around 261 mins. The captured temperature evolutions of these two tests substantiates that supercooling impedes heat transfer during freezing desalination and prolongs the crystallization period.

3.3. Supercoiling's effect on the desalination efficiency

Similarly, numerous freezing experiments were carried out at 35 g/L NaCl solution to investigate the role of supercooling on the salinity of the early-formed ice. Given that supercooling and recalescence influence the initial crystallization stage, the salinity of the first 2% of the ice (following melting and temperature stabilization) is measured in each experiment. The results of supercooling degree, defined as the difference between the supercooling and melting temperature, of the brine solution versus the ice's salinity are depicted in Fig. 4.

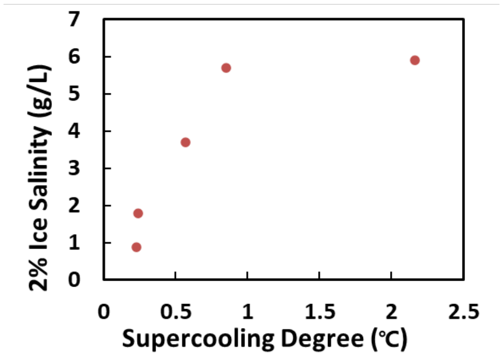

Fig. 4: Ice salinity versus supercooling degree in the freezing experiments of the brine (35g/L, -15℃)

The supercooling degree in the freezing experiments with a 35 g/L brine is small (0.2 ~ 2.2℃). It is evident that a supercooling degree leads to a lower salinity of the early-formed ice. Supercooling induces rapid crystallization during recalescence, and a higher supercooling degree results in faster crystallization in the early freezing stage. The salt ions rejected from the ice lack sufficient time to diffuse into the remaining unfrozen brine, leading to more ions being trapped in the formed ice and resulting in higher salinity. In summary, supercooling diminishes desalination efficiency, with a larger supercooling degree leading to lower desalination efficiency. Therefore, avoiding or minimizing supercooling is crucial for enhancing freezing desalination efficiency and eventually in the pursuing FD as another desalination technology contender.

4. Conclusion

In this work we investigated the role of the supercoiling's effect on the saltwater freeze desalination. Experimental analysis is conducted to understand the temperature jump of supercooling and recalescence. The analysis shows that supercooling hinders the heat transfer and prolonged the freezing time. Moreover, higher supercooling degree leads higher ice salinity and lower desalination efficiency. Thus, supercooling should be minimized or avoided in the saltwater freezing desalination.

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