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Nucleating agent enhanced thermal desalination at the triple point

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ABSTRACT

An energy-efficient desalination process based on spray vacuum freezing of seawater at the triple point of seawater is developed. Freezing and vaporization of water happen simultaneously at the triple point with net-zero thermal energy consumption, both of the processes generates purified water in form of ice and vapor, correspondingly. The vapor is then compressed to a pressure above the triple point and condensed on ice to produce fresh liquid water. Since no thermal energy input is required in the simultaneous phase transition processes, the majority of energy consumption of this technology is used for vapor compression from below-triple point pressure to above it to allow condensation of vapor. The initial pressure of vapor is under equilibrium with the sprayed water droplets, the temperature of which depends on the degree of subcooling during the vacuum freezing process of the droplets. By using proper nucleating agents in seawater, the subcooling is suppressed within 1 ˚C of the theoretical melting point. As a result, the energy consumption for vapor compression is dramatically decreased by 83%. In addition, ice produced by spray freezing is easy to handle and transport comparing to conventional freezing desalination technologies. Applications that can directly benefit from the use of this desalination technology include seawater desalination, brackish water treatment, as well as fresh water supply for remote communities.

KEY WORDS: Desalination, Water, the Triple Point, Subcooling, Nucleating Agent.

1. Introduction.

Fresh water is a vital cornerstone of everything accomplished in modern society. Of all water in the planet, 97% of the earth's water is contained in the oceans. [1] The oceans represent a virtually unlimited supply of water, yet unsuitable for human consumption without treatment. Thus, desalination techniques/processes are required in order to convert this vast volume of water into a usable resource. Among the 3% of total water sources other than seawater, 2% is fresh water trapped in icecaps and glaciers by natural freezing desalination process. Inspired by the natural process, vacuum freezing desalination system aims to couple the evaporation and freezing of seawater droplets at its triple point to improve the energy efficiency. [2-5] Due to the potential advantages of vacuum freezing such as significant energy consumption reduction, these processes have been studied since 1950s, when several pilot plants of vacuum-freezing desalination process had been designed and built up in Israel and the US. [4] However, there has not yet been a successful commercial vacuum freezing process in desalination, due to the lack of reliable water freezing control and ice handling, as well as low-cost vapor transportation at sub-triple-point pressure.

The process of freezing desalination is based on the natural phenomenon of pure ice formation in a saline solution such as seawater. In this process, impurities tend to remain in the liquid phase, leaving a pure solid phase. The phase change of water freezing requires the removal of the heat of fusion (H_f = 334 kJ/kg) of ice. This heat is nearly 1/7 of the heat of vaporization of water (H_{vap} = 2500 kJ/kg) at the same temperature and pressure. Specifically, if operates at the triple point of water, vapor and crystalline ice are formed simultaneously from liquid without the need of external thermal energy, due to the energy balance of the endothermic vaporization and the exothermic freezing:

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$$m_s H_f = m_v H_{vap} \quad (1)$$

where m_s m_s and m_v m_v are the mass of ice and vapor generated from liquid phase, respectively. The net thermal energy consumption for the phase transition desalination processes is zero, during which about 7/8 of the fresh water extracted from seawater is converted to ice and about 1/8 to vapor. The amount of vapor to transport in the process is only about 1/8 of the total processing water, resulting much less pumping power requirement. This low energy consumption is one of the main reasons for the continuous interest in vacuum freezing desalination. In addition, the low operation temperature (< 0 °C) significantly reduces the corrosion issue, which enables the use of much lower cost engineering materials.

In a conventional prototype of vacuum freezing desalination plant, the triple point process is completed in a vacuum freezing chamber. [5] By drawing vacuum from this chamber, the evaporation of water removes heat from seawater and decreases the temperature. When temperature drops below freezing point, ice formation starts in random locations in the chamber. An agitator or scraper is used to break ice and mix it with the liquid to form ice slurry, which is then taken out of the chamber for further treatment. The major problems of this process are a) the lack of uncontrollable water freezing and b) high cost of vapor compression at near-vacuum pressure. Due to the subcooling phenomena of the freezing process, water and aqueous solutions do not readily freeze below the triple point temperature, but rather can be subcooled to form metastable liquids. [6] It is reported that the metastable liquid of water may exist until as low as -38°C. [7] The subcooled water has been one of the major issues in most freezing processes including those in freezing desalination, since it freezes on the container wall and turns to the stable solid phase (i.e., ice) with uncontrollable ice size and shape that induce difficulties in ice handling downstream.

In addition to the ice handling issue, the subcooling of water also increases the energy consumption on the side of vapor operation. [3] The major energy consumption and principal difficulty in vacuum freezing processes is the handling of large volumes of water vapor produced per unit of water. Subcooling of water brings the freezing temperature down in the vacuum freezing chamber, where the equilibrium vapor pressure also drops with temperature; on the other hand, it requires a certain pressure to regenerate liquid water by condensation on ice at the triple point of water. A vapor compression process is used to bring the lower-pressured vapor from the freezing chamber to the water regenerator. The energy consumption of the vapor compression process is the major cost of the vacuum freezing desalination process, which is determined by the pressure increase from the freezing chamber to the water regenerator. The subcooling of water at freezing decreases the temperature at the freezing chamber, which further decreases the equilibrium vapor pressure, and thus increases the energy consumption of the vapor compression and the desalination process.

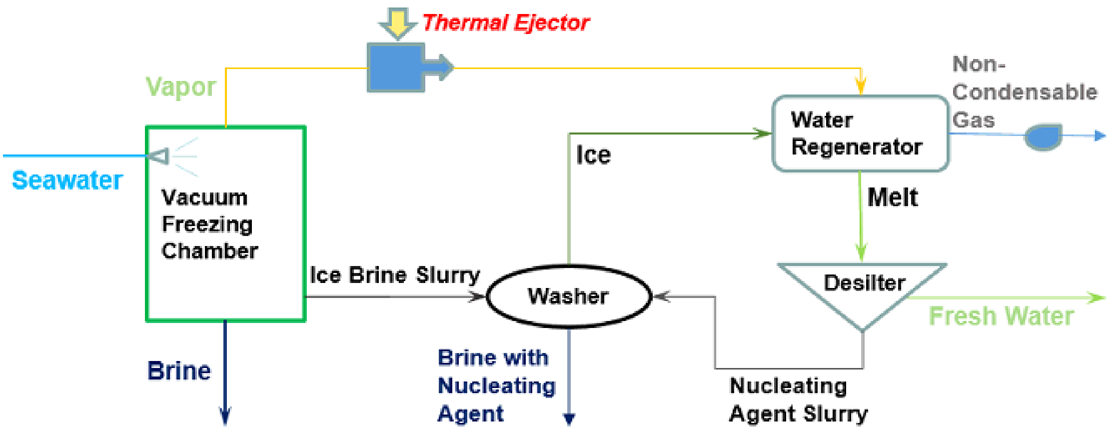

Figure 1. Schematic of a sub-scale prototype of the innovative spray freezing desalination at the triple point.

To summarize, the mutual reason of the two major problems (ice handling and vapor compression) of vacuum freezing desalination is the subcooling of water freezing. Advanced Cooling Technologies, Inc. (ACT) has investigated the feasibility of the vacuum freezing system that meet the energy consumption limit

(2 kWh/m^3) to compete with state-of-the-art techniques in the market. According to our investigation, to meet the energy requirement, the degree of subcooling of seawater needs to be less than 2 ˚C. In this work, ACT proposes and demonstrates the concept to use nucleating agents in water to prevent the subcooling of water droplets at freezing, therefore increases the temperature of freezing and limits energy consumption of the vacuum freezing desalination process. The nucleating agent can be removed from the fresh water product with a desilter under vortex separation process using the balance of buoyancy force on the particles in the fluid and the inertial forces of the vortex flow.[8] The proposed spray freezing system is illustrated in Figure 1.

2. Experimental.

The AgI-based nucleating agents for water were synthesized in house with chemicals purchased from Sigma-Aldrich and used as is. The crystal structure of the nucleating agents were tuned by doping with different elements to further improve the performance of subcooling suppression. Size and shape of the nucleating agent particles are observed with a Scanning Electron Microscope (SEM). The as-synthesized nucleating agents were then added to water and tested in a differential scanning calorimeter (DSC) for the freezing performance.

Vacuum freezing process of water with nucleating agents are evaluated in a vacuum chamber. A beaker partially filled with water was set in the vacuum chamber and two thermal couples are used to measure temperature on the surface and in the bulk water. To start the test, a vacuum pump is used to draw vacuum in the vacuum freezing chamber. Pressure drop and the vaporization induced temperature drop were recorded for further analysis. The experimental setup is shown in *Figure 2*.

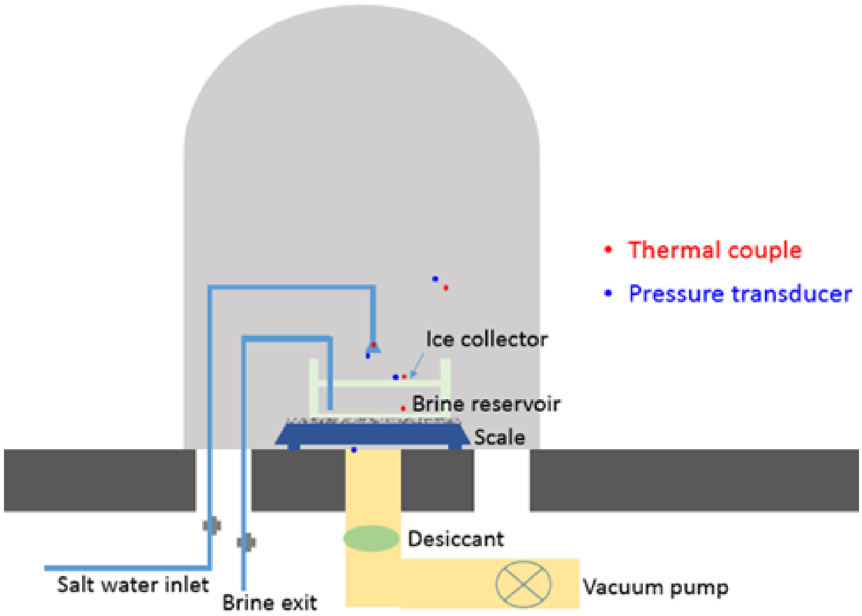

Figure 2. Schematic of the experimental setup of the vacuum chamber for the vacuum freezing process.

3. Results and Discussions.

Figure 3 shows the DSC curve of the melting and freezing process of water with nucleating agents. It is found that pure water starts freezing at -21.8 ˚C in DSC testing cell, i.e., the subcooling of pure water is 21.8 ˚C before it starts freezing on the testing cell wall, lower than that of homogeneous subcooling (38 ˚C). Before doping, the nucleating agent can suppress the subcooling of water and elevate the freezing point to -3.2 ˚C, in which the subcooling of water is significantly suppressed by the using of AgI as nucleating agents but still insufficient to match the target of this project. With the tuned crystal structure by doping the AgI nucleating agents, the doped nucleating agent developed in this work is able to suppress subcooling to 1˚C. The particle size average of the doped nucleating agent is around 0.2 μm as shown in the SEM image in Figure 4, which is suitable for both nucleating in seawater and separation from fresh water after production.

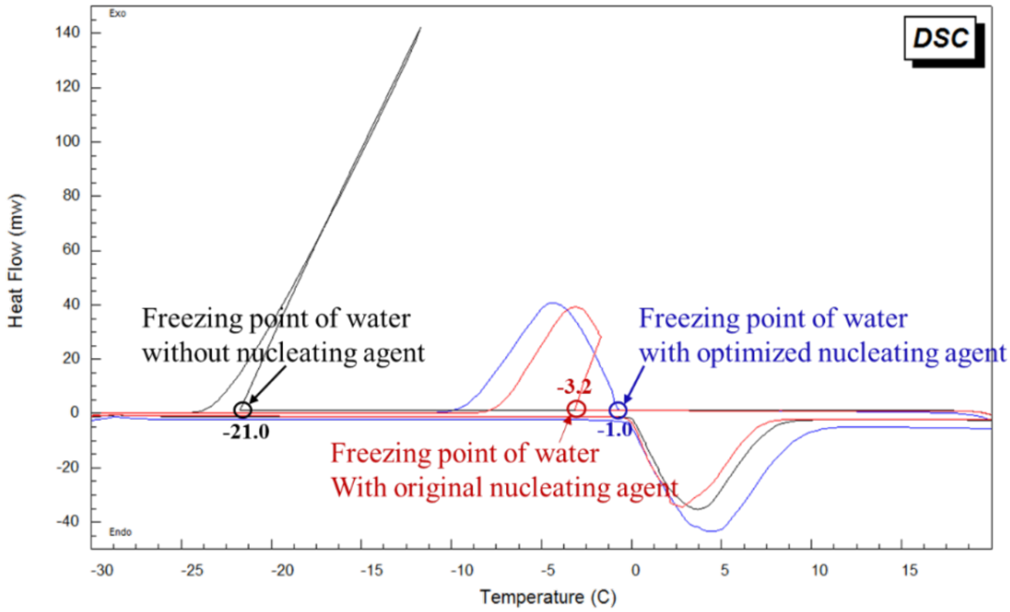

Figure 3. DSC curves of pure water (black) and water with original nucleating agents (red) and doped nucleating agents (blue).

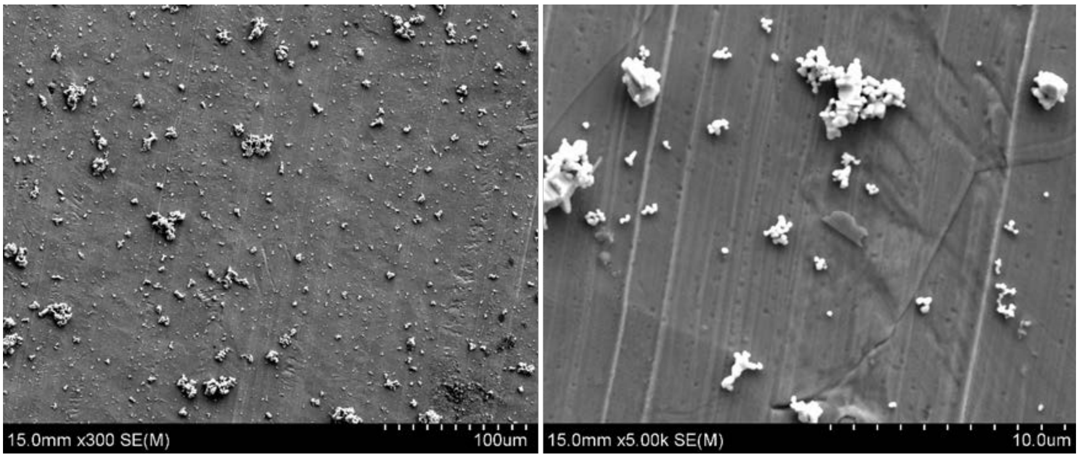

Figure 4. SEM images of the doped nucleating agents. A closer view of the sample is shown on the right.

The tuned nucleating agent is then used in the test of vacuum freezing process. As shown in Figure 3, as the pressure drops in the vacuum chamber, temperature of water also drops both on the surface and in bulk water due to the evaporation of water. Pressure keeps dropping to lower than the triple point pressure $P_{tr,water}$, which brings the surface temperature of water below the triple point temperature $T_{tr,water}$. Due to subcooling, the surface water in the pure water beaker is not frozen immediately after $T_{tr,water}$ is reached. The subcooling condition of pure water maintains for a while until it reaches to a lower limit of temperature at the metastable status, when freezing starts from a random spot on the surface of water. The difference of the lower limit of temperature and the triple point temperature is the subcooling of water in this test, which is about 4 ˚C. The subcooling of bulk water freezing is much smaller than that of droplet freezing, as the large volume of the sample provides more probability to initiate the freezing process by forming initial ice nuclei. [9]

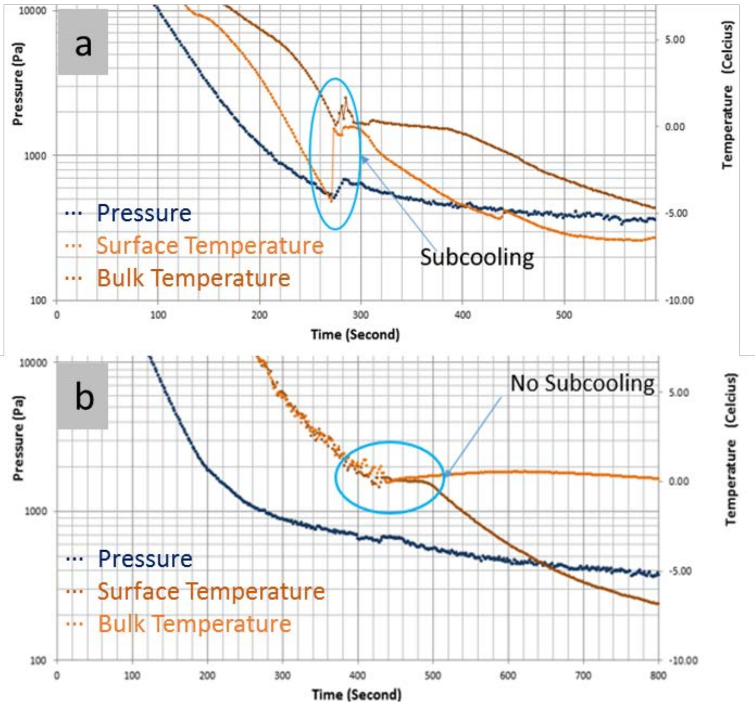

Figure 5. Vacuum freezing test of pure water a) without using of nucleating agent and b) with doped nucleating agent.

The subcooling of water with the doped nucleating agents during vacuum freezing is much smaller. Similar as that of pure water without nucleating agents, temperature drops as pressure decreases in the beginning of the process. However, when pressure reaches the triple point, water on the surface also reaches the freezing temperature and starts to freeze immediately, with no significant subcooling has been found. This is also lower than the 1 ˚C subcooling of similar samples in droplet freezing test in DSC, because of the same reason that bulk water provides more probability of ice nuclei formation. Comparing Figure 5a and b, it can be concluded that the nucleating agents function not only in freezing process induced by temperature drop at atmosphere pressure, but also works in the freezing processes induced by evaporative cooling under vacuum .

Based on the subcooling suppression capability of the doped nucleating agent, a system design of the spray freezing desalination is developed and presented in Figure 1. Different from the conventional freezing desalination techniques involving a cooling source in bulk water, [2-5] this system involves spray freezing in the freezing chamber driving by the low vapor pressure. Subcooling of the sprayed droplets is suppressed using the doped nucleating agents, so that the vapor pressure in the freezing chamber can be maintained at a relatively high value and the energy consumption of the vapor compression process downstream can also be decreased. Since the majority cost of the vacuum freezing desalination process is the energy consumption of the vapor compression, fresh water price of the spray freezing desalination system can also be decreased. Figure 6 shows the subcooling induced pressure decrease in the freezing chamber and correspondent energy consumption of the vapor compression process. It is indicated that with the 1 ˚C degree of subcooling supported by the doped nucleating agent, the energy consumption can be limited to 1.4 kWh/m^3 for low pressure vapor transportation from the vacuum freezing chamber to the water regenerator, 48% lower than using conventional original nucleating agent and 83% lower than that without using nucleating agent, as shown in Figure 6. With the dramatically reduced energy consumption, the potential application of the spray freezing desalination technology is promising in the desalination market.

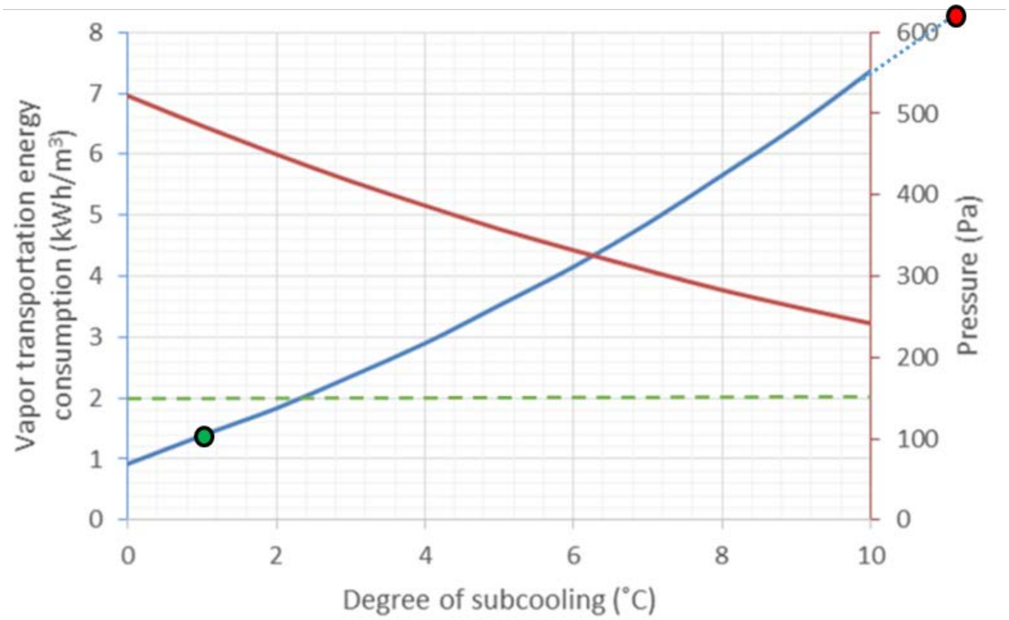

Figure 6. Decrease of vapor pressure (red) in the vacuum freezing chamber and increase of vapor pumping energy consumption per m^3 fresh water production (blue) vs. the increase of subcooling of water at freezing. The significant difference of energy consumption with nucleating agent (green circle) and without nucleating agent (red circle) are also shown. The green dash line represents 2 kWh/m^3.

4. Conclusion.

ACT has developed an innovative technical concept of spray freezing desalination at the triple point of water and overcame key technical challenges in this technology proposed. The subcooling of water is suppressed to 1 ˚C with doped nucleating agent developed in this work, much lower than 4 ˚C of using original nucleating agent. The effectiveness of the doped nucleating agent is also verified in vacuum freezing tests. Our model shows that with the use of the doped nucleating agents, energy consumption of the proposed spray freezing desalination process can be decreased below that of state-of-the-art techniques. It is shown that the energy consumption of this process is only 1.4 kWh/m^3 fresh water, 83% lower than the vacuum freezing desalination process without using nucleating agent. Applications that can directly benefit from the use of ACT's spray freezing desalination technology include seawater desalination, brackish water treatment, as well as fresh water supply for remote communities.

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