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Enhanced vacuum freezing for thermal desalination at the triple point

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ABSTRACT

Nucleating agents are developed to suppress the subcooling of freezing water. By tuning the synthesis parameters of silver copper iodide particles, the capability of subcooling suppression by the nucleating agents is maximized. This is to maintain the actual freezing point of brackish water with nucleating agents close to the triple point temperature of the brackish water. The nucleating agents are applied to a thermally-driven vacuum freezing desalination process under development to minimize the total energy consumption of the desalination process. In this process, freezing and vaporization of water happen simultaneously at the triple point with net-zero thermal energy consumption, where both of the processes generate 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 liquid freshwater. No thermal energy input is required in the simultaneous phase transition processes. To enable simultaneous condensation of vapor and melting of ice, the majority of energy consumption of this technology is used for vapor compression to the triple point pressure or higher from below-triple point pressure in the subcooled vacuum freezing process. The nucleating agents are used to suppress the subcooling and elevate the equilibrium vacuum freezing pressure to decrease the power requirement for vapor compression and the overall desalination process. The enhanced nucleating agents developed can suppress subcooling within 1˚C of the theoretical melting point, thus significantly decreasing the desalination energy consumption. 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, Vacuum Freezing, the Triple Point, Thermal Energy, Nucleating Agent.

1. Introduction.

The need for fresh water supply with an increasing population growth is critical. However, there are areas that are significantly limited by access to freshwater. Most of water in the planet is seawater and brackish water, which represent virtually unlimited supply of water yet unsuitable for human, agricultural, or industrial consumption before treatment. Effective and affordable desalination techniques are required in order to convert this vast volume of water into a usable resource.

The process of vacuum freezing desalination is based on the natural phenomenon of pure ice formation in a saline solution such as seawater. Impurities remain in the liquid phase during the freezing process, leaving behind a pure solid phase of ice. Freezing of water requires the removal of the heat of fusion (H_f = 334 kJ/kg) of ice at the melting point of water, nearly 1/7 of the heat of vaporization of water (H_{vap} = 2500 kJ/kg) at the same temperature and pressure. Specifically, when freezing occurs at the triple point of water where vapor and crystalline ice are formed simultaneously from liquid without the thermal input, the energy is balanced with the endothermic vaporization and the exothermic freezing:

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

where m_s and 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 ice and vapor can then be transported to a water regeneration chamber to produce liquid freshwater by the concurrent melting-

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condensation process on the interfcace of ice and vapor. The amount of vapor to transport in the process is only about 1/8 of the total processing water, resulting in a smaller pumping power requirement and lower energy consumptioon. [1,2] In addition, the low operation temperature (< 0 ˚C) significantly reduces the corrosion issue, which enables the use of much lower cost engineering materials. 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. [1]

There has not yet been a successful commercial vacuum freezing process in desalination, partially due to the cost of vapor transportation at sub-triple-point pressure induced by the lack of reliable water freezing control. [2] The majority of energy consumption and principal difficulty in the vacuum freezing process 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. However, it requires a certain pressure higher than the saturated vapor pressure to regenerate liquid water by condensing vapor on ice at the triple point of water. A vapor compression process is then required to bring the low-pressure vapor from the freezing chamber to the water regenerator. Since the energy consumption for vapor compression is the major operation cost for vacuum freezing desalination, the energy cost of the vacuum freezing desalination is largely determined by the pressure increase from the freezing chamber to the water regenerator. The subcooling of water during freezing decreases the temperature in the freezing chamber, which further decreases the equilibrium vapor pressure; thus, subcooling of water increases the energy consumption of the vapor compression and desalination process.

In order to suppress the subcooling of water during freezing and decrease the cost of vapor transportation in vacuum freezing desalination, Advanced Cooling Technologies, Inc. (ACT) had demonstrated the concept to use nucleating agents in water to prevent the subcooling of water droplets at freezing. With the use of nucleating agents in the vacuum freezing process, this technology suppresses the subcooling, increases the temperature of freezing and limits energy consumption of the vacuum freezing desalination process.[3] The nucleating agent can be recycled with a desilter after the production of the fresh water.[4] The proposed vacuum freezing system is illustrated in Figure 1. In this work, the AgI-based nucleating agent that is able to suppress the subcooling of water within 1 ˚C has been further developed for the vacuum freezing application.

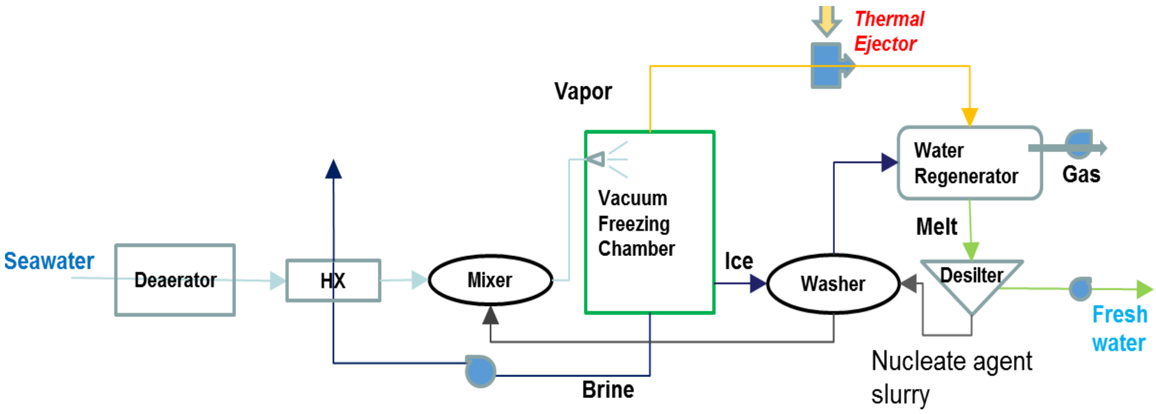

Figure 1. Schematic of a sub-scale prototype of the innovative spray freezing desalination at the triple point.

2. Experimental Results and Discussions.

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 was tuned by doping with different elements to further improve the performance of subcooling suppression. The as-synthesized nucleating agents were then added to water and tested both in a differential scanning calorimeter (DSC) and a vacuum chamber as shown in Figure 2 for the freezing performance.

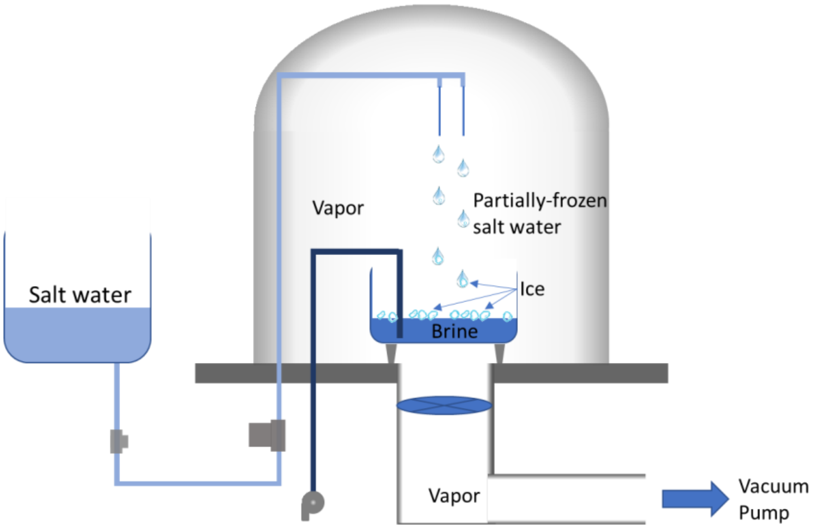

Figure 2. Schematic of the experimental setup of the vacuum chamber for the vacuum freezing process.

It is known that β-AgI can serve as a nucleating agent to supress the subcooling of water due to the similar crystal structure between the iodide and ice. Ice at the triple point of water presents a hexagonal crystal structure, with lattice parameters a_{ice}=4.52Å and c_{ice}=7.36Å. With similar hexagonal crystal structure and lattice parameters a_{AgI}=4.52Å and c_{AgI}=7.36Å, β-AgI can suppress the subcooling of water on its surface to 4 ˚C (i.e., water starts freezing at -4 ˚C), much lower than the reported the homogeneous subcooling of water as large as 38 ˚C. By doping AgI with copper, $Ag_xCu_{1-x}I$ can be produced with smaller difference of lattice parameters with hexagonal ice. The enhanced nucleating agents thus present better capability of subcooling suppression. As shown in Figure 3, when *x*=0.7, $Ag_{0.7}Cu_{0.3}I$ shows the optimum subcooling suppression capability, decreasing the degree of subcooling to 1.0 ˚C, much lower than that by pure AgI (*x*=1). Further experiments (not shown) indicated that the synthesis of effective nucleating agents favor both lower reagent concentration and lower reaction temperature.

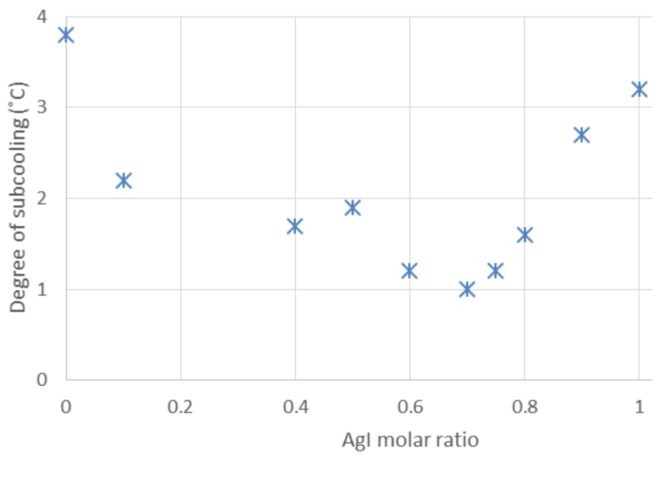

Figure 3. Subcooling of water samples with nucleating agents $Ag_xCu_{1-x}I$, with doping ratio (1-x) from 0 to 1.

The tuned nucleating agent $Ag_{0.7}Cu_{0.3}I$ is then used in the test of vacuum freezing process as shown in Figure 2, where salt water at varying concentrations were introduced to the vacuum chamber with vacuum applied by a vacuum pump. As the pressure drops in the vacuum chamber, temperature of water also drops due to the evaporation of water. Freezing of salt water starts when the subcooled freezing point is reached with the use of the nucleating agent. Figure 4 shows the starting pressure of the freezing process of salt solutions with different concentration. Without the nucleating agents, no freezing occurs with any concentration of salt water or freshwater above 300 Pa. With the use of nucleating agents, the equilibrium vapor pressure is increased for salt water at all concentrations, therefore decreases the pumping power requirement of vapor from vacuum freezing chamber to the condensation chamber to regenerate liquid freshwater with fixed pressure at 620 Pa or higher.

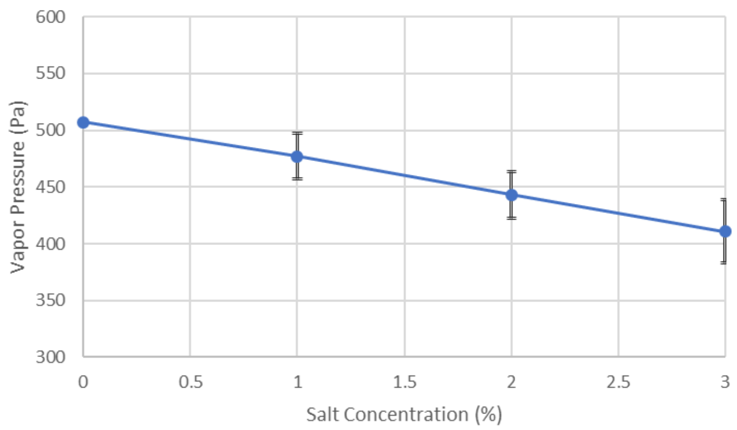

Figure 4. Vacuum chamber pressure when the salt water starts freezing.

Since the majority cost of the vacuum freezing desalination process is the energy consumption of the vapor compression, freshwater price of the vacuum freezing desalination system can be decreased with increased salt water freezing point by the nucleating agents developed in this research. As indicated in our previous cost model [3], with the 1 ˚C degree of subcooling supported by the enhanced 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. With the dramatically reduced energy consumption, the potential application of the spray freezing desalination technology is promising in the desalination market.

3. Conclusion.

ACT developed an innovative technical concept of vacuum freezing desalination at the triple point of water and overcame key technical challenges of developing specific nucleating agents in this technology. The subcooling of water is suppressed to 1°C with doped nucleating agent developed in this study, much lower than the 4°C subcooling using original nucleating agents. 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 vacuum freezing desalination process can be decreased significantly comparing with the process without using nucleating agent.

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