Freezing of mineralized water droplets in winter sprinkling

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Abstract. Drip congelation is an effective method of desalination of salt water. The results of mathematical modelling of freezing of fresh and salt water droplets in conditions of free fall at negative air temperatures are presented. Different options of salt rejection from the frost boundary and mineralization growth in the unfrozen part of the drop are considered.

1. Introduction
Intensive economic development of Arctics has resulted in pollution of sewage waters of water bodies. For purification and desalination of large volumes of natural and technogenic waters, including for the purposes of water supply of the population, it is necessary to use lean processing based on the use of renewable natural energy. Our research has shown [1] that one of the most efficient method of desalination and purification of large volumes of mineralized water is the method of drip freezing. The method is based on the use of long-range sprinklers plants to create a drip torch and the formation of porous ice bodies. Water consumption of the most common sprinklers, based on DTT-70 system with nozzle diameter 55 mm is 240 m³/hour, with a jet range 70 m. In the Arctic zone the performance of freezing with winter sprinkling can reach 10⁶ tons of porous ice per month. Currently, winter sprinkling is widely used for the construction of ice crossings and ice roads. Experiments with salt water and estimations show that this method allows, even at the freezing stage, to reduce the mineralization of porous ice body by 10–12 times. When the water droplets are freezing, the salt pushed away off into the central unfrozen drop core. When the water drops fall on the ground and their ice shells destruct, the unfrozen brine is filtered away from the porous ice body that considerably reduces its mineralization. With increase of mineralization of initial water, the mineralization of the unfrozen water drop core grows, and, as a result, the desalination productivity decreases [2].

The aim of the paper is to assess the influence of water mineralization on freezing of droplets in winter sprinkling.

2. Problem statement
At winter sprinkling the height of the drip torch reaches 20 meters. The average diameter of drops of modern sprinklers units of the "Grad" series applied for winter sprinkling is 1.5 mm with diameter range 1-2 mm. The fall time of water droplets 1 to 2 mm in diameter from a height of 20 m is 3 – 5 seconds. Application of winter sprinkling allows to create in a drip torch a water/ice mixture which forms the monolithic ice used for construction of ice crossings and dams. The water drops in the mixture should not freeze completely, and at falling the ice shell of a drops should be destroyed and release unfrozen water. Otherwise, dry granulated ice will be formed, which is not suitable for the construction of ice crossings. Experimental studies have shown that for water droplets with a radius of
1.5 mm, the proportion of ice in a drop should not exceed 50 – 60 %. The same conditions are necessary at application of winter sprinkling for desalination of mineralized waters. This imposes restrictions on the parameters of the drip torch depending on the air temperature. Restrictions on the share of ice in freezing drops and the fall time will be used in calculating of water mineralization effect on freezing of drops at winter sprinkling.

3. Mathematical modelling

At freezing of drops of fresh water or water with low mineralization (up to 5-10 g/L) the ice shell is formed on a surface of a drop and it thickens, reducing the radius of the liquid part. For water with high mineralization, the growth of branchy crystals into the depth of the liquid part of the drop is possible. This increases the mineralization of the liquid part of the drop. However, the growth of branchy crystals is difficult to predict. Therefore, as well as in case of a drop of fresh water, the scheme of freezing is accepted with the formation of the ice shell and its symmetrical development to the center of the drop. It is assumed that the initial drop temperature is equal to the freezing temperature of water at initial salinity.

The transfer of heat and freezing water is described by a boundary problem with a moving phase boundary

\[
\frac{\partial T_i}{\partial \tau} = a_i \left( \frac{\partial^2 T_i}{\partial r^2} + \frac{2}{r} \frac{\partial T_i}{\partial r} \right), \xi(\tau) < r < R, \\
\frac{\partial T_w}{\partial \tau} = a_w \left( \frac{\partial^2 T_w}{\partial r^2} + \frac{2}{r} \frac{\partial T_w}{\partial r} \right), 0 < r < \xi(\tau).
\]

The condition of heat exchange at a drop boundary is

\[-\lambda_i \frac{\partial T_i}{\partial r} \bigg|_{r=R} = \alpha_{ai} (T_i(R) - T_{ae}).\]

Stefan's condition at the freezing boundary at \( r = \xi(\tau) \) is

\[
\lambda_i \frac{\partial T_i}{\partial r} - \lambda_w \frac{\partial T_w}{\partial r} = -L \frac{d\xi}{d\tau}.
\]

At freezing boundary when \( r = \xi \) the temperature in solid and liquid parts suggested to be equal to the freezing temperature of saline water \( T_d(s) \) with different salinity \( T_i = T_w = T_0(s) \).

In the central part of the drop when \( r = 0 \) the following condition is accepted

\[
\frac{\partial T_w}{\partial r} = 0.
\]

In the initial period when \( \tau = 0 \) the water temperature is assumed to be equal to the freezing temperature \( T_w = T_0 \).

Accepted designations: \( T \) is temperature, \( \tau \) is time, \( a \) and \( \lambda \) are coefficients of thermal diffusivity and thermal conductivity; \( L \) is the volumetric heat of the water-ice phase transition, \( R \) is the radius of the drop; \( \alpha_{ai} \) is a heat-exchange coefficient of falling drops; \( \xi \) is the position of the crystallization front (radius of the liquid core). Indexes \( w \) and \( i \) correspond to water and ice; \( T_{ae} \) is an effective air temperature.
Thermal diffusivity is \( a = \lambda / (c \rho) \), where \( c \) and \( \rho \) are heat capacity and density, respectively. Factor heat-exchange coefficient on the drop surface and effective air temperature are taken from [3]. They were obtained using criterial dependencies of heat and mass exchange in relation with water vapor pressure and temperature.

The phase composition of the salt ice depends on the temperature and mineralization. At the temperature of salt ice above \(-8\ldots-10 \, ^\circ C\), as a first approximation one can take a linear dependence between the concentration of brine \( S_b \) (kg/m\(^3\)) in ice and ice temperature \( t_i \) [4]

\[
S_b = S \cdot t_i, \tag{1}
\]

where is \( t_i = T_i - 273 \); values of factor \( \sigma \) depend on the freezing temperature of different salts, and for sea water \( \sigma = -18.2 \, \text{kg/(m}^3 \text{ grad}) \).

The efficient heat capacity of salt ice \( c_{ie} \) is taken into account for heat-physical calculations and is equal to the average value of the sum of the heat capacities of the crystal ice \( c_i \) and brine \( c_b \), and the heat of phase transitions \( L \). The value of \( c_{ie} \) is determined by the equation [4]

\[
c_{ie}(T_i) = c_i + (c_b - c_i) \left( \frac{S}{\sigma(T_i - 273)} \right) - L \frac{S}{\sigma(T_i - 273)^2}. \tag{2}
\]

4. Calculation results

Calculations were carried out for fresh water and water with mineralization 35 g/L with freezing temperature \(-1.8 \, ^\circ C\). For calculations, the drop diameters accepted as 1, 1.5, and 2 mm. On the freezing boundary of a saline water drop a layer of water with increased mineralization can develop. This process is difficult to predict. Therefore, as a first approximation, extreme cases of salt rejection from the freezing boundary into the liquid part of the drop were considered: 1) salt at drops freezing is not rejected in the liquid part of the drop, the salinity of the ice shell and the liquid core are equal to the freezing temperature; and at the same time the effective heat capacity of ice is determined by the equation (2); 2) salt during freezing is completely rejected into the liquid part of the drop, and the heat capacity of the ice shell is equal to the heat capacity of crystal Ice \( c_i \), and the temperature of the phase transition is calculated according to the equation (1) taking into account the growing salinity of the liquid core of the drop; 3) the ice shell contains 1/3 part of the salt what often corresponds to the salinity of the young sea ice, and equations (1) and (2) are used to calculate the effective heat capacity of the ice and the freezing temperature of the liquid core.

The intensity of drops freezing depends on temperature difference between air and ice shell surface. Calculations showed, that in the first case the surface temperature of drops with radius of 0.5 and 1 mm when half of its volume frozen are \(-2.0 \) and \(-2.2 \, ^\circ C\); and in second case \(-3.6 \) and \(-3.9 \, ^\circ C\), respectively (Figure 1).

When half of a drop volume is frozen, radius of a liquid part is about 0.8 from a radius of a drop. For a drop of 1.5 mm in diameter the thickness of the ice shell is 0.15 mm. For this ice thickness the temperature difference between the freezing boundary and the drop surface (ice shell) is usually not more than 0.3 °C.

For heat exchange between the air and the falling droplet, an important parameter is the time-weighted value of drop surface temperature. For instance, at the time of half-volume freezing of the droplet 1.5 mm in radius, its surface temperature is about \(-3.8 \, ^\circ C\) (second case of calculations), whereas the average time-weighted temperature of its surface is \( C \) with air temperature \(-20 \, ^\circ C\). Meanwhile the effective air temperature reaches \(-29 \, ^\circ C\) because of heat exchange by evaporation. The average time-weighted temperature of droplet surface (in first case) is \(-2.0 \, ^\circ C\) and (in third case) \(-2.6 \, ^\circ C\). The temperature of the surface depends mainly on the ice share freezing drop and, in a lesser degree, on air temperature. For example, for a drop of 1.5 mm in diameter, its surface temperature at the moment of half-volume freezing is \(-3.7 \, ^\circ C\), \(-3.9 \, ^\circ C\), and \(-4.1 \, ^\circ C\) at air temperatures \(-10 \, ^\circ C\), \(-20 \, ^\circ C\), and \(-40 \, ^\circ C\) accordingly (second case of calculations).
Figure 1. Surface temperature of a droplet depending on the share of ice in its volume. Curves 1, 2 and 3 correspond to three cases of salt rejection from the freezing boundary into the liquid part (details in text).

The results of calculations (for second case) of freezing time of a drop of 1.5 mm diameter depending on ice fraction are given in Figure 2. The fall time of the drop from a height of 18 m is 3.3 sec. During this time 0.14, 0.20, 0.24, or 0.39 of its volume freezes at air temperatures –10, –15, –20, or –40 °C, respectively (Figure 2).

Figure 2. Freezing time of a droplet of 1.5 mm in diameter depending on ice volume fraction in it. The time is estimated for second case (see text) at different air temperatures: curve 1 is for –10 °C, curve 2 is for –15 °C, curve 3 is for –20 °C, and curve 4 is for –40 °C.

Effect of droplet size on freezing is shown in Figure 3. It can be seen that at air temperature –20 °C the half-volume freezing time (second case of calculations) is 4.9, 8.4, and 13.4 sec for drops of 1, 1.5, and 2 mm in diameter, respectively.
Figure 3. Freezing time of a droplet with a diameter of 1 mm (4), 1.5 mm (1, 3), and 2 mm (2) depending on ice volume fraction. The time is estimated for second case (see text) at different air temperatures: curve 1 is for –10 °C, curves 2, 3 and 4 are for –20 °C.

Freezing of half volume of a drop of 1.5 mm in diameter at air temperature –20 (–10) °C requires 8.5 (15.2) seconds for fresh water and 9.9 (19.0) seconds for water with mineralization of 35 g/L (third case of calculations). On the first case of calculations it takes 9.7 (17.8) seconds and on the second case 9.4 (18.2) seconds. This result is explained by the fact that the average time-weighted surface temperature differs slightly (relatively to effective air temperature) at freezing to the half of the drop volume. While retaining some salt in the ice in the form of brine cells significantly increases the effective heat capacity of ice, according to the equation (2). Thus, for various variants of salt rejection, the results of calculating the freezing time of the droplet to half its volume are determined both by the effective heat capacity of the ice and by the freezing temperature of the liquid part of the drop. The latter depends on the mineralization of the liquid core, which increases during freezing and is determined by the mechanism of rejection of salt ions from the freezing boundary.

5. Conclusions
Results of mathematical modeling of freezing of drops of fresh and salt water in conditions of free fall at negative temperatures of atmospheric air were presented. The Stefan condition was adopted at the freezing front. Various variants of the growth of mineralization of the unfrozen part of the drop during its freezing were considered. For drops of water with mineralization of 35 g/L and diameter of 1.5 mm, the freezing time of half the volume of the droplet at an air temperature of –10 °C is 25 % longer than for fresh water, and 17 % at an air temperature of –20 °C, when ice retains 1/3 of the salt.

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