Experimental study and numerical simulation of the salinity effect on water-freezing point and ice-melting rate

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Abstract. In this paper, based on the background of snowmelt de-icing tools, we studied the effect of salt on freezing point and melting rate of ice through laboratory test and FLUENT numerical simulation analysis. It was confirmed that the freezing point is inversely proportional to the salt solid content, and with the salt solid content increasing, the freezing process of salt water gradually accepts the curing rule of non-crystal solids. At the same temperature, an increase in the salt solid content, the ice melting rate increase by the empirical formula linking the melting time with temperature and salt content. The theoretical aspects of solid/fluid transformation are discussed in detail.

1. Introduction
In cold seasons, snow/ice cover on the roads strongly deteriorate transportation conditions and public safety, which makes the problem of snow cover melting quite topical [1, 2] As the most commonly and largely used snow-melting agent, salt has a great contribution to snow- and ice-melting. However, the utilization of salt causes irreversible pollution to the environment. Thus, it is important to reduce the dosage of salt during the snow-melting process or research environmentally friendly snow-melting agent to replace salt. In the winter of 2008, a one-off snowstorm occurred in south China. The roads were slippery and crowded due to continuous snowstorm and low temperature, numerous areas experienced a blackout/power loss due to high-voltage electric lines were covered by ice and torn. According to statistics, the total direct economic loss caused by the snowstorm amounted to 130 billion yuan (19.5 billion USD). Therefore, the research of transformation about water and ice is emergency due to the theoretical significance and applied value. In publication [3], the author studied the fluid-solid transformation theory based on transformation thermo dynamics and molecular dynamics, and the author deduced the melting speed formula. Authors [4] studied the influence of humidity and temperature on the water-ice fluid-solid transformation and deduced the empirical formula linking the melting time and humidity at different temperatures. In study [5], the influence of pH value and pressure on melting rate was investigated, and the empirical formula linking the pH value, pressure, and melting time was proposed.

The research object of our study is the salinity effect on water freezing point and ice melting rate. The results of this study can provide theoretical substantiation of snow melting process and the respective solid-flow transformation mechanism.

2. Solid-flow transformation mechanism of ice and water
In the field of heat transfer, the solid-flow transformation of ice and water is called Stefan Problem [6]. It bases on thermodynamics and heat transmission science, and the research contains four parts: (a) impact of external environment on the solid-flow transformation process; (b) distribution of temperature field; (c) impact of free convection or forced convection of the solid-flow transformation process; and (d) motion rule of the phase variation interface.

2.1 Differential equation of heat conduction
Practice shows that the quantity of heat transmission per second and per square meter is directly proportional to the temperature alteration ratio in the normal direction $x$ to the cross-section:
\[
\frac{\phi}{A} \sim \frac{\partial T}{\partial x}
\]  

(1)

where \( \phi \) is constant.

Formula (2) is Fourier heat conduction law

\[
\phi = -\lambda A \frac{\partial T}{\partial x}
\]  

(2)

where \( \lambda \) is heat conductivity coefficient (where “minus” sign in formula(2) means the direction of heat transfer is opposite to the direction of temperature rise); \( A \) is the cross-sectional area; \( T \) is the temperature; \( \frac{\partial T}{\partial x} \) is the gradient of temperature along the direction of \( x \).

In a rectangular coordinate system, consider a random micro parallelepiped (figure 1) derived from heat conductor, which is assumed to be isotropic.

Figure 1. Thermal analysis of the infinitesimal parallelepiped

According to the quantity of heat through following infinitesimal area in figure 1, we can deduce the general type of three-dimensional heat conduction differential equation in the Cartesian coordinate system using the Fourier heat conduction law and the energy conservation law (i.e., the first law of thermodynamics).

\[
\rho \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left( \lambda \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left( \lambda \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left( \lambda \frac{\partial T}{\partial z} \right) + \phi
\]  

(3)

In equation (3), parameters \( \rho, c, \phi, \) and \( t \) represent density, specific heat capacity (i.e., heat from internal heat source per second and per square meter), and time, respectively.

2.2 Model of ice melting

Every mathematical description of physical phenomenon needs approximate treatment, the governing equation of phase change problem based on the concept of continuous medium, we suppose that each material is homogeneous and isotropous. The sketch map of the solid-flow two-phase system is shown in figure 2. Here \( V \) means a random control body of the space, the value of \( V \) is invariable. At the time of \( t \), the control body is divided into two parts by phase interface, which are liquid zone (\( V_L \)) and solid zone (\( V_s \)). \( V_n \) means the speed of liquid arise from density fluctuation or other possible convection reasons. The motion of ice-water interface and the system’s temperature field are controlled by the thermal boundary condition on the surface \( S \), the distribution of initial temperature and the thermo-physical property of ice. The subscripts \( L \) and \( S \) represent the related properties of liquid and solid, respectively.

Figure 2. The system of solid phase and liquid phase [5]
The models of heat transfer with phase transformation account can be classified into two types: (i) temperature-based ones, which treat the temperature as a single variable and apply two energy conservation equations to solid and liquid phases; and (ii) enthalpy-based ones, which regard enthalpy and temperature as two variables and do not use the governing equations. In this study, the former type of (temperature-based) model is used to analyze the ice-melting process and the solid-flow transformation process of ice and water.

According to the energy conservation law, the governing equations of the temperature-based model are as follows:

\[ \rho \varepsilon \left( \frac{\partial T}{\partial t} + \nabla \cdot \mathbf{v} \right) = \nabla \cdot \left( \lambda \nabla T \right) + \dot{\phi} \]  \tag{4}

\[ \rho_s \varepsilon_s \frac{\partial T_s}{\partial t} = \nabla \cdot \left( \lambda_s \nabla T_s \right) + \dot{\phi}_s \]  \tag{5}

In Eqs. (4) and (5), \( \rho \) is density, \( c \) is specific heat, \( T \) is temperature, \( \nabla \) is gradient operator, \( t \) is time, \( \mathbf{v} \) is velocity vector of liquid phrase, \( \lambda \) is heat conductivity coefficient, and \( \dot{\phi} \) is volumetric heat source.

3. Solid-flow transformation test of ice and water

3.1 Test tools and instruments

The used equipment and materials include: an RPH-800 temperature and humidity chamber, the Agilent 34972 data acquisition unit, measuring temperature gun, refrigerator, computer, slot type screwdriver, temperature sensing wires, salt, measuring glass, electric saw, 20-mm cubic molds, vernier caliper, ruler, knife, and paper cups.

3.2 The experimental operation process

3.2.1 Solidification Test of Salt. The following procedure is recommended. Connect Agilent 34972A data acquisition unit to computer and set the temperature in RPH-800 at -20°C, as shown in figure 3.

![Laboratory equipment and parameter settings](image)

Firstly, prepare salt water; then measure the water and salt weight with electronic scales. The solid content is assessed as follows:

\[ C = \frac{G_{\text{salt}}}{G_{\text{water}} + G_{\text{salt}}} \times 100\% \]  \tag{6}

where \( C \) is solid content of salt; \( G_{\text{water}} \) is weight of water; \( G_{\text{salt}} \) is weight of additive salt.

According to formula (6), prepare salt solution with the solid content of salt at the ratio of 5%, 8%, 10%. The Agilent 34972A data acquisition unit has multi-channels data acquisition [7]. Put three kinds of salt solution into temperature and humidity chamber and collect test data. Ensure the environment of salt solution with different solid content of salt is uniform, which will enhance comparability of the data acquired from the test. Repeat each test three times and average the data. Plot temperature variation curve of salt solution with different solid content of salt in the process of freezing with MATLAB program.

3.2.2 Melting test of brine ice. Firstly, prepare pure water and salt solution with three values of salt solid content, then put them into refrigerator for 24 hours. Due to water evaporation, once the solution is prepared, the pure water and salt solution should be placed into refrigerator immediately to ensure accurate and comparable test results. Secondly, the surface of ice is irregular after freezing, so it is necessary to smooth
the surface of the ice before the test and ensure the size of the ice is uniform, which can enhance the comparability of the results. Then, put the ice into thermal/constant humidity chamber to observe the melting, record the temperature and time. In the test, the error is reduced by repeating the ice-melting tests for three times with the same temperature and solid content of salt, and averaging the data.

4. Test data analysis and discussion

4.1 Results and analysis of salt solution freezing tests

The time step of data acquisition is 20 seconds, export the data into computer for analysis. The process of pure water freezing can be divided into three steps; in the first step, the temperature is dropping continuous from initial temperature to freezing point. In the second step, the temperature is stable around the freezing point of salt solution. In the third step, the temperature continuously drop until it is equal to the setting temperature of incubator.

4.1.1 Process of pure water freezing. The temperature variation behavior during the process of pure water freezing is shown in figure 4.

As shown in figure 4, pure water freezing can be divided into three steps, the first step is temperature drop process before freezing. The second step is temperature-constant process, the average freezing point of 0.44℃ can be obtained by averaging the temperature of three tests. The third step is the temperature drop process after freezing.

There are two kinds of change in the first step, the one is the temperature continuous drop, the other one is the temperature going back to the freezing point and remaining unchanged. The freezing point means that water starts to freeze. By analyzing the first step, we can conclude that the reason why the temperature decreased at first and then increased is that the temperature of environment is below that of pure water, so the heat is transferred from pure water to the environment. At the moment, the internal resistance of water is the intermolecular cohesion, only the molecular force greater than intermolecular cohesion can violate the stable state conditions [8]. This is why the temperature drops to the freezing point at first.

It is known that the higher the temperature, the greater the potential energy, while the potential energy of liquid water exceeds that of ice. Energy release from water to the environment occurs when liquid turns into ice, which results in the temperature rise. When temperature increases to the freezing point, the energy balance occurs: the temperature exhibits a continuous drop after pure water is completely frozen.

4.1.2 Data analysis of salt solution freezing test. As seen from table 1, with salt solid content increase, the freezing point of salt solution is reduced, and since salt solid content is inversely proportional to freezing point, the second step shorter. A probable reason is that pure NaCl is a crystal, but table salt contains some iodine, which makes it non-crystal. With the increase in the solid content of salt, salinity has a stronger impact on the freezing of salt solution. Generally, the freezing curve of salt solution tends to non-crystal behavior.
Table 1. Freezing points of salty water for different solid content values

| Solid Content/% | data | T/min | Ice Point/℃ |
|----------------|------|-------|-------------|
| 5              | 55   | 18    | -2.62       |
| 8              | 46   | 15    | -5          |
| 10             | 31   | 10    | -6.32       |

Figure 5. Temperature evolution for freezing of water with four different salinity levels (0, 5, 8, and 10%)

We can see from figure 5 that a higher salinity of water results in a sharper temperature drop and less duration of freezing point attainment. Moreover, there is no distinct transition between the second and third steps, which is characteristic of non-crystal behavior.

4.2 Results and analysis of salt ice melting test

The initial temperature of salt ice taken out of refrigerator is -30.9℃. The melting test data for the ice from pure and salty water are shown in table 2.

Table 2. Summary melting process data (temperature T, time t, salt solid content s)

| T   | s  | 0%  | 5%  | 8%  | 10% |
|-----|----|-----|-----|-----|-----|
| 10  | 4823| 3024| 2806| 2407|
| 20  | 3864| 2300| 1872| 1742|
| 30  | 2652| 1470| 1374| 1231|
| 40  | 1734| 1054| 935 | 864 |
| 50  | 1235| 810 | 769 | 704 |
| 60  | 864 | 430 | 340 | 286 |
| 70  | 653 | 319 | 279 | 243 |
| 80  | 428 | 285 | 237 | 198 |

4.2.1 The relationship of pure water ice melting time and temperature

The test data are listed in table 2. They are incorporated into M file, which is imported to Matlab. The curve of pure water ice melting time evolution with temperature is then constructed. By fitting different kinds of function, we find two kinds of functions which can fit the data properly, that is \( f(x) = a \cdot e^{bx} \) and \( f(x) = a \cdot e^{cx} + c \cdot e^{dx} \). Hereinafter, the two functions are referred to as Power1 and Power2.
Power1-fitting formula is:

\[ t_{1} = 8937 \times e^{-0.0419T} \]  

(7)

Power2-fitting formula is:

\[ t_{2} = 3.711 \times 10^{12} \times e^{-0.26T} + 6990 \times e^{-0.0335T} \]  

(8)

Hereinafter, \( t \) is melting time, in s; \( T \) is temperature, in °C.

As shown in figure 6, the amplitude of Power1 is higher than that of Power2, which means Power2 is better-fitting than Power1. The fitting degree index of Power1 and Power2 are 0.9643 and 0.9971, which means the fitting degree of Power2 is better than Power1.

The curve of Power2 has a sudden inflexion point, whereas the curve of Power1 has no polar axis around the freezing point, so we choose Power2 as the empirical formula for the melting temperature-time variation of ice from pure water.

4.2.2 Temperature variation of melting time of salty ice with 5%, 8%, 10% solid contents. For the salty ice with three levels of salt solid content, the fitting curves of melting time and temperature are depicted in figures 7, 8, and 9.

Power1-fitting formula is:

\[ t_{1} = 5515 \times e^{-0.0450T} \]  

(9)

Power2-fitting formula is:
When the solid content of salt is 8%, the curves are fitted by the respective test data. Power1-fitting formula is:

\[ t_1 = 5064 \cdot e^{-0.0463T} \]  \hspace{1cm} \text{(11)}

Power2-fitting formula is:

\[ t_2 = 3883 \cdot e^{-0.0356T} + 1134 \cdot e^{-0.2639T} \]  \hspace{1cm} \text{(12)}

Figure 9. The melting curve of salty ice with 10% solid content of salt

When the solid content of salt is 10%, the curves are fitted by the respective test data. Power1-fitting formula is:

\[ t_1 = 3998 \cdot e^{-0.0410T} \]  \hspace{1cm} \text{(13)}

Power2-fitting formula is:

\[ t_2 = 3465 \cdot e^{-0.0351T} + 0.6681 \cdot e^{-1.434T} \]  \hspace{1cm} \text{(14)}

As shown in the residual analysis of figures 7, 8, and 9, in each couple of melting curves, the amplitude of Power1 is higher than that of Power2, so that Power2 is better than Power1. In each couple of melting curves, the fitting degree index \( R^2 \) values in Power1 and Power2 are: 0.9935 and 0.9981; 0.985 and 0.9989; 0.9859 and 0.9986; respectively, which means that fitting degree of Power2 is better than that of Power1. Since there is no polar axis near the freezing point, we selected formulas (10), (12), and (14) as salt's empirical formulas for the 5%, 8%, 10% solid content, which are the formulas for the temperature variation with melting time.

4.2.3 The curve of different solid content of salt. As shown in figure10, for the same temperature, the higher the solid content, the quicker the melting. Analysis based on energy, the reason is that with the increase of solid content of salt, the freezing point of salt ice is decreased. In the melting process under same temperature, the smaller of freezing point, the bigger temperature difference between salt ice and external environment, and the more heat can be absorbed in the same time, which means melting is faster. Analysis based on enthalpy value, the lower the temperature, the lower the enthalpy value, which means the less energy of specific salt ice has, the less heat can be absorbed during the temperature-rise period. In conclusion, the addition of salt decrease the freezing point, which bring two main advantages in the melting process, (a) the one is increase the temperature difference; (b) the other one is decrease the absorption of heat, that means melting process is accelerated and melting time is shorter.

We can see from Figure10 that four curves tend to straight line \( y=0 \), which means the temperature tends to infinity, the melting time tends to 0. On the left of freezing point, the melting time tends to infinity, which confirms the rationality of the fitting curves.
5. Numerical simulation of solid-flow transform for ice-water with FLUENT
In order to contract the test melting time with simulation melting time, we choose salt ice with solid content of 5% to simulate the process of melt, using the melt/freezing model in FLUENT [9]. The freezing point of the salt ice is 270.52K and the initial temperature is 243.15K, we suppose the undersurface of the salt ice is insulating. Boundary condition of undersurface is 270.52K, and the environment temperature is 313.15K.

![Figure 10. The melting curve of salt ice with different solid contents](image)

(a) ![Figure 11. Melting process of ice with 5% solid content: after 100s (a), 500s (b), and 982s (c).](image)

The melting time from the test is 1024s, whereas the value obtained by the numerical simulation is 982s. The main reasons of the difference can be as follows: (i) the temperature of saline ice will increase during its transfer from refrigerator to incubator; (ii) the temperature in incubator will decrease when the saline ice is placed into incubator; (iii) the enthalpy value changes after the saline ice freezing point drops; and (iv) the heterogeneity of saline ice: the closer to the center of salt ice, the higher the salt content. Thus, the simulation results have a good fit with the experimental data.

6. Conclusions
From the above findings for three different solid contents of salt (5, 8, and 10%), the following conclusions can be drawn:

1. The relationship between freezing point and solid content of salt is inversely proportional, the freezing point decreases with the solid content of salt.
2. At the second step, the duration of freezing point attainment is reduced, and the freezing process of saline solution tends to non-crystal pattern.
3. By analyzing the data from laboratory test for different solid contents of salt, the empirical formulas between ice-melting time and temperature were derived, which provide the theoretical basis for further study.
4. Under the same temperature, with the increase of solid content of salt, the melting time decreases, which implies higher melting rates.

Acknowledgments
This research was financially supported by the National Natural Science Foundation of “Research of theory and technology on rheological, creep and solid-fluid transformation of deep soft rock” (51674149).

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