Experimental Study on Crystallization Process and Freezing Properties of Ice Slurry Generation Based Sodium Chloride Solution

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Abstract

The crystallization process of ice slurry plays an important role in the cooling capacity and other freezing properties of the new-type cool agent. An experimental study on the important parameters during the crystallization process of ice slurry has been carried out and reported in the paper. The ice slurry is produced from sodium chloride solution using a scraper. It has been found that the liquid’s temperature experiences four stages during the crystallization process. This variation trend keeps accordance with literatures’ results, which verifies the responsibility of the test. It has also been investigated that the concentrations of sodium chloride solution have effects on several freezing properties of the ice slurry generation. In addition, a mathematical correlation between the latent heat and concentration has been developed eventually by polynomial fit. The error between the fitting curves and original experimental data is less than 10%. Overall the correlations and curves obtained in this paper can be used to predict the freezing point and the solidification time practically. It is of great significance that the concentration of brine water used for making ice can be estimated and controlled to meet the cooling capacity requirement.

Keywords: Sodium chloride; Scraper; Solution temperature; Freezing point; Latent heat

1. Introduction

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Ice slurry, a mixture of ice crystals, liquid water and some kind of antifreeze, is a promising working fluid due to its good flow characteristics and large energy density[1-2]. Scraped surface heat exchanger has been widely used in food industry, such as making ice cream[3-4]. Jacques Guilpart[5] compared the performance of several commonly used organic and inorganic ice slurry secondary refrigerants. Sodium chloride solution is an environmentally friendly phase change material (PCM). It is a widely available, less-expensive, and non-toxic secondary refrigerant with high latent heat and high thermal conductivity.

M. Akyurt a,b[6] briefly reviewed the physicochemical processes that occur during a freezing process. Many experimental studies of ice crystal growth in supercooling pure water have been carried out[7-10]. Hiroyuki Kumano et.al[11] reported the production of apparent latent heat from ice in aqueous solutions, which was defined as the effective latent heat. Measurements of effective latent heat of fusion of ice in aqueous solutions were carried out with liquid ice slurry, and ice was considered as a thermal energy storage material in the thermal energy storage system. Sawada et.al[12] attempted to measure latent heat of fusion of ice slurry, but their study was not satisfactory with regards to dilution heat due to variations in the concentration of solutions. Some measurements using differential scanning calorimetry (DSC) have also been carried out [13-14].

An experimental study on the important parameters during the crystallization process of ice slurry has been carried out and reported in the paper. It has been found that the liquid’s temperature experiences four stages during the crystallization process. Freezing properties which depend on the concentrations of sodium chloride solution are investigated systematically.

2. Experimental test rig

The ice slurry system with a surface-scraped heat exchanger, as shown in Fig.1, was designed for gaining the information about the crystallization process and properties of ice slurry. The test rig consists of the following three parts: the vapor compression refrigeration cycle, ice slurry forming unit and the chilled water circulation unit. The vapor compression refrigeration cycle includes the compressor, the condenser, the throttle valve and the evaporator which simultaneously act as the ice generator in ice slurry forming unit.

![Fig. 1 The principle diagram of the dynamic ice slurry producing device](image1)

![Fig. 2 Schematic plot of scraped device](image2)

Internal structure of ice generator is shown in Fig.2. The ice generator, one of the most major component, is made up of two concentric cylinders of different sizes between which some pieces of scraped blades are installed to prevent accumulation of the ice crystals. Series of brine solution with different concentrations in a range from 0.01 to 0.09 are pumped into the evaporator i.e. ice generator and then are transported out of it in the form of flowable ice slurry. The IPF (ice packing fraction) varies approximately within 30%-60%.
The experiment was operated under 0.1 MPa and room temperature. The evaporating temperature is adjusted at -12°C while the condensing temperature is adjusted at 40°C.

Temperatures are measured by sheathed thermocouple of T type. Distant data acquisition system is adopted in order to collect data and information from sheathed thermocouple of T type and then transform these data to the personal computers.

3. Theoretical analyses on freezing process

Fig.3[15] shows the temperature variation in the freezing process of pure water (ABCDE) and aqueous solutions (A'B'C'D'E'). As shown in Fig.3, the initial temperature at point A dropped fast below the freezing point \( t_f \), which is equal to the melting point \( t_m \), before the induction of crystallization. From A to B(B'), the ice slurry is at a nonequilibrium, metastable state, which is so-called supercooling. Many substances do not crystallize at the melting temperature \( t_m \) (liquid – solid equilibrium) but at a lower temperature[16]. Once the water or the solution reaches the minimum value at point B(B'), which is also called degree of supercooling, the nucleation phenomenon occurs. In this section, latent heat released from the solid ice to the liquid is more than the heat removed from the system. Therefore, in the following stage from B(B') to C(C'), the temperature jumps up to a certain value.

In pure water (or brine water), the line from C(C') to D(D') in the figure reflects that fast cool rates promote the formation and growth of many small ice crystals. What focus attention is that trend of line CD is more steady and of higher level in comparison with trend of line C'D' due to the presence of solutes, which results in depression of the freezing point based on Raoult’s Law. In addition, as above diagram indicates, the point B' which represents degree of supercooling of the aqueous solutions looks a little higher than the corresponding point B. The added solute promotes heterogeneous nucleation, thereby accelerating the nucleation process. In general, the additive of solute has a major influence on faster nucleation and lowered freezing point[17].

At point D', solution may become supersaturated and large latent heat of crystallization is released, causing a slight jump in temperature. From D(D') afterward, continuous crystallization occurs until the system is completely crystallized or solidified at very low temperatures.

Equilibrium curves of some common inorganic compounds studied by J. Guilpart[18] are shown in Fig.4.

4. Results and discussion

4.1. The crystallization process
Experimentally obtained temperature changing in the crystallization process of pure water and 3% sodium chloride are plotted in Fig.5. It can be seen that initial liquid temperatures in both of them descend down to the degree of the supercooling followed by a slight recover, which agree with the results described in the theoretical analyses section. Due to the effect of additive solute which act as anti-freeze depressant, the whole temperature and freezing point of brine solution become lower than pure water’s, which corresponds to the Fig.3[15].

![](image1)

**Fig.5** Solution temperature in pure water and sodium chloride solution of 4% concentration compared with each other

**Fig.6** The temperature changes of sodium chloride solution in evaporator export

It’s shown in Fig.6 that the temperature changes in the same trends when the concentrations of NaCl vary as listed: 1%, 5% and 9%.

It is considered that the above plots drawn from the experiment has verified the accuracy of the theoretical analyses to some extent. Above all, the experiment is reliable to study the correlation between concentrations and other factors.

### 4.2. Freezing properties influenced by solution concentration

![](image2)

**Fig. 7** The comparison of experimental and alkali manual freezing temperature values for sodium chloride solution

**Fig.8** The relationship of the concentration of sodium chloride and phase interface

To determine the relationship between the freezing point and variable concentrations of the sodium chloride solution, the experimental value and manual value referring to <Physicochemical parameters manual in chlor alkali industry> are compared in the Fig.7. It can be remarkably seen from the two curves that the freezing points decrease with increasing solution concentrations. However, except for the first point, each of the experiment value appears a little higher than manual ones, which is mainly caused by the scraping ice-making device. Scraped blades rotating at extremely high speeds strongly interfere the
brine water. It results in an enhancement of the heat transfer coefficient and more of that, the interference break the degree of supercooling before nucleation so that solidification formed in advance.

In Fig.8, comparison of 5 pairs of point has been apparently marked. Totally solid phase of ice appears 560s later than the mixture phase does in 1% concentration solution. The rest can be described in the above way, like 660s later in the 3% concentration solution, 770s later in the 5% concentration solution, 950s later in the 7% concentration solution and 1270s later in the 9% concentration solution.

It can be checked that the appearance of the mixed phase or totally solid phase become later with the increasing concentrations of solution. Moreover, the growth rate of arising time is adding more and more higher when concentrations is high enough, as shown in Fig.8. This phenomenon can be explained by that freezing points of the solution go down with increasing concentrations, so that those aqueous solutions of higher concentrations desire to absorb much more heat from the system which also needs longer time.

Latent heat of the phase change absorbed by sodium chloride solution of different concentrations is recorded utilizing DSC scanning thermal analyzer and is plotted in Fig.9. It can be seen that the latent heat does not change so much when the concentrations are under 5%. Otherwise, after the concentrations are more than 5%, the latent heat seems goes down obviously. In order to obtain the correlation between latent heat and the concentrations, the original curve is fitted, as the fitting curve shows. The finally determined mathematical correlations is as follows:

\[ y = 0.0157x^4 - 0.357x^3 + 2.584x^2 - 11.88x + 320.611 \]  \hspace{1cm} (1)

Where \( y \) stands for the phase change latent heat and \( x \) represents the concentration of the sodium chloride solution. Results calculated by the fitting model only have errors within 10%, comparing to the initial experimental data.

5. Conclusions

Experimental investigation of important parameters in the process of crystallization based sodium chloride solution was conducted. According to the foregoing description and analyses several conclusions could be drawn as follows:

(1) There are remarkably four zones within the whole process of the solidification. The temperature of the liquid drops directly to the degree of supercooling in the initial stage and then rise up a little. Once the nucleation occurs the temperature value keeps gentle decrease (keeps constant in pure water). In the fourth, namely, the last stage, totally solid phase turns out and temperature continue to drop more rapidly.

(2) It has been found that the tested trend of temperature change in the freezing process keeps accordance with the theoretical analyses. Therefore, the experimental results are reliable for further study.
(3) The mathematical correlation between the concentrations and the phase change latent heat is finally determined. Practically, correlations and curves obtained in the paper can be used to predict the freezing point and the solidification time. It is of great significance that the concentration of brine water used for making ice can be estimated and controlled to meet the cooling capacity requirement. Deeper research may be focused on relation between concentrations and particle diameter of ice crystals which play an important role in application systems.

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References


**Biography**

Professor Shengchun Liu went to the West Virginia University in United States to be a visiting scholar from Feb., 2014 to Aug., 2014. His researches focus on the refrigeration system optimization and energy saving (ice production systems research), heat transfer and heat exchange study on refrigeration and air conditioning systems, performance study of natural refrigerants.