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# Density modification of ice particles in ice slurry



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## ARTICLE INFO

### Article history:

Received 31 March 2015  
 Received in revised form 30 September 2015  
 Accepted 1 October 2015  
 Available online 13 October 2015

### Keywords:

Ice slurry  
 Crystallization  
 Density  
 Nucleation

## ABSTRACT

One of the characteristic properties of ice slurry is the buoyancy of ice particles, which leads to ice separation in unmixed ice slurries and the necessity to agitate storage vessels if ice slurry is to be extracted. Based on this, an investigation into the density modification of ice particles has been undertaken. Additional particles with higher density than ice should act as ice forming nuclei during ice generation, for which suitable particles have been determined and tested. It was possible to show that not all added particles act as ice forming nuclei in the role of a cell nucleus. Furthermore, it can be assumed that various particles agglomerate on the surface of ice particles; hence the density of ice particles increased more than expected due to the incorporation of several particles in each ice particle. These modified ice particles may sediment to the bottom of the container due to the high density of the numerous heavy foreign particles.

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# Modification de la densité des particules de glace dans un coulis de glace

Mots clés : Coulis de glace ; Cristallisation ; Densité ; Nucléation

## 1. Introduction

Cooling a mixture of water and a freezing point depressant – like ethanol, glycol or salt – until small ice particles are formed, leads to a secondary refrigerant known as ice slurry. Ice slurry, as a two-phase heat transfer fluid, is being increasingly applied as a secondary refrigerant in industry (Egolf and Kauffeld, 2005). The advantages are many; due to the stored latent heat – caused by the phase change from water to ice and ice to water – it is an excellent medium for energy storage. Compared to liquid refrigerants, ice slurry shows a two to three times better heat

transfer and up to ten times higher energy density for a given temperature change, as a result of which pipe dimensions and pumping power for cold distribution can be reduced. Furthermore, ice slurry is – depending on the additive – an environmentally benign, harmless and non-toxic secondary refrigerant and is also being used in direct contact cooling of diverse food articles like fish or vegetables (Kauffeld et al., 2010).

Another characteristic property of ice slurry is the density difference between the carrier fluid and the ice particles. Owing to their lower density compared to the carrier fluid, the ice particles experience buoyant force within the fluid. This aspect leads to some challenges when operating ice slurry-systems

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<http://dx.doi.org/10.1016/j.ijrefrig.2015.10.001>

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### Nomenclature

$L_{crit}$	critical cluster size [m]
$\Delta G$	Gibbs' free energy [J]
$A_c$	surface of a critical cluster [m <sup>2</sup> ]
$\gamma_{cl}$	interfacial tension [J m <sup>-2</sup> ]
$\Theta$	contact angle [°]
%( <i>w/w</i> )	mass fraction [-]

as well as having an impact on ice slurry storage. As a result, most storage tanks need propellers or agitators to avoid ice separation at the top of the tank. There are also special requirements for the piping in ice slurry systems. If the flow velocity in pipes is too low – depending on ice particle size and pipe dimension below approximately 0.6 m s<sup>-1</sup> – there might be undesired flow patterns like “heterogeneous flow”, “moving bed” or even “stationary bed” (Kitanovski et al., 2002). Connections with vertical upward outflow should be avoided to prevent accumulation and blockage caused by floating ice particles in case of no flow in the vertical branch (Kauffeld et al., 2005). Based on these challenges the density modification of ice particles has been investigated. The fundamental idea is to create modified ice particles by using particles, which act as ice forming nuclei. If the density of the additional particles is higher than the density of ice, the total density of the modified ice particle increases. This combination would affect the buoyancy of the modified ice particles. In this study, modified and pure ice particles are defined as ice particles with and without additional particles.

## 2. Nucleation theory

At this point it is necessary to presuppose basic knowledge of crystallization in order to determine the particles that can act as ice forming nuclei. Crystallization is a combination of nucleation and crystal growth (Chegnimonhan et al., 2009). In terms of the target modification of the ice particles the mechanism of nucleation becomes important.

### 2.1. Homogeneous nucleation

Homogeneous nucleation is by definition the nucleation in a pure solution without any impurities. If a solution resides in a metastable state, molecular collisions occur and small “clusters” (Gnielinski et al., 1993) or “embryos” (Kauffeld et al., 2005) build up. In the initial phase these clusters have a short lifetime and decay again. They have to reach a critical cluster size  $L_{crit}$  in order to become a stable nucleus and grow to the size of a crystal. The driving force of this mechanism is the reduction of Gibbs' free energy  $\Delta G$  in the system, also called the nucleation barrier (Günther et al., 2009). Gibbs' free energy can be written as (Gnielinski et al., 1993):

$$\Delta G = \Delta G_A + \Delta G_V \quad (1)$$

where  $\Delta G_A$  is the positive surface free energy, which has to be supplied to the system. The volume-free energy  $\Delta G_V$  is released

during the growing process of the nucleus and is therefore negative. According to this relation, a nucleus smaller than  $L_{crit}$  can reduce its overall free energy  $\Delta G$  by shrinking and decay, a nucleus larger than  $L_{crit}$  can reduce its  $\Delta G$  by growing (Günther et al., 2009). For homogeneous nucleation the critical cluster size depends on the degree of supersaturation – in the case of ice formation called the degree of supercooling. The higher the supersaturation (supercooling), the smaller is the critical cluster size (Vali, 1995). In order to form a critical cluster into a solution, the work of nucleation can be described as (Volmer and Weber, 1926):

$$\Delta G_C = 1/3 A_c \gamma_{cl} \quad (2)$$

where  $A_c$  is the surface of a critical cluster and  $\gamma_{cl}$  the interfacial tension between crystal and liquid.

### 2.2. Heterogeneous nucleation

Heterogeneous nucleation is defined as the nucleation on a surface of a foreign substrate. The aspired modification of the ice particles by using ice forming nuclei is based on the process of heterogeneous nucleation. With the presence of impurities in a solution, the work of nucleation can be reduced due to the lower energy barrier at the additional surface. The reduction is described by the factor  $f$  and can be written as (Gnielinski et al., 1993):

$$\Delta G_{C,het} = f \Delta G_C = f 1/3 A_c \gamma_{cl} \quad (3)$$

with

$$f = [(2 + \cos \Theta)(1 - \cos \Theta)^2] / 4 \quad (4)$$

where  $\Theta$  is the contact angle between the substrate and the growing crystal. Depending on the wettability of the substrate the contact angle may range between 0° and 180°. For a contact angle of 180° (unwettability of the substrate) one would obtain  $f \rightarrow 1$  and nucleation takes place under the conditions of homogeneous nucleation. For a contact angle of 0° (complete wettability of the substrate) one would obtain  $f \rightarrow 0$  and the work for nucleation tends to be zero (Gnielinski et al., 1993).

## 3. Requirements for ice forming nuclei

The main goal of this work is to modify the density of ice particles by using particles, which act as ice forming nuclei. Shirai et al. explored that polymers suppress the secondary nucleation of ice crystals (Shirai et al., 1985). Obviously, the process of ice forming is very selective. For this purpose, the particles used must have some specific characteristics in order to serve as ice forming nuclei.

In view of the good environmental performance of ice slurry, the additional particles must also be environmentally safe. Environmentally harmful substances should be omitted.

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