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Solute inclusion and freezing rate during progressive freeze concentration of sucrose and maltodextrin solutions

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ABSTRACT
Progressive freeze concentration is an alternative method to concentrate aqueous industrial streams compared to evaporation or membrane separation. In this research sucrose and maltodextrin solutions were concentrated in a stirred progressive freeze concentrator. The solute inclusion in the formed ice was studied using varying stirring speeds, initial concentrations and freezing plate temperatures. Under constant freezing plate temperature, a lower limit was found for the solute inclusions with increasing stirrer speeds. To improve the freeze concentration process, a decreasing temperature ramp was applied to the freezing plate. This yielded 2 to 3 times less solute inclusions in the ice, while maintaining similar ice yields.

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Freeze concentration; sucrose; solute inclusion

Introduction

Concentration of aqueous food streams is a routine operation in the food industry to prepare for (spray) drying, to increase shelf-life and to reduce transportation volumes. Multiple techniques are available, based on evaporation or freeze concentration. While thermal evaporation is the most common industrial technique and is readily applicable to many streams, such as dairy or sugar, it has drawbacks for streams containing heat-sensitive components.[1] Components such as proteins and flavors either become damaged through the heat-treatment or may co-evaporate with the water from the product stream, resulting in a loss of product quality. During freeze concentration, these components are only exposed to low temperatures and therefore suffer minimal thermal damage. It is therefore considered a mild concentration technique.[2,3]

During freeze concentration water is frozen as ice crystals, which excludes the solute molecules, when the degree of supercooling is not too high.[4] Supercooling is the process of lowering the temperature below the freezing point while the ice crystals are not yet formed due to absence of nucleation.[5] Sudden nucleation then leads to the formation of small crystals, which will enclose much of the solutes between the ice crystals. When the freezing surface is at low temperatures, the ice crystals tend to grow in dendritic shape. Between the dendrites concentrated solution may be trapped, which decreases the overall separation between ice and solution.[6–8] At lower rates of freezing, the crystals will be larger, the solute will have time to diffuse into the solution, and the entrapment of solutes is much lower.[9]

Freeze concentration can be performed in three main ways: suspension freeze concentration, block freeze concentration and progressive freeze concentration. These have been extensively reviewed by various authors for applications in fruit juices, coffee extracts, dairy and desalination.[1,10–12] During suspension freeze concentration, the ice growth and the degree of supercooling are maintained by continuously seeding the suspension with fresh crystals. The ice crystals are then washed and melted in a continuous washing filter.[13] This technique is commercially available and has applications in the fruit juice and beer industry.[1,14] Advantage of this form of freeze concentration is the ease of creating pure ice by the high surface area of the crystals.[4] Drawback of the technology is the need for a continuous wash filter, which requires precise operation to melt the ice to remove it from solution.[1] During block freeze concentration the product is nearly completely directionally frozen and selectively thawed to retrieve the concentrate.[15,16] The advantage

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of this method is the simple equipment although there should be a precise control of the freezing rate to achieve good separation.[16] During progressive freeze concentration the ice crystal(s) are grown on the wall of a heat exchanger and the ice layer is removed after the concentration process. Leaving the ice on the wall eliminates the need for a washing filter, which reduces the complexity of the system. A drawback of progressive freeze concentration is however that it is a batch operation. After growth of the ice layer the concentrate is removed and the ice is melted and removed from the system. Subsequently, the system is filled with a next batch. By operating at least two freeze concentration units in a parallel mode, they may be heat integrated by using a heat pump. This approach reduces the total energy usage of the process and thus increases the economic feasibility of the progressive freeze concentration process.[17]

Many researchers studying progressive freeze concentration have focused on the inclusion of solute in the ice. Parameters that determine solute inclusion are especially the initial solution concentration, the cooling temperature and the agitation or flow rate.[6,18–20] Recent research has investigated these parameters applying freeze concentration to various food products, such as for example apple juice, dairy and coffee extract.[21–25] A common problem is that with increased product concentration, the viscosity of most concentrates will increase. This increase in viscosity will hinder mass transfer of solutes from the boundary layer to the bulk and therefore enhance solute inclusion. The cooling temperature determines the ice growth rate and therefore has large influence on solute inclusion. In most work the temperature was kept constant. The most commonly studied solutes are sugars or salts.[13,18,26,27]

Due to the ice growth and solute exclusion by the ice, concentration polarization occurs at the boundary.[6,28,29] The concentration polarization leads to increased concentration close to the ice layer. The concentration difference between the layer close to the ice and the bulk will lead to diffusion of solutes back into the concentrate. With forced convection the transport of solute molecules can be enhanced and the diffusive boundary layer is minimized in thickness. Forced convection can thus contribute to less solute inclusion in the ice.

In this study a small stirred tank was used for progressive freeze concentration, in which the ice was grown on a heat exchanger plate at the bottom of the tank. The influence of convection was studied by varying stirrer rate in the tank. This system may be effectively scaled to a progressive freeze concentration system using for example heat exchanger plates on which ice is grown and in which hydrodynamics are varied with variable flow rates. Sucrose and maltodextrin were selected as model solute components in this study. Sucrose was selected as it is a major constituent of fruit juices.[1] Maltodextrin was selected as a larger molecule which has a lower diffusion coefficient in water.[30,31]

The objective of this study is to investigate the relationship between inclusion behavior of solutes and hydrodynamic conditions near the growing ice layer during progressive freeze concentration. Previous studies have often used progressive freeze concentration systems, which are optimized for studying solute partitioning behavior at the ice water interface.[27] In this study we chose a different set-up which can apply more realistic cooling and hydrodynamic conditions, when scaling up to a plate heat exchanger for ice growth. This is especially relevant for scaling-up the progressive freeze concentration process.

Material and methods

Experimental set-up

The film freeze concentration experiments were conducted in a small-scale test apparatus.[32] The test apparatus was constructed from an acrylic cylinder with 90 mm internal diameter (Figure 1). The bottom of the cylinder was a stainless-steel chamber that was flushed with cooling fluid. The vessel was equipped with a pitched two-bladed stirrer. To monitor the temperature during the experiments, thermocouples were placed in the vessel at 1, 2, and 5 mm from the bottom surface, plus one thermocouple at 10 mm below the liquid surface and two thermocouples in the in- and outgoing liquid flow. All thermocouples (type T) were connected to 24-bit data logger (National Instruments, cDAQ-9214, ±0.01 °C relative accuracy, USA).

Materials

Sucrose and maltodextrin solutions with various concentrations were used as feed solutions. Sucrose (342.30 g mol^{-1}) was obtained from Sigma-Aldrich (BioXtra, >99.5%) and maltodextrin DE12 (≈ 3423.0 g mol^{-1}) from Roquette Freres (Glucidex 12). The feed solutions were pre-cooled to 4 °C before use. To determine the sucrose concentration in the sample, we used a refractometer (Anton Paar, Abbemat 500, Germany). To determine the maltodextrin concentration, we heated the pre-weighed solutions overnight in an oven at 105 °C and weighed them afterwards. The

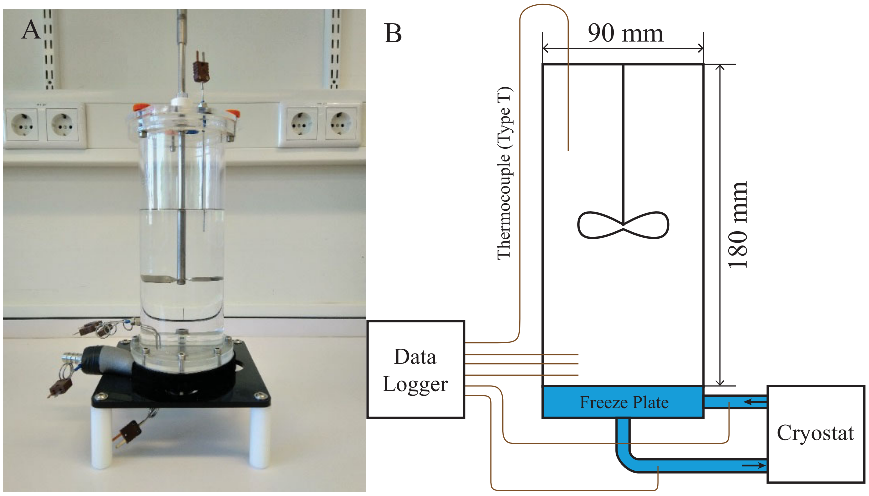

Figure 1. Small-scale stirred tank with cooling plate and ice growth at the bottom for progressive freeze concentration, (A) Picture of set-up, (B) Schematic representation with dimensions.

Table 1. Measured freezing points using DSC.

Sucrose concentration % (w/w)	Measured freezing point (°C)
6	−0.3
18	−1.9
36	−4.5
Maltodextrin concentration % (w/w)	
6	0.0

solutions were reused for a maximum of 5 days and separate solutions were used for experiments on the same day.

Freeze concentration experiments

The first set of freeze concentration experiments were conducted with constant cold wall temperatures, ranging from 5 °C, 7.5 °C, and 10 °C below the freezing point of the solution. The freezing points were determined using differential scanning calorimetry (TA instruments DSC250, USA, 20 µg sample, 10 °C/min cooling rate, 1 °C/min heating rate from −30 °C to 10 °C). The determined freezing points can be found in Table 1.

The stirrer speeds were varied between 50, 150, 300, and 500 rpm. Sucrose solutions of 6, 18, and 36%(w/w) and a 6%(w/w) maltodextrin DE12 were concentrated for 30 minutes. A second set of freeze concentration experiments was carried out with a decreasing cold wall temperature (Figure 2) to avoid the high initial ice growth rate when using a constant cold wall temperature. We chose a linear decreasing (equation 1) and a quadratically decreasing (equation 2) cold wall temperature. All profiles start at −2.8 °C, which is 2.5 °C below the freezing point of the 6%(w/w) sucrose solution used.

$$T = \min(-\alpha\ t,\ \ -2.8°C) \tag{1}$$

$$T = \ \ -\beta\ t^2 - 2.8°C \tag{2}$$

Where α is the slope of the cooling profile in °C/min and where β is the coefficient for the parabolic equation in °C s^{-2}. These experiments ran for 60 minutes at a stirrer speed of 500 rpm, with a 6%(w/w) sucrose solution.

At the start of the freeze concentration experiments, a droplet (100 µL) of pure water was deposited on the freeze plate, which forms a seed crystal preventing high initial super cooling. If initial super cooling is not prevented, sudden, very fast initial ice growth may lead to excessive inclusions at the start of the process[6] or may lead to ice crystals forming in suspension rather than on the freeze plate. When the droplet was completely frozen, the feed solution was introduced via a filling port at the top of the cylinder. To prevent air inclusion the stirring was only started after the solution had submerged the stirrer blades. At the end of the experiment the liquid was removed by pouring it from the cylinder and the ice was melted. Both fractions were weighted, and the sucrose content was determined with a refractometer (Anton Paar Abbemat 500, Germany). The dry matter content of the maltodextrin solution was determined drying the samples, in pre-weighed pans overnight in an oven at 105 °C. All experiments were carried out in duplicate.

Data analysis

To compare the intensity of the convective flow in a stirred vessel for the different concentrations and solutes, the impeller Reynolds number is computed:

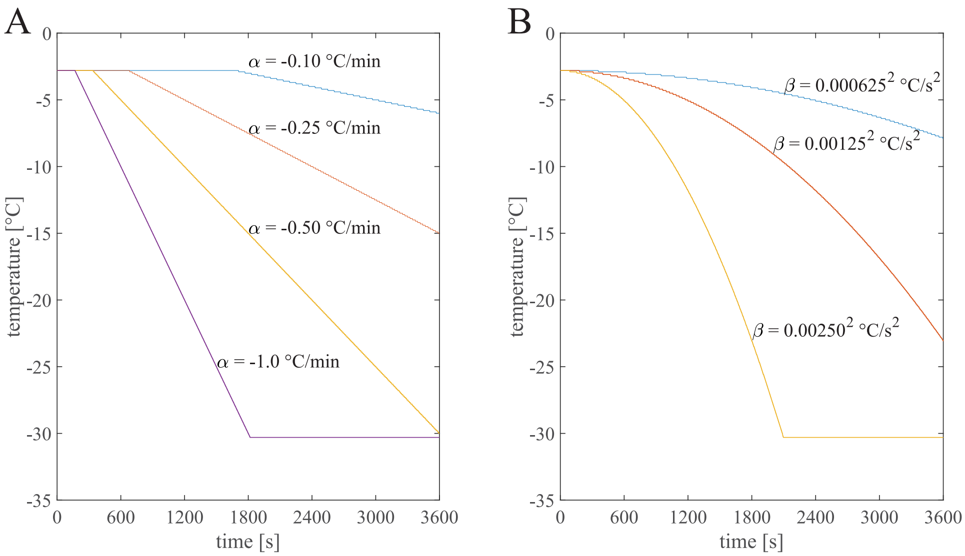

Figure 2. Applied temperature profiles for the decreasing cold wall temperature experiments in this study A) Linear (equation 3), B) Parabolic (equation 4).

$$Re = \frac{\rho N D^2}{\mu} \tag{3}$$

The average solute inclusion can be expressed with the ratio of the solute concentration in ice and the solute concentration in the original solution:

$$K = \frac{C_S}{C_L} \tag{4}$$

Results and discussion

Ice formation

The ice yield of progressive freeze concentration was compared for different stirrer rates and cold wall temperatures (Figure 3A). The yield showed little dependence on the stirrer rate. Only at 50 rpm we did observe a minor increase in ice yield, but higher stirrer speed yielded always similar amounts of ice. At the lowest agitation rates, the heat transfer from the bulk of the solution toward the ice is slow and will therefore result in faster ice growth. However, the heat transfer in general is relatively fast compared to the mass transfer of the solute and is not limiting at somewhat better agitation.[33]

A clear dependence was found on the cold wall temperature. Lower temperatures yielded more ice because the driving force for heat transfer is higher. The ice yield was found to decrease somewhat with increased solute concentration due to the increased freezing point depression at higher sucrose concentrations (Figure 3B), especially when considering that the concentration of solute at the ice-solution interface is much larger than in the bulk, due to the concentration polarization.[34] The maltodextrin solutions show a lower ice yield than the 6%(w/w) sucrose solution. This is caused by the higher viscosity of the solution compared to the 6%(w/w) sucrose. A higher viscosity hinders the ice formation.[35] In fact, viscosity may also be an additional explanation for the decrease in ice yield with increasing concentration of sucrose.

Sucrose and maltodextrin inclusion in ice

The degree of solute inclusion in ice depends on the hydrodynamics close to the ice layer.

In Figure 4A the average solute inclusion (equation 4) is plotted versus the Reynolds numbers (equation 3) for different solute concentrations. The solute inclusion decreased at increasing Reynolds numbers for all different solutions and cold wall temperatures. As expected, the 18%(w/w) and 36%(w/w) sucrose solutions showed more inclusion than the 6%(w/w) sucrose solutions (Figure 4A). This is most probably caused by the strong increase in concentration at the ice-liquid boundary leading to more favorable circumstances for solute inclusion, plus the increased viscosity of these solutions in the concentration polarization layer, contributing to a thicker boundary layer.

An increase of the stirrer speed increases the shear above the ice surface, which improves the transport of the solute away from the ice-liquid boundary and therefore reduces the diffusion limitation in the boundary layer during freeze concentration.[36] We observe that the dependence on the Reynolds number

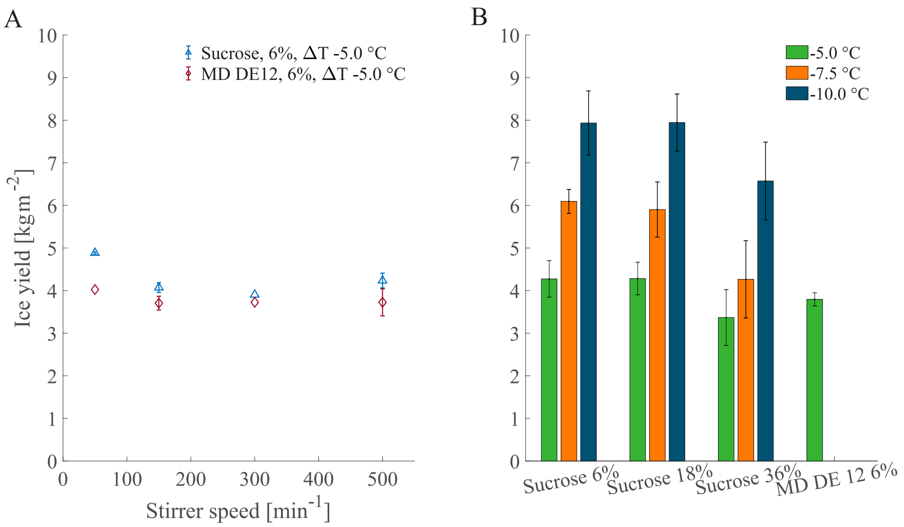

Figure 3. Effect of applied freeze plate temperature and solute concentration on the ice formation after 30 minutes of freeze concentration. (A) Ice yield for sucrose 6%(w/w) and maltodextrin DE12 6%(w/w) vs. stirrer speed. (B) Ice yield for sucrose and maltodextrin DE12 solution averaged over the stirrer speeds. The error bars indicate the standard deviation.

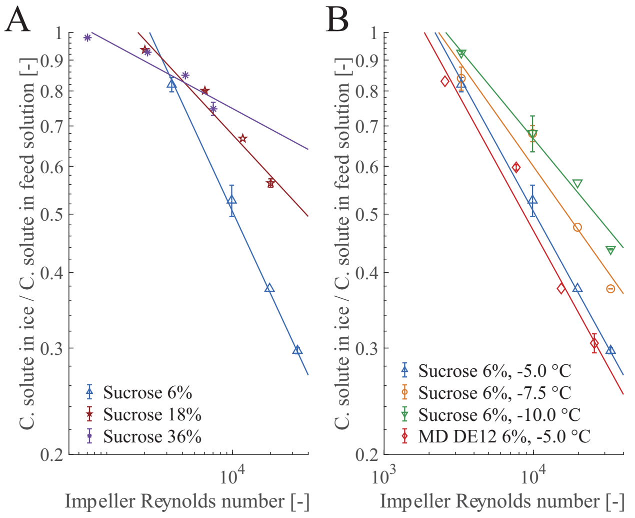

Figure 4. Effect of impeller Reynolds number on the effective solute inclusion after 30 minutes. A.) The effect of increasing sucrose concentration at −5.0 °C below the freeze point of the solution. B.) The effect of decreasing freeze plate temperature. The error bars indicate standard deviation.

or stirrer speed becomes stronger for lower concentrations (Figure 4A). This can be explained because at increasing concentrations viscosity increases rapidly, which again hinders mass transfer and promotes inclusion. For freezing rates, we also observe a dependence on Reynolds number, where solute inclusion increases with faster freezing rates (Figure 4B). This can be explained as the ice growth rate increases with increasing freezing rate, while the stirring rate remains the same. This is in line what has been found by Liu et al.[19] and Jusoh et al.[18]

Perhaps surprisingly, the freezing of the 6%(w/w) maltodextrin solution is quite comparable to that of 6%(w/w) sucrose (Figure 4B). Maltodextrins, being larger molecules, diffuse more slowly and give rise to higher viscosities, but give less freezing point depression due to the larger molecular weight. These effects may cancel out each other at least partially.

Decreasing cold wall temperature

With a constant cold wall temperature, freezing initially proceeds much faster and then slows down. The decrease in ice growth is due to the increasing thickness of the ice layer, which reduced the heat transfer from the ice growth front to the cooling plate. The higher initial ice growth rate leads more inclusion during the initial period compared to a later stage. To avoid this initial strong inclusion, we adjusted the cold wall temperature such that the temperature difference with the ice growth front starts relatively small and then gradually increases during the process leading to more constant ice growth rates.

The used temperature profiles can be found in Figure 2. Initially a certain degree of supercooling is necessary to ensure nucleation and have the freezing process started. The ice yield was comparable for the cooling programs with −5 °C constant temperature (average ice growth rate $= 1.30 \times 10^{-3}$ mm/s), −0.1 °C/min linear profile (average ice growth rate $= 1.31 \times 10^{-3}$ mm/s) and $(6.25{\cdot}10^{-4})^2$ °C/s^2 quadratic profile (average ice growth rate $= 1.29 \times 10^{-3}$ mm/s), and was larger with steeper decrease of the applied temperature profiles (Figure 5A). The larger ice yield is achieved by a larger heat removal from the system. The slopes of −1.0 °C/min (average ice growth

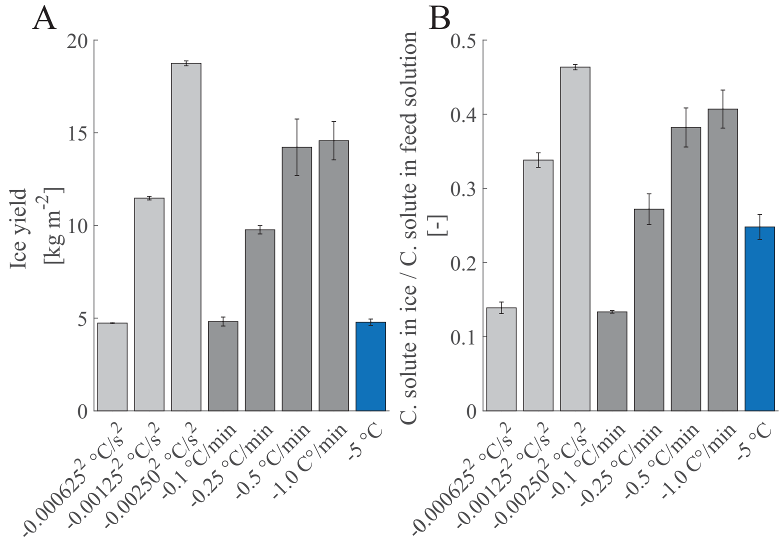

Figure 5. Freeze concentration ice yield and solute inclusion after 60 minutes for the temperature profiles in Figure 2. The light gray bars indicate linear decreasing temperature profiles, the dark gray bars indicate parabolic temperature profiles, the blue bar indicates constant temperature profile.

rate = 3.96×10^{-3} mm/s) and $(2.50 \times 10^{-3})^2$ °C/s^2 (average ice growth rate = 5.10×10^{-3} mm/s) were limited by the minimum temperature of the cryostat (−30 °C), thus giving a lower ice yield, than what would be expected if the profile would continue below this temperature. The sucrose inclusion, for the −0.1 °C/min and $(6.25 \times 10^{-4})^2$ °C/s^2, could be reduced by approximately a factor two when compared to the constant temperature operation (Figure 5B), while having the same ice yield. The other profiles include more sucrose but also yield more ice. The higher ice yield in these cases will lead to a higher concentration in the remaining solution, but the overall separation is worse. These experiments show that for successful operation of progressive freeze concentration, good control of the ice growth rate is necessary for optimal separation and concentration. Modeling of the ice growth rate and the inclusion behavior of the solute could assist in optimizing the ideal temperature profile for the cold wall temperature, increasing the ice yield and lowering the solute inclusion.

Yield versus purity

The aim of a concentration method is to concentrate a solution as much as possible, while minimizing the losses of the solute. When comparing solute losses, we observe a distinct grouping of the freeze concentration processes employing a constant temperature, which have a lower yield and significant inclusions (Figure 6, group 1). In this group, the level of inclusion increases with increasing solute concentration. A lower cold wall temperature increases the ice yield but reduces the purity, mostly due to high initial inclusion during the fast initial freezing. This is evident in the observation that extending the freezing time from 30 to 60 minutes gives a less than proportional increase of the ice yield, but lower overall solution inclusion (Figure 6, group 3). This shows that the slowing of the freezing process reduces the solute conclusions over time.

Therefore, experiments were carried out with varying ramps (Figure 2). It could be observed that indeed a cold wall temperature profile that decreases in time gives significantly lower solute inclusion (Figure 6, group 2), mostly because of the reduced initial degree of supercooling near the cold wall, while the lower temperatures at later stages, increase the ice yield. The rate of progression in cooling, must be balanced with the rate mass transfer of the solute from the freezing plane toward the solution bulk. A ramp that is too steep will result in more inclusion, caused by the ice growth rate and the drag by the water flux becoming higher than the diffusion rate of the solute away from the ice boundary, causing it to accumulate in the boundary layer.[27,37] Too much concentration polarization may even lead to phase changes and precipitation of the solute, which again will favor solute inclusion.[38] These relative inclusions get higher with increasing feed concentration. This is supported by Miyawaki et al.,[27] who conclude that the ice growth rate should be low enough to prevent strong concentration polarization in the boundary layer. For this, the velocity of the ice front should be balanced with

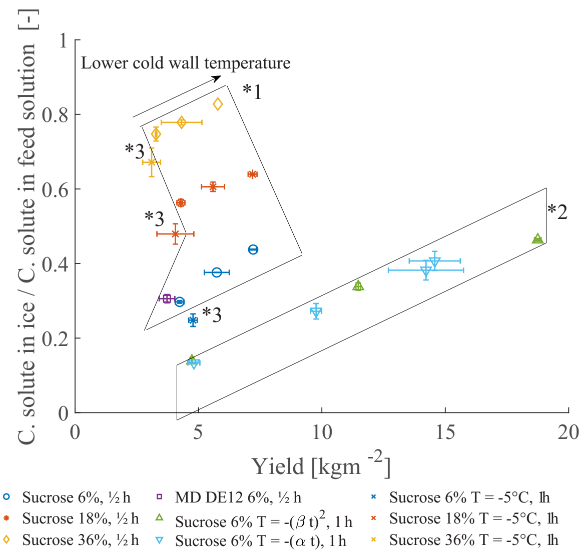

Figure 6. Yield versus impurities in the ice for different operating conditions. Group 1 represents operation at constant temperature for 30 minutes. Group 2 represents operation with variable cold wall temperature. Group 3 represents operation at constant temperature for 60 minutes.

the diffusion in the boundary layer and the transport in the bulk of the liquid.

The yields reported show the amount of ice formed for the given duration of the experiment. When comparing the ice yield from the experiments with constant temperature at −5 °C for ½ h and 1 h, then one can observe that the yield is similar or increases a little bit for the lowest sucrose concentration. This shows that the majority of the ice is formed at the beginning of the process and the minor increase in ice yield in time shows that the system is near its steady state in terms of heat transfer. It is interesting to note that the sucrose inclusions decrease during the second half hour, which may be explained by diffusion of sucrose from the concentrated domains in the ice layer into the bulk liquid.

Conclusion

The inclusion behavior of sucrose and maltodextrin during progressive freeze concentration was closely coupled to agitation rate and ice growth rate in the stirred tank set-up. Agitation should be large to reduce concentration polarization in the boundary layer and thus minimize undesired solute inclusion. Operating at a constant cold wall temperature led initially to high solute inclusions due to the high ice growth rate at the start of the process. To improve this, we investigated application of variable cooling profiles with a linear or progressive decrease of temperature over time. This approach was found promising to increase the ice yield while at the same time reducing solute inclusion. Ideally, the ice growth rate is thus controlled at a constant value to minimize solute inclusions, while still having a significant ice yield. This would allow better scaling of the results to larger scale progressive freeze concentrators. The more accurate control of ice growth rate the availability of predictive models that describe ice growth and solute inclusion over time is indispensable.

Symbol list

Symbol	Description	Unit
C_L	Concentration of solute in feed solution	% (w/w)
C_s	Concentration of solute in ice	% (w/w)
D	Diameter of stirrer	m
K	Average solute inclusion	–
N	Rotational speed	rad s^{-1}
Re	Reynolds number	–
t	Experimental time	s
α	Slope of cooling curve	°C min^{-1}
β	Coefficient of quadratic decreasing cooling curve	°C s^{-2}
μ	Dynamic viscosity	Pa s
ρ	Liquid density	kg m^{-3}

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