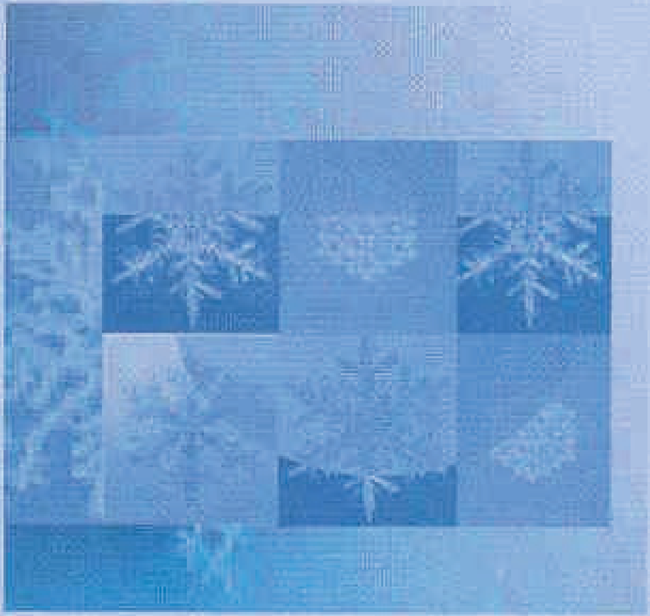
IIR Guides

Handbook on Ice Slurries

- Fundamentals and Engineering -

Editors:

Michael Kauffeld, Masahiro Kawaji, Peter W. Egolf



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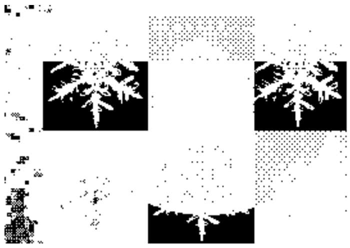

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CHAPTER 9. DIRECT CONTACT CHILLING AND FREEZING OF FOODS IN ICE SLURRIES

by Kostadin Fikiin, Ming-Jian Wang, Michael Kauffeld and Torben M. Hansen (see specific list of symbols in Appendix 3)

Ice slurry has received increasing attention and demand for refrigeration processes in different industries because of the widespread concerns over product quality, process efficiency and environmental friendliness. This chapter deals with the application of ice slurry technologies to direct contact chilling and freezing of foods. As a rule, direct contact cooling in ice slurries improves the product quality. To date this technology has mainly been used in the fish industry (by employing sea-water-based ice slurry) but its recent applications to the fruit and vegetable processing sectors revealed a very promising potential as well. Both laboratory and industrial trials demonstrated convincingly the superiority of the ice-slurry-based immersion methods over conventional modes of food refrigeration.

Direct contact cooling by dried ice slurries has lately been applied in supermarket display cabinets. Ice slurry is thereby used similarly to flake ice, but the slurry handling is much easier because it can be pumped to the display cases and released via a hose, whereas the ice flakes have to be shovelled. Moreover, there are no traumatic effects on the food surface, which may occur when flakes are involved. Although the cooling ability of the ice slurry is very similar to that of flake ice in this particular application of dried ice slurry, ice slurry shows heat transfer benefits for the direct contact/immersion applications described below.

9.1. State of the art and conventional modes of food refrigeration

Let us, for instance, illustrate the ice slurry capabilities for food freezing applications as compared with the most common techniques known so far. In the early 1900s, many people were experimenting with mechanical and chemical methods to preserve food. As an industrial process, quick freezing began its history some 70 years ago when Clarence Birdseye found a way to flash-freeze foods and deliver it to the public – one of the most important steps forward ever taken in the food industry. During his stay in the Arctic, Birdseye observed that the combination of ice, wind and low temperature almost instantly froze just-caught fish. More importantly, he also found that when such quick-frozen fish were cooked and eaten, they were scarcely different from the fresh fish in taste and texture. After years of work, Birdseye invented a system that packed dressed fish, meat or vegetables into waxed-cardboard boxes, which were flash-frozen under pressure (US Patent No. 1,773,079, 1930). Then he turned to marketing and a number of ventures were initiated to manufacture, transport and sell frozen foods (e.g. construction of double-plate freezers and grocery display cases; lease of refrigerated boxcars for railway transport; and retail of frozen products in Springfield, Massachusetts, in 1930). These technological achievements constituted the world's first cold chain for frozen foods, which became shortly a legend (Fikiin, 2003).

Thus, quick freezing has further been adopted as a widespread commercial method for long-term preservation of perishable foods, which improved both the health and convenience of virtually everyone in the industrialised countries. Freezing rate affects strongly the quality of frozen foods, in which the predominant water content should quickly be frozen in a fine-grain crystal structure in order to prevent damages to the cellular tissues and to inhibit rapidly the spoiling microbiological and enzymatic processes.

Basic heat transfer considerations (Fikiin, 2003) clearly suggest that the desired shortening of freezing duration and a resulting high throughput of refrigerating equipment could be achieved by means of: (i) lower refrigerating medium temperature (which generally requires greater investment and running costs for the refrigeration machines to be employed), (ii) enhanced surface heat transfer coefficients (by increased refrigerating medium velocity and boundary layer turbulence, involvement of surface phase-change effects and less packaging), and (iii) reduced size of the refrigerated objects (by freezing small products individually or appropriately cutting the large ones into small pieces).

Air-blast and multiplate freezers are most widespread, while air fluidizing systems are used for individual quick freezing (IQF) of small products. The cryogenic IQF is still very restricted because of the high prices of the liquefied gases used.

Fluidized-bed freezing systems

Air fluidization has been studied extensively and used commercially, with increasing popularity, over the last forty years (Fikiin et al., 1965, 1966, 1970; Fikiin, 1969, 1979, 1980). This freezing principle possesses many attractive features, including:

- High freezing rate due to the small sizes and thermal resistance of the IQF products, large overall heat transfer surface of the fluidized foods and high surface heat transfer coefficients.
- Good quality of the frozen products, that have an attractive appearance and do not stick together.
- Continuity and possibilities for complete automation of the freezing process.

In spite of these advantages, fluidization freezing by air has some drawbacks, such as:

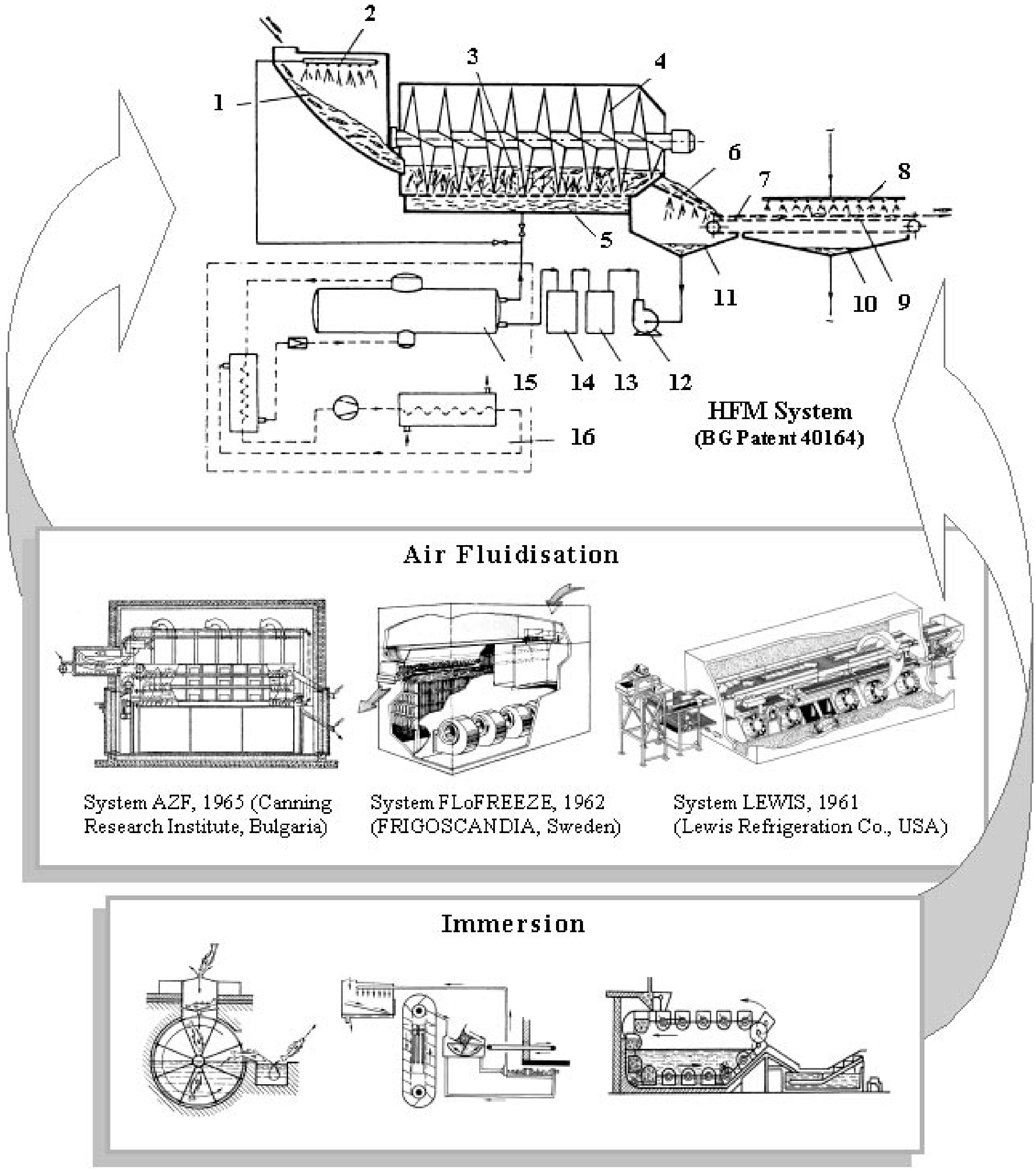
- Necessity of two-stage refrigerating plants (often using large quantities of CFC-, HCFC- or HFC-based refrigerants with significant ozone depletion or global warming potentials) to hold an evaporation temperature of about –45°C, which results in high investment and power costs.
- Lower surface heat transfer coefficients and freezing rates in comparison with the immersion methods described below.
- Need for a high speed and pressurized airflow, that results in large fan power consumption.
- Some moisture losses from the product surface and rapid frosting of the air coolers, caused by the large temperature difference between the products and the evaporating refrigerant.
- Excessive sensitivity of the process parameters to the product shape, mass and size, that requires careful control specific to every separate food commodity.

Freezing by immersion

The immersion freezing in non-boiling liquid refrigerating media is a well-known method having several important advantages: high heat transfer rate, fine ice crystals in foods, high throughput, low investments and operational costs (Woolrich, 1966; Tressler, 1968; Fleshland and Magnussen, 1990; Lucas and Raoult-Wack, 1998). The immersion applications have been limited because of the uncontrolled solute uptake by the refrigerated products and operational problems with the immersion liquids (high viscosity at low temperatures, difficulty in maintaining the medium at a definite constant concentration and free from organic contaminants). Recent achievements in heat and mass transfer, physical chemistry, fluid dynamics and automatic process control make it possible to solve these problems and to develop advanced immersion individual quick freezing (immersion IQF) systems (Fikiin and Fikiin, 1998, 1999a, 2002, 2003a,b; Fikiin, 2003).

9.2. Unfreezable liquids and pumpable ice slurries as refrigerating media and fluidizing agents

The *Hydro Fluidization Method* (HFM) for fast freezing of foods was suggested and patented recently to overcome the drawbacks and to bring together the advantages of both air fluidization and immersion food freezing techniques (Fikiin, 1985, 1992, 1994). The HFM uses a circulating system that pumps the refrigerating liquid upwards, through orifices or nozzles, in a refrigerating vessel, thereby creating agitating jets. These form a fluidized bed of highly turbulent liquid and moving products, and thus evoke extremely high surface heat transfer coefficients. The principle of operation of an HFM freezing system is illustrated in *Figure 9.1*.



System AZF, 1965 (Canning Research Institute, Bulgaria)

System FLoFREEZE, 1962 (FRIGOSCANDIA, Sweden)

System LEWIS, 1961 (Lewis Refrigeration Co., USA)

Figure 9.1. Possible arrangements of a HFM-based freezing system combining the advantages of both air fluidization and immersion food freezing techniques (Fikiin and Fikiin, 1998, 1999a): (1) charging funnel; (2) sprinkling tubular system; (3) refrigerating cylinder; (4) perforated screw; (5) double bottom; (6) perforated grate for draining; (8) sprinkling device for glazing; (7 and 9) netlike conveyor belt; (10 and 11) collector vats; (12) pump; (13 and 14) rough and fine filters; (15) cooler of refrigerating medium; (16) refrigeration plant

Unfreezable liquid refrigerating media as fluidizing agents

Although various immersion techniques have been known for a long time, until now hydrofluidization principles have not been used for chilling and freezing of foods. Experiments on HFM freezing of small fish and some vegetables through an aqueous solution of sodium chloride showed a much higher freezing rate when compared with other IQF techniques (Fikiin, 1992, 1994). The maximum surface heat transfer coefficient achieved exceeded 900 W/(m^{2}K), while this was 378 W/(m^{2}K) when immersing in a flowing liquid, 432 W/(m^{2}K) for sprinkling and 475 W/(m^{2}K) for immersion with bubbling through (Fikiin and Pham, 1985). Even at a slight or moderate jet agitation and a comparatively high refrigerating medium temperature of about –16°C, scad fish were frozen from 25°C down to –10°C in the centre within 6-7 minutes, sprat fish and green beans within 3-4 minutes and green peas within 1-2 minutes. As an illustration *Figure 9.2* shows recorded temperature histories during hydrofluidization freezing of scad and sprat fish, green beans and peppers.

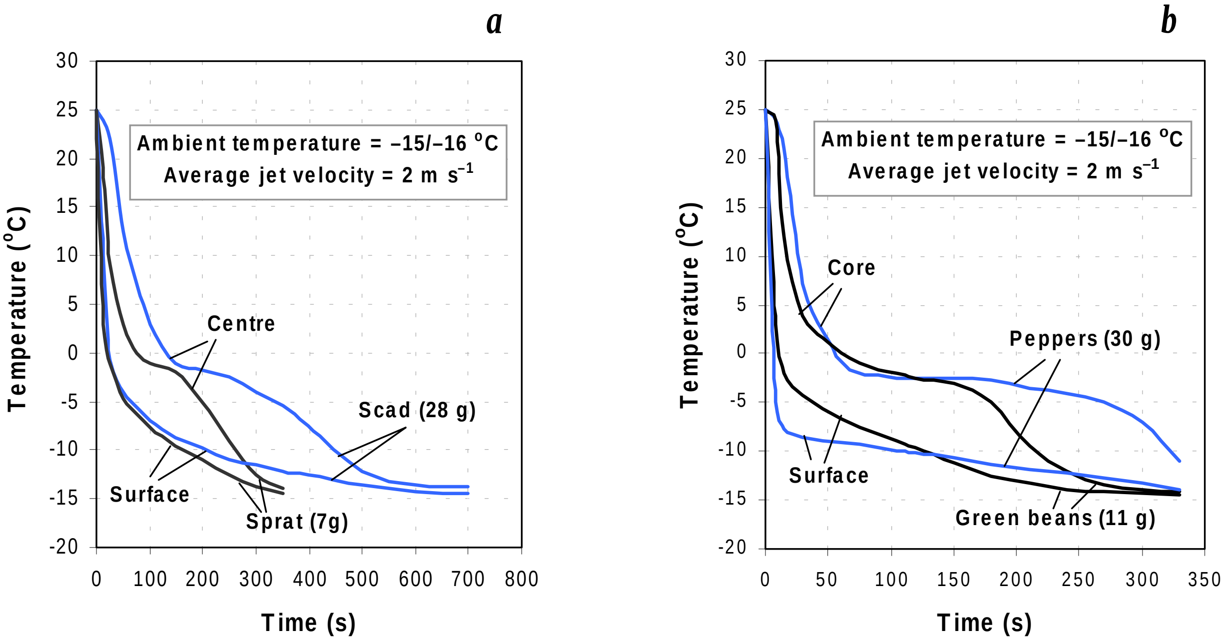


Figure 9.2. Experimental temperature histories during HFM freezing of some kinds of (*a*) fish and (*b*) vegetables, when using sodium chloride solution (without ice slurry) as a fluidizing agent (Fikiin, 1992; Fikiin and Fikiin, 1998, 1999a)

Two-phase ice slurries as fluidizing agents

Pumpable ice slurries (known under different trade names, such as *FLO-ICE*, *BINARY ICE*, *Slurry-ICE*, *Liquid ICE*, *Pumpable ICE* or *Fluid ICE*) were proposed recently as environmentally benign secondary coolants circulated to the heat transfer equipment of refrigeration plants, instead of the traditional ozone-depleting CFC- or HCFC-based refrigerants (Paul, 1995; Ure, 1998, Egolf *et al.*, 1996; Bel and Lallemand, 1999; Pearson and Brown, 1998). Promising attempts to refrigerate foods by immersion in such slurries have already been carried out. As already discussed, fish chilling in sea water-based ice slurries has good potential to replace the traditional use of ice flakes (Fikiin *et al.*, 2002). A number of foods immersed in slurries with various ice contents are shown in *Figure 9.3*.

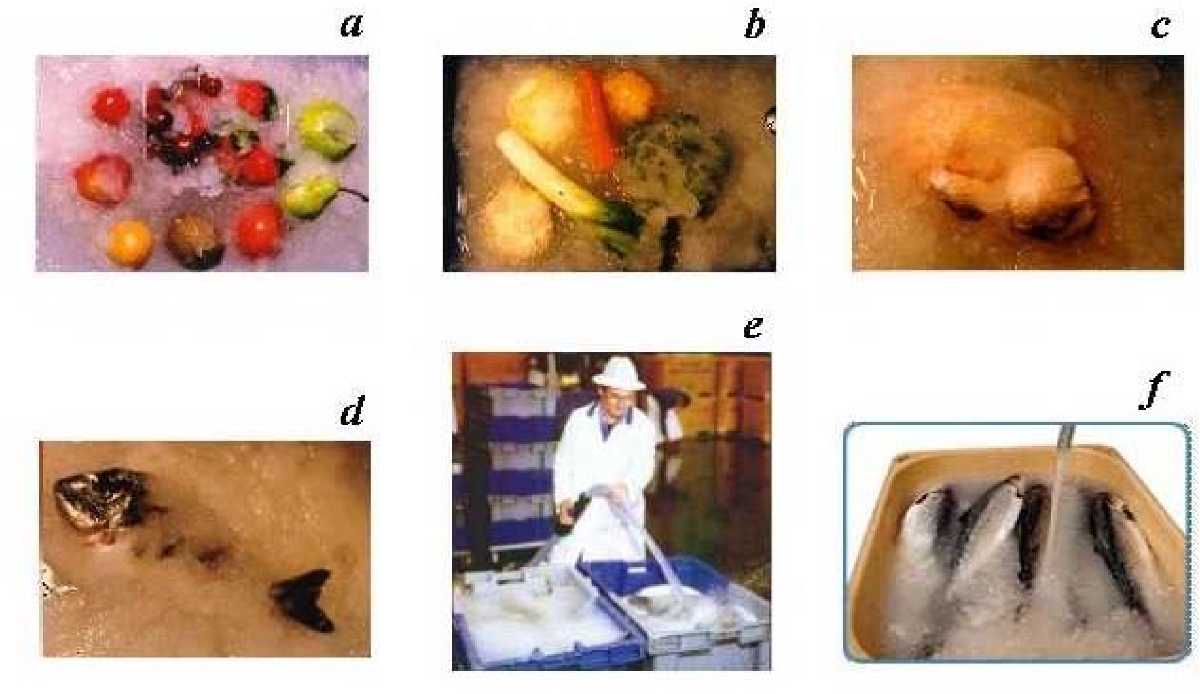


Figure 9.3. Different foods immersed in slurries with various ice concentrations: (*a*) fruits; (*b*) vegetables; (*c*) chickens; (*d*), (*e*) and (*f*) fish (Fikiin *et al.*, 2002)

Fikiin and Fikiin (1998, 1999a) launched, therefore, the idea to enhance the advantages of hydrofluidization (described above) by employing two-phase ice suspensions as fluidizing media. Ice slurries possess a large energy potential as HFM refrigerating media whose small ice particles absorb latent heat when thawing on the product surface. Hence, the goal of ice slurry usage is to provide a high surface heat transfer coefficient (of the order of 1000-2000 W/(m^2K) or more), shortened freezing time and uniform temperature distribution in the whole volume of the freezing apparatus. The combination of the HFM with the high heat transfer efficiency of the ice-slurry-based refrigerating media represents a new interdisciplinary research field whose development would advance essentially the refrigerated processing of foods. The HFM freezing with ice slurries can acquire a process rate approaching that of the cryogenic flash freezing modes. For instance, at a refrigerating ice-slurry temperature of –25°C and a heat transfer coefficient of 1000 W/(m^2K), strawberries, apricots and plums can be frozen from 25°C down to an average final temperature of –18°C within 8-9 minutes; raspberries, cherries and morellos within 1.5 to 3 minutes; and green peas, blueberries and cranberries within about 1 minute only. The general layout of an ice-slurry-based system for hydrofluidization freezing is shown in *Figure 9.4*.

Advantages of hydrofluidization freezing with ice slurries

As described above, the novelty of the hydrofluidization method lies in the involvement of unfreezable liquids or pumpable ice slurries as fluidizing agents. It is well-known that the immersion freezing history began with the use of brines to freeze fish, vegetables and meat. Binary or ternary aqueous solutions containing soluble carbohydrates (e.g. sucrose, invert sugar, glucose [dextrose], fructose and other mono- and disaccharides) with additions of ethanol, salts, glycerol, etc., have been studied as possible immersion media. There are practically unlimited possibilities to combine constituents and to formulate appropriate

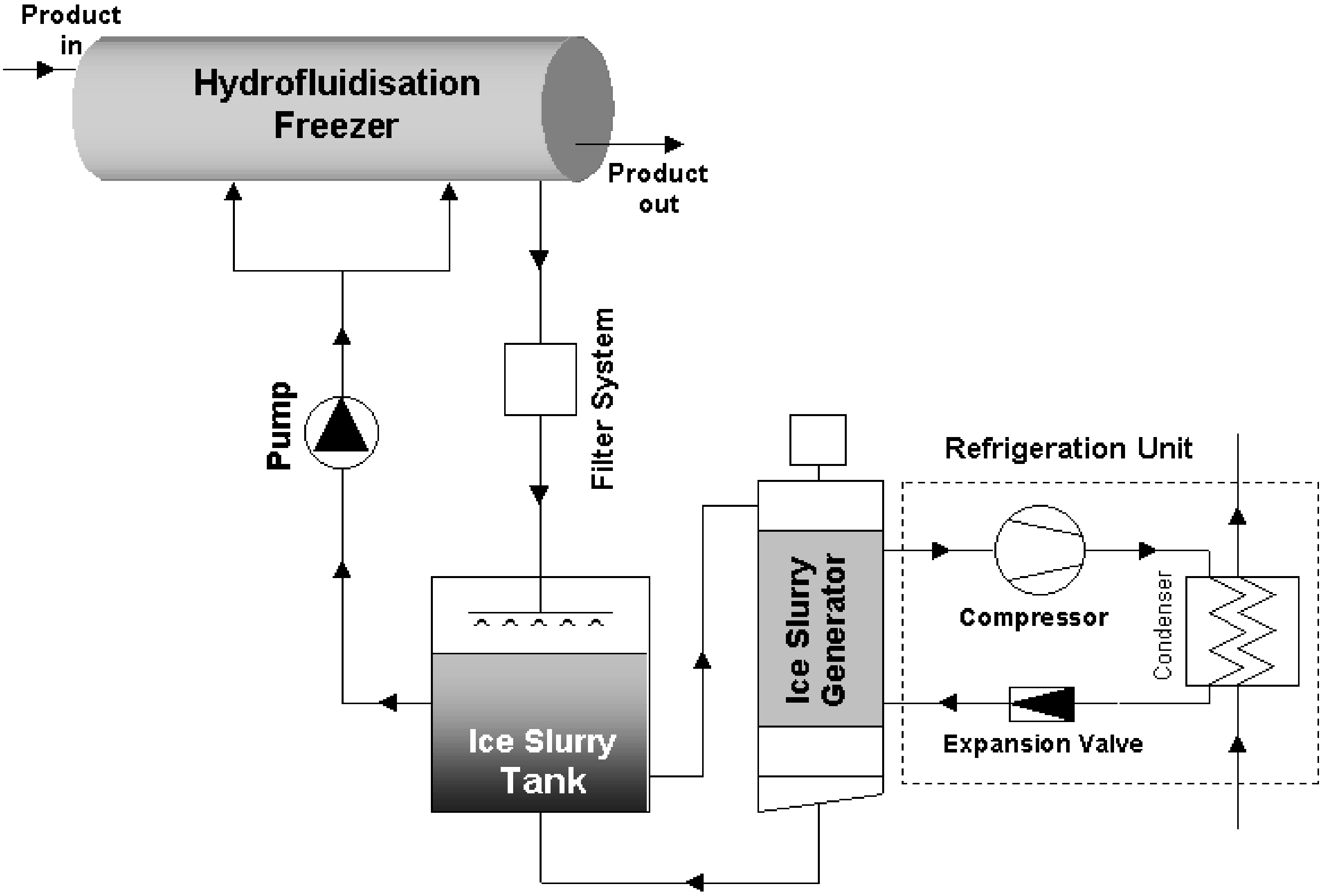


Figure 9.4. Schematic diagram of an ice-slurry-based hydrofluidization system *HyFloFreeze*®
(Fikiin and Fikiin, 1998, 1999a)

multicomponent HFM refrigerating media based on single-phase liquids or two-phase ice slurries, which have to be both product- and environment-friendly and to possess a low enough viscosity in terms of pumpability and good hydrofluidization.

The main advantages of hydrofluidization over the conventional freezing modes can be summarized as follows:

- The HFM facilitates a very high heat transfer rate with a small temperature difference (product to cooling medium). The evaporation temperature can be maintained much higher (at –25/–30°C) achievable by a single-stage refrigerating machine with much higher COP and nearly half the investment and energy costs as compared with the conventional air fluidization. Cold dissipation through the freezer walls is subsequently also lower. The water flow rate or fan power consumption for cooling the condenser decreases as well, due to the reduced mechanical work of the refrigeration unit running at higher evaporation temperature.
- The critical zone of water crystallization (from –1 to –8°C) is quickly passed through, which ensures a fine ice crystal structure in foods preventing the cellular tissues from perceptible damage.

- The product surface freezes immediately in a solid crust that hampers the osmotic transfer and gives an excellent appearance. The water losses tend to zero, while in air freezing tunnels the moisture losses are usually 2-3%.
- Delicious new products can easily be formulated by using some selected product-friendly HFM media (for example, fruits frozen in syrup-type sugar solutions turn into dessert products with beneficial effects on colour, flavour and texture). Such media can also include appropriate antioxidants, flavourings and micronutrients to extend the shelf life of the products and to improve their nutritional value and sensory properties.
- The HFM freezers use environmentally friendly secondary coolants (for instance, syrup-type aqueous solutions and ice slurries) and the primary refrigerant is closed in a small isolated system, in contrast to the common air fluidization freezers where large quantities of ozone depleting and/or high global warming potential CFCs, HCFCs or HFCs are circulated to remote evaporators with a much greater risk for emission to the environment.
- Fluidized state is acquired with low velocity and pressure of the fluid jets due to the Archimedes forces and buoyancy of the products, that lead to both energy savings and minimum mechanical action on the foods.
- The operation is continuous, easy to maintain, convenient for automation and the labour costs are substantially reduced. Further processing or packaging of the HFM-frozen products is considerably easier since they emerge from the freezer in a “free-flowing” state, i.e. do not stick together.
- Ice-slurry-based HFM agents may easily be integrated into systems for thermal energy storage, accumulating ice-slurry during the night at lower electricity costs.

The top view photos on *Figure 9.5* show how a hydrofluidized bed of highly turbulent ice slurry is formed inside the *HyFloFreeze*® prototype's freezing compartment.

Figure 9.5. *HyFloFreeze*® prototype: hydrofluidized bed of highly turbulent ice slurry (Fikiin, 2003).

International research co-operation

Two main applications of the suggested HFM freezing technique can clearly be distinguished: (i) employment of unfreezable liquids as fluidizing agents and (ii) use of pumpable ice slurries as fluidizing media. This freezing principle provides an extremely high heat transfer rate, short freezing times, great throughput and better product quality at higher refrigerating temperatures. Thus, only about half the investment and power costs are necessary as compared with the popular individual quick freezing methods. Moreover, such hydrofluidization freezing systems are less hazardous from an environmental viewpoint, since the primary refrigerant is limited to a small isolated circuit.

The emerging HFM technology has attracted the attention of a number of academics and industrialists. The identification of optimal design specifications for HFM freezing systems requires an interdisciplinary approach by researchers with complementary skills. The *HyFloFreeze* project was, therefore, funded by the European Commission and performed by an international research consortium of six participating organisations (four universities and two SMEs) from Belgium, Bulgaria, Russia and the UK (Fikiin, 2003).

9.3. Cooling of fish with ice slurries

The use of ice for extending the storage life of fish dates back many millennia. Up to the middle of the last century all ice used for fish cooling was from natural sources (winter snow or imported arctic ice). With the introduction of mechanical cold production, ice was and is produced in different forms, e.g. block, cube, tube or flake ice. Most of these forms need a certain degree of manual operation for transportation from one place to another, and have rather sharp edges capable of damaging the fish surface. Furthermore, they are usually quite coarse, resulting in poor heat transfer. The introduction of ice slurry for direct contact cooling of fish (*Figure 9.6*) presents several attractive features to the process operation over other forms of ice (Wang *et al.*, 2000).

For quality assurance it is essential that effective product cooling be provided throughout the entire production chain, from catch at sea, to storage, transportation, and processing. Cooling technologies employed often use refrigerated seawater and/or different types of fresh ice. Sea water systems placed on board large vessels maintain fish, by sea water circulation, at a mean temperature of about 2-4°C. Disadvantages of such systems are the volume taken up by the refrigeration machinery, difficult working conditions and salt uptake by the fish, especially in smaller species like sardine. Onboard smaller ships, fresh ice is normally loaded from harbour, stored and eventually mixed with the catch. The tendency of fresh ice to re-crystallize and agglomerate in many cases limits the quality of icing, since the ice has to be loosened by manual means before mixing. Often large blocks of ice mixed with the fish result in uneven cooling rates.

Bacterial growth is highly temperature-dependent. As a rule of thumb, the shelf life of fish kept at 0°C is more than doubled compared to +5°C; the closer to the freezing point of the fish, the better the product quality. Bearing in mind that bacterial growth rates can not be stopped, but only decelerated, it is also important to minimize the bacterial level by a rapid temperature drop in each part of the process. Possible freezing of the fish anticipated for chilling may result in decreased sensory perception (Sørensen, 1999) and should therefore be avoided. Intuitively, the use of ice slurry could improve cooling of fish by exploiting properties such as (Wang *et al.*, 2000):

- narrow approach to the freezing point of fish;
- close to isothermal heat exchange during melt-off;
- smooth surface preventing fish from damage;
- easy dosing, mixing, handling and pumping;
- possible drainage of salty water to minimize salt uptake.

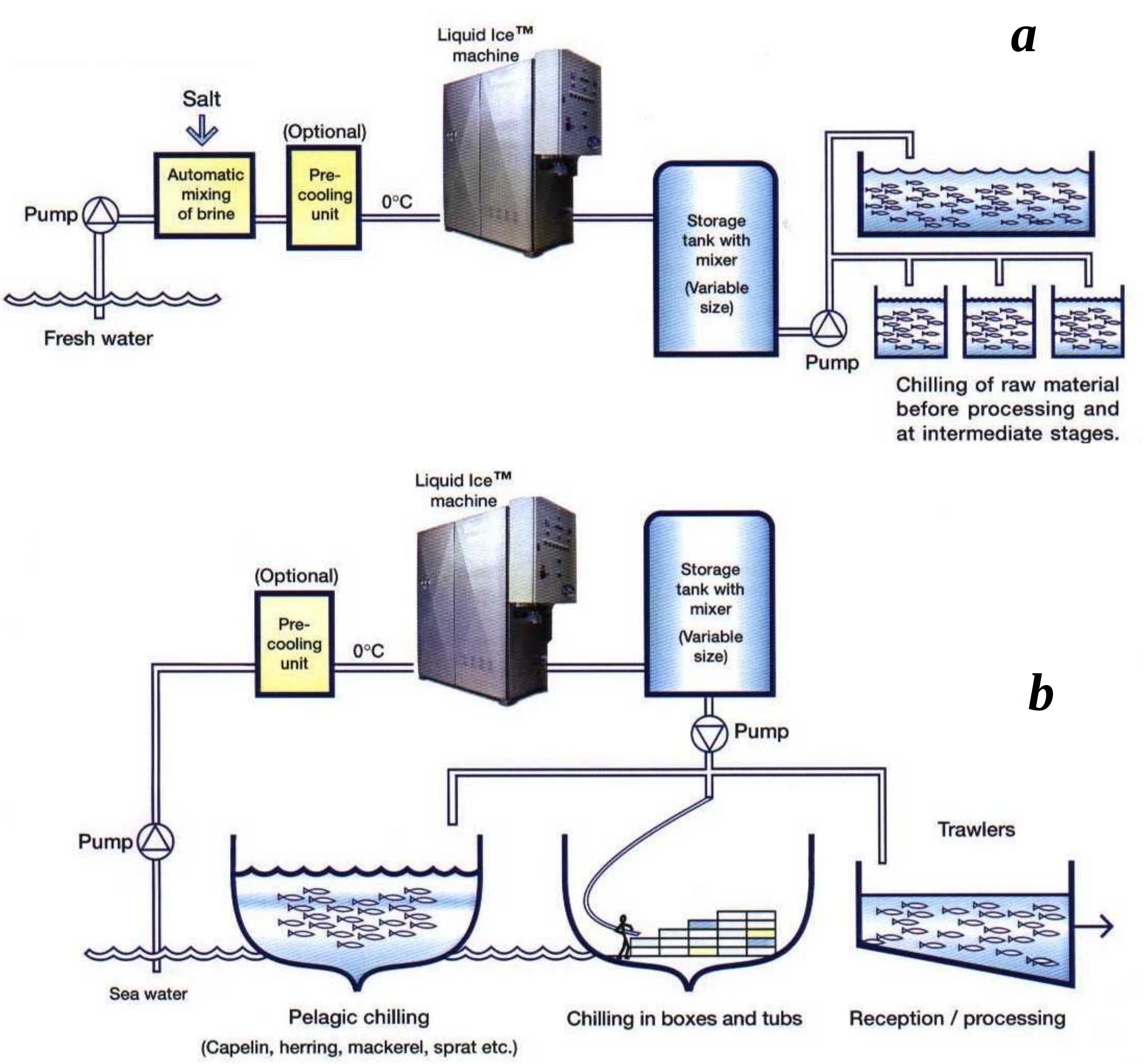


Figure 9.6. Fish chilling in ice slurry (Fikiin *et al.*, 2002): (*a*) land-based systems and (*b*) on-board systems (Liquid Ice^{TM}, Brontec, Iceland)

Because of its tiny ice crystals, ice slurry is soft and flexible for the chilled product. It effectively avoids any hot spots in the fish container, and provides excellent contact with fish without bruising. As fish are surrounded by numerous ice crystals, high cooling rate is achieved. This significantly retards bacterial growth and reduces fish tissue degradation.

Analysis of cooling methods and process simulation

Ice slurry for fish cooling and controlling temperature during storage can be implemented in different ways. In order to verify the aforementioned advantages of ice slurry a simulation model has been developed and related experiments have been carried out (Hansen *et al.*, 1999). To simulate the cooling process and to check whether freezing occurs near the fish surface, a differential heat conduction equation was solved by using finite-element-based CFD software:

$$div(k\,grad T)=\rho\cdot c_p\frac{\partial T}{\partial \tau} \tag{9.1}$$

Thermal properties are calculated by considering that phase change of water will occur over a wide temperature interval (see *Figure 9.7*). The majority of water (70-90%) is mechanically trapped in and between cells, and is relatively easy to freeze. During freezing the salt content increases, resulting in a temperature glide of phase change. Individual freezing curves may vary among species, although the characteristics remain the same, i.e. thermo-physical properties are strongly influenced down to a temperature of approximately –10°C. The behaviour of phase change described has a large effect on the thermo-physical properties that vary with the temperature throughout a frozen fish. The composition of fish changes a lot among species and depends on the place and season of harvesting, which may also affect thermo-physical properties. White fish may be considered relatively stable containing about 80% water and 20% dry materials. For fatty fish like horse mackerel and sand eel, the content of dry materials may remain approximately 20% during the season whereas the oil content varies from 1 to 20%. Temperature-dependent thermo-physical properties for white fish (80% water) and fatty fish (70% water, 10% oil) are shown in *Figure 9.7*.

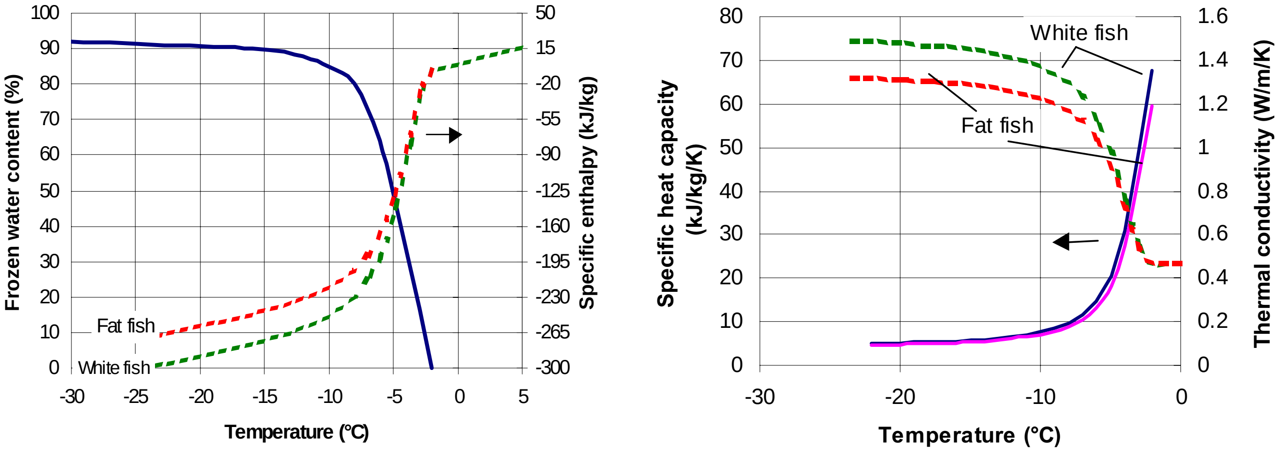


Figure 9.7. Enthalpy-temperature curve from differential scanning calorimetry of cod fillets (Sørensen and Spange, 1999) and calculated thermophysical properties

Based on the freezing curve, the enthalpy can be calculated as a function of temperature by assuming constant heat capacities of constitutient substances. For fat fish neglecting the effect of oil on crystallization may cause some errors. The specific heat capacity of fish is calculated as follows:

$$\Delta h = \Delta T \cdot \left(X_d\, c_{p,d} + X_{oil}\, c_{p,oil} + (X_w - X_i)\, c_{p,w} + X_i\, c_{p,i} \right) + X_i\, L \tag{9.2}$$

$$c_p = \left(\frac{\partial h}{\partial T} \right)_P \tag{9.3}$$

The thermal conductivity, k, is determined by the assumption that the overall resistance to conduction is due to the resistance of parallel layers of each substance in parallel (=) or perpendicular (⊥) to the heat flow direction. It is further assumed that both cases are equally represented, i.e.:

$$k = \tfrac{1}{2}(k_{=} + k_{\perp}) \tag{9.4}$$

Experiments with artificial and real fish samples

To eliminate biological and seasonal variation of fish properties when comparing cooling methods, artificial fish samples with thermophysical properties close to those of white fish have been made out of Karlsruhe food simulator (a mixture of methylcellulose, sodium chloride and water). The aim of the experiments was to compare cooling of fish in containers by using ice slurry or flake ice. The distribution of fish is assumed to be in perfect layers of fish and ice respectively. Three different cooling scenarios were set up, two of them representing an ideal distribution of either flake ice or ice slurry on top of each fish layer, and the third assuming larger re-crystallized/agglomerated blocks of ice covering only 25% of the total surface area, while liquid film heat transfer is present on the remaining surface.

Measurements were made for an artificial fish model with thermocouples placed internally. The fish was placed between artificial dummies in the middle of the container. A total of 20% pure ice was employed for each experiment. Results obtained were compared with the data for horse mackerel. For modelling purposes, fish were assumed to be cylinders of infinite length with adiabatic contact lines between fish. Temperatures of flake ice and ice slurry were set to 0 and –3°C, respectively. The heat transfer coefficient between the ice particles and fish was estimated to be 750 W/(m²K), a value affected by the resistance of the melting liquid layer between the fish surface and ice. Liquid film heat transfer coefficient was assumed to be 50 W/(m²K).

Figure 9.8 shows a reasonable agreement between calculated and measured temperature histories. However, it is also evident that a simple set of boundary conditions is not sufficient to describe the real situation in the container and some deviation may exist, especially for the time interval when almost all the ice has melted (1200 to 1600 seconds). Furthermore, it appears that the centre temperature decreases at a higher rate when using ice slurry at –3°C. This is even more obvious at the surface. The calculated temperature histories indicate that freezing does not occur at the outer shell if the ice slurry is kept at above –3°C. The final equilibrium temperature of the fish was approximately 1 K lower when using the same amount of ice slurry versus using flake ice. The difference is caused by the larger enthalpy change of the melting ice slurry.

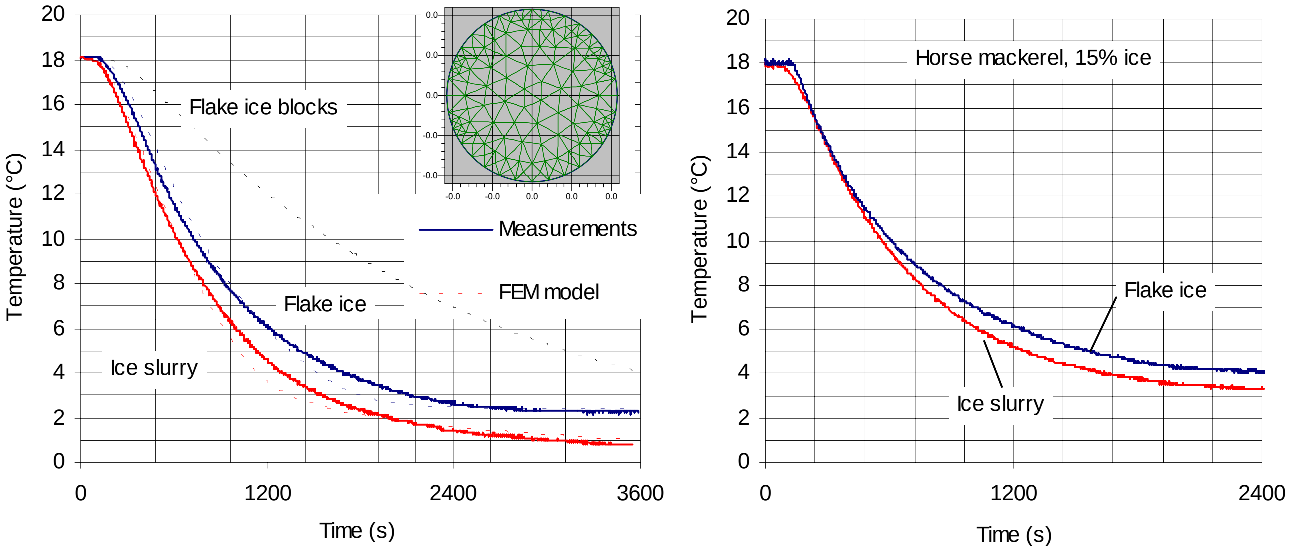


Figure 9.8. Variation in centre temperature (left graph) measured in an artificial fish model (43 mm diameter) cooled in a container with ice slurry at –3°C and with flake ice at 0°C, together with calculated temperatures (initially 20% ice in the container). Temperature measurement (right graph) in horse mackerel cooled in a container with ice slurry and with flake ice (initially 15% ice in the container)

The results from the experiments with the artificial fish model were comparable with those with horse mackerel. A similar tendency was found, i.e., faster temperature drop and about 1 K lower final temperature when using ice slurry. The end cooling temperature was, however, different because of the smaller amount of ice. If the distribution of flake ice is not ideal because of re-crystallized blocks, *Figure 9.8* reveals that cooling with flake ice is less effective than with ice slurry.

Cooling experiments with a fish model immersed into a flowing stream of ice slurry with different velocities and ice concentrations were also conducted to identify any advantages of pre-cooling before container storage. Measurements were performed for flow velocities of 0.1 and 0.2 m/s and at ice concentrations of 10, 20 and 30 wt-%. Results showed that there is no major difference in terms of cooling time for different combinations of these parameters. Compared with the immersed fish model, no significant difference was detected when cooling a container with perfect distribution.

9.4. Ice-slurry-based cooling of fruits and vegetables

The ice-slurry cooling method for fish can also be employed for fruit and vegetables, along with other food commodities to be chilled or frozen. In many cases the uncontrolled uptake of solutes (salt or alcohol) on the product surface is more undesirable than for fish (unless osmotic phenomena are exploited to give added value to the product). Similar to the fish cooling, much faster heat transfer rates can be obtained. Most notable is the improvement when comparing previously air cooled products versus ice slurry cooled products. For instance, the Danish Technological Institute investigated the chilling and freezing of pig carcasses in ice slurry with good results, while a number of researchers around the world performed promising experiments with various fruits and vegetables.

When using suitable product-friendly media, the osmotic phenomena on the surface can be exploited to give added value to the products. In particular, by freezing of fruits in sugar-ethanol-based aqueous solutions or pumpable ice slurries new delicious dessert products can be formulated with beneficial effect on colour, flavour and texture due to the enzyme-inhibiting action of the sugar (Fikiin and Fikiin, 1998, 1999). In addition, the take-up of food additives (antioxidants, flavourings, aromas and micronutrients) is improved, which can result in a better quality and extended shelf-life of the end product. Nevertheless, the available data for the physical properties and the performance of such secondary fluids in food freezing equipment are still too scarce. A set of predictive equations for the density, viscosity, thermal conductivity and specific heat capacity of sugar-ethanol aqueous refrigerating media are given by Fikiin *et al.* (2001).

Sugar-ethanol aqueous solutions and ice slurries suitable for immersion freezing of fruits

Several important criteria must be taken into consideration when selecting liqueur-type refrigerating liquids and ice-slurries pertinent for fruit freezing applications: (i) product friendliness with regard to the end product quality, (ii) environmental friendliness, (iii) suitable rheological properties in terms of good pumpability, and (iv) appropriate initial freezing temperature (Fikiin *et al.*, 2001). A number of test solutions were therefore prepared at the St. Petersburg State University of Refrigeration and Food Technologies by using distilled and deionized water, pure ethanol of food-admissible class and sugar (sucrose or glucose). Solution compositions and freezing points are presented in *Table 9.1*. The estimated uncertainty in the mass fraction data was ±0.1%.

Table 9.1. Compositions and initial freezing temperatures of the studied solutions

Solution Number	**Composition (mass fraction)**			**t_f (°C)**
	water, x_w	**ethanol**, x_e	**sucrose**, x_s	
1	0.55	0.25	0.20	–28.0
2	0.60	0.25	0.15	–25.0
3	0.65	0.25	0.10	–22.0
4	0.55	0.20	0.25	–26.5
5	0.60	0.20	0.20	–23.5
6	0.65	0.20	0.15	–19.5
7	0.55	0.15	0.30	–23.0
8	0.60	0.15	0.25	–20.0
9	0.65	0.15	0.20	–16.5
Solution No.	**water**, x_w	**ethanol**, x_e	**glucose**, x_s	**t_f (°C)**
10	0.60	0.25	0.15	–24.5

An international taste panel considered that solutions No. 1, 2 and 10 posessed the best sensory and physical properties, but some other solutions (such as No. 4, 5 and 6) were also acceptable.

Predictive equations for the thermophysical and rheological properties of sugar-ethanol aqueous solutions and ice slurries

A series of experiments were carried out and some theoretical approaches were employed to determine basic thermal and rheological properties of the studied single- and two-phase refrigerating media and to establish resulting regression relationships. The following assumptions were made when deriving the predictive equations: (i) water is the only freezable component of the solution (because, at atmospheric pressure, all the ethanol remains unfrozen above –114.5°C), (ii) the temperature-dependent properties of the liquid solution are extrapolated below the initial freezing point to estimate the unfrozen fraction properties, and (iii) the ice fraction variation with the temperature conforms with the Raoult's Law (Fikiin *et al.,* 2001).

Initial freezing temperature

Typical gradients of the time-temperature curves during slow freezing or thawing (~0.5°C/min) were registered to measure the initial freezing points of the studied solutions (*Table 9.1*) and the following empirical equations were then established by a regression analysis:

$$t_f = a_0 + a_1.\, x_e + a_2.x_s + a_{12}.x_e.x_s \qquad (9.4)$$

where $0.15 \leq x_e \leq 0.25$, $0.10 \leq x_s \leq 0.30$, and $a_0 = 10.9$, $a_1 = -103.33$, $a_2 = -51.67$ and $a_{12} = -66.67$.

Density

The liquid densities were determined by a piezometric technique, which was previously tested with reference liquids (water, ethanol and other well-investigated solutions). The resulting regression equation is:

$$\rho_l = (b_0 + b_1\, x_e + b_2\, x_s + b_{12}\, x_e\, x_s) + (c_0 + c_1\, x_e + c_2\, x_s + c_{12}\, x_e\, x_s)\, t \qquad (9.5)$$

for $t_f \leq t \leq 21$°C, $0.15 \leq x_e \leq 0.25$, $0.10 \leq x_s \leq 0.30$ and coefficients are given in *Table 9.2*.

Table 9.2. Coefficients of Eq. (9.5)

b_0	b_1	b_2	b_{12}	c_0	c_1	c_2	c_{12}
981.8	–67.556	481.111	–255.556	0.30483	–3.10689	–2.06289	9.18444

Furthermore, the ice-slurry density can be expressed as follows:

$$\rho_{is} = [x_i / \rho_i + (1 - x_i)/ \rho_l]^{-1} \qquad (9.6)$$

where x_i is the mass fraction of ice, the ice density $\rho_i = 916.8\,(1 - 0.00015\, t)$ and ρ_l is determined by Eq. (9.5) for $x_s = x_s^{in} / [1 - (1 - t_f / t)\, x_w^{in}]$ and $x_e = x_e^{in} / [1 - (1 - t_f / t)\, x_w^{in}]$.

Viscosity

Measurements of the liquid viscosity were carried out by using glass capillary viscometers and the results obtained were approximated by the following equation:

$$\eta_l = D + E\, t + F\, t^2 \qquad (9.7)$$

where: $D = d_0 + d_1 x_e + d_2 x_s + d_{12} x_e x_s$, $E = e_0 + e_1 x_e + e_2 x_s + e_{12} x_e x_s$, $F = f_0 + f_1 x_e + f_2 x_s + f_{12} x_{es}$, $t_f \leq t \leq 21$°C, $0.15 \leq x_e \leq 0.25$ and $0.10 \leq x_s \leq 0.30$. The empirical coefficients are given in *Table 9.3*.

Table 9.3. Coefficients of Eq. (9.7)

d_0	–17.325	e_0	1.556	f_0	–0.04318
d_1	79.222	e_1	–6.162	f_1	0.15612
d_2	100.822	e_2	–7.486	f_2	0.18694
d_{12}	–181.778	e_{12}	15.611	f_{12}	–0.40644

The model of Thomas (1965), valid for ice particle diameters between 0.1 and 45 µm, can further be employed to evaluate the apparent viscosity of the ice slurry (please refer to Chapter 3 for a detailed description of rheological ice slurry properties):

$$\eta_{is} = \eta_l \, [1 + 2.5\, \varphi_i + 10.05\, \varphi_i^2 + 0.00273 \exp (16.6\, \varphi_i)] \qquad (9.8)$$

where the volumetric ice fraction $\varphi_i = x_i\, [\, x_i + (1 - x_i)\, (\rho_i \,/\, \rho_l)\,]^{-1}$ may vary between 0 and 0.625, while η_l is calculated by Eq. (9.7) for $x_s = x_s^{in} / [1 - (1 - t_f / t)\, x_w^{in}]$ and $x_e = x_e^{in} / [1 - (1 - t_f / t)\, x_w^{in}]$.

Thermal conductivity

As is well-known, the thermal conductivity of a ternary solution does not comply with the additive principle and cannot, therefore, be rigorously expressed through the properties of the different constituents. Nonetheless, by using a quasi-binary assumption the overall liquid conductivity could be considered as a compound function of the conductivities of ethanol and water-sugar system. It turned out that the liquid thermal conductivity predominantly depends on the ethanol content and could roughly be estimated on the basis of the ethanol fraction only:

$$k_l = (i_0 + i_1 x_e + i_2 x_e^2) + (l_0 + l_1 x_e + l_2 x_e^2)\, t \qquad (9.9)$$

for $t_f \leq t \leq 20$°C, $0.10 \leq x_e \leq 0.35$ and equation coefficients are shown in *Table 9.4*.

Table 9.4. Coefficients of Eq. (9.9)

i_0	I_1	i_2	l_0	l_1	l_2
0.50686	–0.573278	0.2401997	0.001347	–0.0028111	0.0011861

In accordance with the Maxwell model, the apparent thermal conductivity of the ice slurry could be written in the form of Jeffrey (1973):

$$k_{is} = k_l\, (1 + 3\, \varphi_i\, \beta + 3\, \varphi_i^2\, \beta^2\, \chi) \qquad (9.10)$$

where $\chi = 1 + 0.25\, \beta + 0.1875\, \beta\, [\, (\alpha + 2) \,/\, (2\, \alpha + 3)\,]$, $\beta = (\alpha - 1) \,/\, (\alpha + 2)$, $\alpha = k_i \,/\, k_l$, $k_i = 2.22\, (1 - 0.0015\, t)$, φ_i is as in Eq. (9.8), and k_l is calculated by Eq. (9.9) for $x_e = x_e^{in} / [1 - (1 - t_f / t)\, x_w^{in}]$.

The dimensionless apparent ice-slurry viscosity, $\eta^* = \eta_{is} / \eta_l$, and thermal conductivity, $k^* = k_{is} / k_l$, determined by Eqs (9.8) and (9.10) as a function of the volumetric ice fraction, φ_i, are shown in *Figure 9.9*.

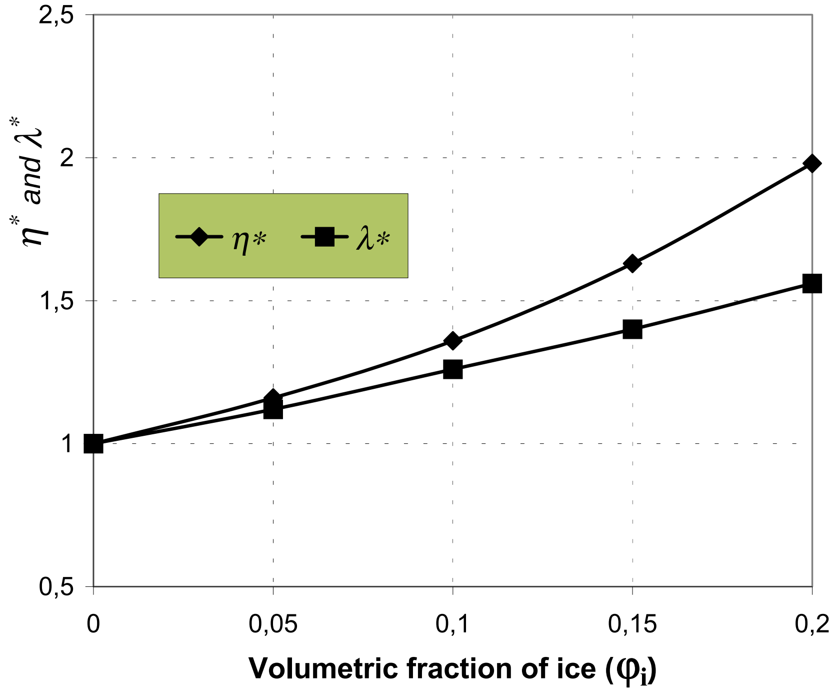


Figure 9.9. Dimensionless apparent viscosity, $\eta^* = \eta_{is} / \eta_l$, and thermal conductivity, $k^* = k_{is} / k_l$, versus φ_i. (The notation for thermal conductivity in the figure follows the symbol tradition of Continental Europe, i.e. "λ" is used instead of "k")

Specific heat capacity

General thermodynamic considerations make it possible to determine the specific heat capacity of ternary solutions on the basis of the heat capacities of the solution components. The data obtained for liquid sugar-alcohol aqueous solutions were fitted by the following regression equation:

$$c_{p,l} = (m_0 + m_1 x_e + m_2 x_s + m_{12} x_e x_s) + (n_0 + n_1 x_e + n_2 x_s + n_{12} x_e x_s)\, t \qquad (9.11)$$

for $t_f \le t \le 20°C$, $0.15 \le x_e \le 0.25$, $0.10 \le x_s \le 0.30$ and empirical coefficients are presented in *Table 9.5*.

Table 9.5. Coefficients of Eq. (9.11)

m_0	m_1	m_2	m_{12}	n_0	n_1	n_2	n_{12}
4.192	–1.9272	–2.8172	0.0910	0.000020	0.005075	0.002675	0.000459

The apparent specific heat capacity of ice slurries and other water-containing systems can easily be evaluated as follows (Fikiin and Fikiin, 1999b):

$$c_{p,is} = c_{p,l} - d\,[\,x_i\,L\,] \,/\, d\,t \qquad (9.12)$$

where $L = 334.2 + 2.12\, t + 0.0042\, t^{2}$, $x_{\mathrm{i}} = x_{\mathrm{w}}^{\mathrm{in}}\, (1 - t_{\mathrm{f}} / t)$ and c_{l} is determined through Eq. (9.11) for $x_{\mathrm{s}} = x_{\mathrm{s}}^{\mathrm{in}} / [1 - (1 - t_{\mathrm{f}} / t)\, x_{\mathrm{w}}^{\mathrm{in}}]$ and $x_{\mathrm{e}} = x_{\mathrm{e}}^{\mathrm{in}} / [1 - (1 - t_{\mathrm{f}} / t)\, x_{\mathrm{w}}^{\mathrm{in}}]$.

It is obvious that $t < t_{\mathrm{f}}$ in all the ice-slurry related equations, Eqs (9.6), (9.8), (9.10) and (9.12).

A small-size prototype of HFM freezer for testing, demonstration and promotion of the HFM technology is under investigation at the Technical University of Sofia and Interobmen Ltd. – Plovdiv (Bulgaria). The hydrofluidization, conveyor and driving systems of the prototype are shown in *Figure 9.10*.

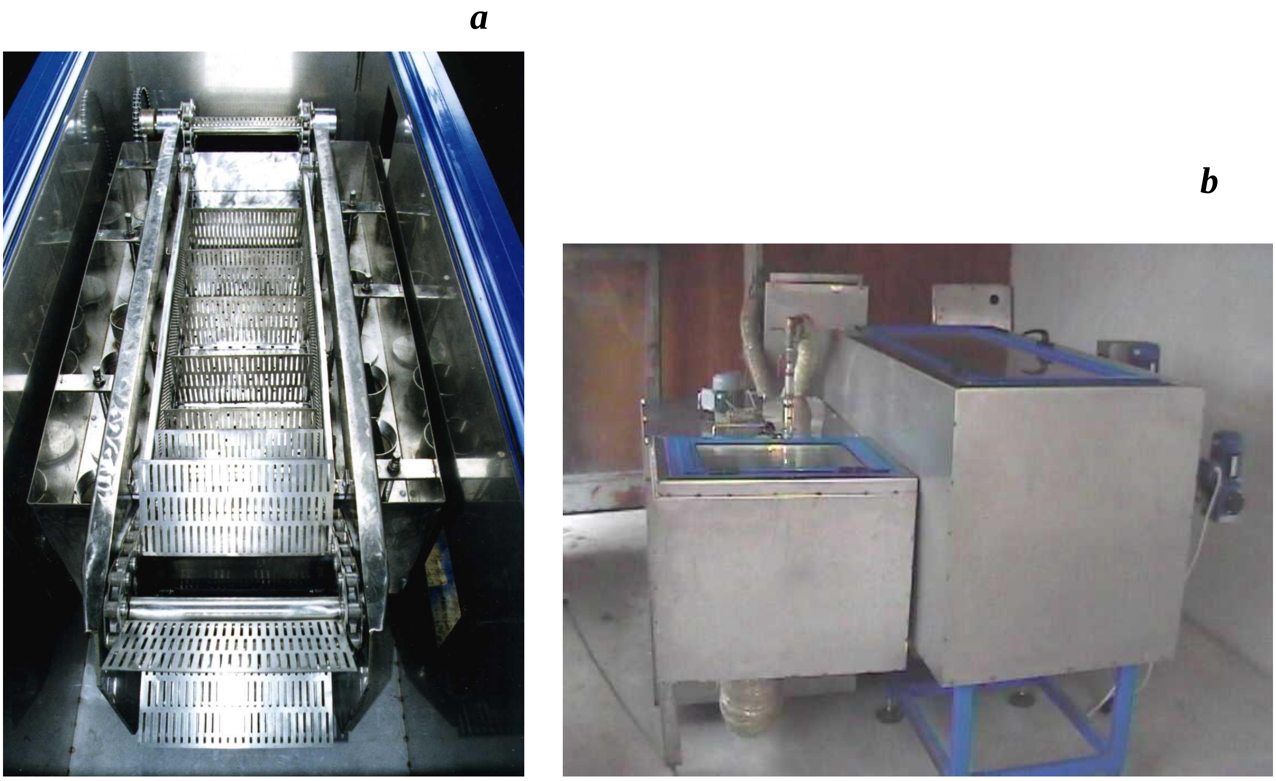


Figure 9.10. Hydrofluidization, conveyor and driving systems of the *HyFloFreeze*® prototype (Technical University of Sofia and Interobmen Ltd.): (*a*) top view, (*b*) overall view

The following <u>initial design specifications</u> were used when putting together the prototype freezer:

(i) *starting selection of fruits to be frozen:* strawberries, raspberries, plums, apricots, morellos, cherries, blueberries and cranberries; (ii) *refrigerating media:* unfreezable liquids or pumpable ice slurries based on sugar-ethanol aqueous solutions, (iii) *refrigerating medium temperature*: –25/–30°C, (iv) *evaporation temperature of the refrigerant:* –30/–35°C, (v) *throughput:* 20-50 kg per hour (depending on the product); (vi) *final temperature in the frozen food centre:* –12/–15°C; (vii) *final average temperature of the product:* –18/–20°C; (viii) *principle of operation:* enhanced hydrofluidization throughout the whole freezer by directed jets of fluidizing agent; and (ix) *conveyor system:* electronic regulation of the driving motor revolutions for smooth variation of the conveyor speed and product residence time depending on the individual freezing duration for each product.

The ice-slurry-based HFM technology possesses a series of advantages over the conventional IQF modes, which can be summarised as follows (Fikiin and Fikiin, 1998, 1999; Fikiin *et al.*, 2001):

- **Frozen fruit quality:** high freezing rate; fine-grain crystal structure; sharp reduction of the surface mass transfer; enzyme-inhibiting action of the sugar; easy incorporation of antioxidants, flavourings, aromas and micronutrients and formulation of delicious dessert-type frozen foods with extended shelf-life and improved nutritional value and sensory properties.
- **Energy and economic efficiency:** higher refrigerating and evaporation temperatures; possibility for single-stage refrigeration machine with reduced investment, maintenance and energy costs; easy connection with systems for thermal energy storage; high throughput and cost efficiency.
- **Environmental friendliness:** use of environmentally friendly secondary coolants (syrup-type solutions or ice-slurries) and primary refrigerant closed in a small isolated system.

At some temperatures and concentrations, the pumping of sugar-ethanol-based slurry through the hydraulic circuit and perforated bottom may be accompanied by intense foaming (*Figure 9.5*). Preliminary tests revealed that this adverse effect could be overcome by adding suitable antifoaming agents.

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