Maximising Quality and Stability of Frozen Foods

A Producers Guide to The State of the Art

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Report 2

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Chapter 1

1.1 Introduction

1.1.1 Who is this booklet written for?
This document has been prepared for manufacturers, large and small, of frozen foods. Growth in the high-quality frozen food market has often been limited by the lack of confidence, on the part of food producers, in the handling of foods by distributors, retailers and indeed the end user. This has limited investment by producers in quality materials and innovation. The producer is not, however, powerless in producing goods that can retain quality even if subjected to what might be termed “reasonable“ degrees of temperature abuse. This document is written for producers who wish to maintain the maximum quality stability in their products.

1.1.2 Why should you read this?
This document can not provide you with a complete understanding of all the research that has been performed on frozen food storage. However we intend that the information in it will provide you with a basic guide to producing products that maintain their quality for the maximum period of time. It will provide an outline to the main points that need to be considered when choosing your starting material, formulation, processing and packaging.

In the course of this document we will refer extensively to quality. Quality here has two meanings. Firstly the attainment of a level of excellence in comparison to other similar products. Secondly, to maintain a consistency of this product at the time of use. This is to be achieved by consistency of production and in spite of handling by distributors and the consumer themselves.

1.1.3 What’s the book going to tell you?
In the remainder of this introduction I will briefly outline the factors affecting frozen food stability, the causes of product instability and how these affect product quality.

In the following chapter we will discuss selection of varieties when freezing fruits and vegetables. Initial selection of species and cultivars plays a major role in determining subsequent resistance to frozen storage. Chapter 3 discusses factors that are important in producing high quality frozen meat and fish products.

We will then address the area of pre-treatments, from long established practices such as blanching to more recently developed techniques such as osmotic dehydration soaking. The transition of the unfrozen portion of a food to a glass has a major effect on stability.
The temperature at which such transitions occur depends on the composition of the food, the variety and pre-treatment.

In Chapter 5, Martin George from Campden and Chorleywood Food Research Association provides a guide to choosing packaging that will optimise the storage potential of frozen foods.

The volume finishes with a little crystal ball gazing. Frozen food is presently receiving considerable attention from both academics and commercial producers. Alfred Jann of Nestle and Geoff Archer of BioFreeze comment on possible future developments.

1.1.4 What do we mean by stability?
Stability is best defined, as the lack of its inverse. We freeze foods to extend their storage life by making them more inert. A range of physical and biochemical reactions continues however and many of these will be accentuated when storage conditions are altered. To a large extent we are unconcerned with the microbiology of frozen foods since no microorganisms grow below -10°C, however freezing and frozen storage is not a reliable biocide. The production of safe frozen foods requires the same attention to good manufacturing practice (GMP) and HACCP principles as the production of their fresh counterparts. A false sense of security, based on the good safety record of frozen foods, should not lead us to reduce our vigilance when preparing or handling these products.

1.1.5 What happens to frozen foods during distribution?
Frozen foods during distribution may reasonably be expected to undergo a range of thermal cycles both large and small. The perfect cold store has yet to be invented. Typical air temperature fluctuations in a cold store can be between 4 and 8°C. Retail cabinets, which require ready access and good product visibility, are often subject to larger fluctuations still. Finally the consumer must return home with their purchase. Although the use of freezer bags is increasing, the producer can certainly not rely on their widespread use. Most products are therefore likely to experience at least one large step up and down in temperature between purchase and storage in the domestic freezer.

Report 1 in this series, "A Practical Guide to The Cold Chain From Factory to Consumer", describes the state of the art in temperature monitoring and control and what developments in that technological field may bring. Here we must address the effects of the problem as it now exists.

1.2 What are the effects of temperature abuse?
Freeze damage occurs by a number of mechanisms that result in loss of quality in a product after thawing. Sometimes, loss of quality may be seen in the frozen product, i.e.
before thawing (freezer burn, discoloration, breakage, etc.). In many (most) cases, the loss of quality is not noticeable until after cooking. Most of these mechanisms are determined by the storage temperature and thus accelerated during storage periods spent above the recommended storage temperatures. Others are determined by temperature gradients caused by fluctuations in the external temperature. Many are affected by both factors. A practical outcome of this is that the quality of a frozen product stored under fluctuating temperature condition cannot be assumed to have the quality parameters of the time weighted mean temperature.

The argument for this is as follows. If the quality parameter is found to be related linearly to the inverse of its storage temperature, the effect of temperature fluctuations will be to increase deterioration when the temperature is higher than the average, and decrease it by the same amount when the temperature falls by the same amount. Because the dependency is linear, the quality of the product will be that which would be expected \( Q_T \) at the time-weighted mean storage temperature \( T \). If, however, the rate of deterioration increases in an exponential (or other higher order) manner with temperature, fluctuations in temperature result in greater quality losses \( Q \) than would be expected from the time weighted mean temperature \( Q_T \). This is illustrated in figures 1.1a and 1.1b.

![Figure 1.1 - diagrams demonstrating the effect of temperature fluctuation between upper \( T_U \) and lower temperature \( T_L \) limits around a time weight mean temperature of \( T \) on the rate of quality loss \( Q \). a) where quality loss varies linearly with temperature and b) where quality losses increase exponentially with temperature.](image)

**1.2.1 How does ice damage food?**

**Damage during freezing**
The direct cause of most ice damage is the rigidity of ice in the food structure. The expansion of water on freezing leads to the stressing of delicate structures, membranes etc, which do not relax back on thawing. Ice can not grow through structures. It grows by adding molecules to an existing crystal. On meeting a boundary, therefore, growth in that direction stops. However, when ice begins to grow in a gap between cells the stress
created by its expansion can cause the gap to open further. This then allows more growth and a run away effect leads to the large voids often seen in frozen materials on thawing. Similar damage occurs to structures within cells as ice crystals grow there. The result for the end user is loss of liquids from within the food on thawing, drip, and changes to the rigidity and texture of the food material.

Figure 1.2 Ice crystals surrounded by an unfrozen matrix.

Ostwald ripening.
Oscillations in temperature manifest themselves primarily in the enhancement of Ostwald ripening. This is a direct effect of the surface energy of ice crystals. The lowest energy state, and hence the equilibrium state towards which a collection of ice crystals will move, has the lowest possible surface to volume ratio. This is achieved by having one large ice crystal.

When a food is frozen a collection of ice crystals is formed, surrounded by a matrix of unfrozen solution, see figure. The ice crystals in a frozen food are in a dynamic equilibrium with this surrounding unfrozen solution. Water molecules are continually leaving and rejoining the crystal. Surface energy kinetics require that water molecules are more readily given off by small ice crystals and more easily collected by large ones, driving the food towards the equilibrium state.

Temperature fluctuations accelerate this process as they result in a small amount of melting, preferentially from the smaller crystals, followed by re-freezing, preferentially on to the larger crystals. The net effect is an increase in stress damage and a build up of local high solute concentrations (see below) as the ice migrates to preferred locations.
**Accretion**

A related phenomenon is the accretion of ice crystals. This is the joining together of two ice crystals that are already in physical contact. This occurs by an Ostwald ripening process accelerated by the crystals’ proximity and a rearranging of surface ice molecules to lower their surface energy. The phenomenon again leads to increased stress and irreversible damage to tissues, and hence increased drip loss and textural changes.

**Vapour migration.**

The final moisture migration phenomenon we need to consider is the migration of moisture into voids. This is most apparent at the surface of frozen foods and results in the familiar build up of ice on the interior of packaging and food surfaces. If unchecked, vapour migration leads ultimately to freezer burn and associated changes in colour and texture.

This type of moisture migration is driven by differences in vapour pressure. Again we are looking at a dynamic equilibrium between an ice surface and this time the vapour phase above it. The variation of vapour pressure above ice with temperature is shown in figure 1.3. Above a relatively warm surface the vapour pressure is higher. Vapour moves to a point above a colder surface due to the pressure difference and will precipitate there. Again, because of the lower energy of the ice in a pure ice crystal, on reversal of the temperature gradient the moisture will not return to its starting point and builds up on surfaces and voids. The greater the frequency and magnitude of fluctuations the greater this effect will be. From figure 1.3 it is also clear that the higher the mean around which the temperature is fluctuating, the larger the volume of moisture that will migrate.

![Vapour pressure over ice verses temperature](image)
1.2.2 Concentration effects

In section 1.2.1, we have outlined the physical effects of ice formation and recrystallisation. As well as these physical effects, the formation and recrystallisation of ice has repercussions for the biochemical stability of frozen foods. This is primarily as a result of the increase in concentration of the solutes in the unfrozen matrix.

Solute concentration
As ice forms during freezing, the concentration of solutes in the unfrozen portion increases. Increases in the strength of ionic solutions can have effects, particularly on charged molecules. This has been shown to lead to the aggregation of biopolymers and precipitation of such molecules from solution. This results in changes to the consistency of the product. It can also lead to the damage of cell membranes with resultant loss of nutrients. The temperature of the unfrozen solution limits these reactions and rapid increases in these temperatures will lead to higher reaction rates, without an accompanying dilution due to ice melting.

Osmotic dehydration
Osmotic dehydration during freezing is dependent on freezing rate. For the majority of foods, ice forms in extra-cellular spaces increasing the concentration of solutes outside the cell and drawing water out of the cell by osmosis. This water will often not return to the cell on thawing. Again the effects of high concentration lead to the deterioration effects listed above. In addition to this osmotic dehydration may result in cell wall damage and loss of turgor in plant tissues. Fluctuations of temperature will result in acceleration of concentration related reactions. They may also undo any advantages obtained by rapid freezing in limiting osmotic dehydration.

1.2.3 Other irreversible changes

Solute crystallisation
As previously discussed, when a food freezes the surrounding unfrozen component increases in concentration. Once the maximum solubility has been exceeded two things may happen. We may obtain a supersaturated solution, which undergoes a glass transition (see chapter 4). More usually the solution stays for a length of time in the supersaturated state before the solute begins to crystallise out. The effects of solute crystallisation are to alter the ionic strength and pH of solutions.

Lipid oxidation
Although temperature reduction reduces the rate of oxidation, increases in concentration due to freezing acts to accelerate this process. The net result is that lipid oxidation can become the shelf life limiting characteristic in some frozen foods. This is particularly
noticeable in the case of fatty fish and some pork products. Lipid oxidation leads to the development of off flavours particularly rancidity.

**Enzymatic activity**
Finally, there are numerous enzymatic reactions that are affected by concentration and temperature. These lead to the development of off colours, off odours and off flavours. Due to the halting of microbial deterioration processes these can become the predominant deterioration mechanism for frozen products.

1.3 Summary
We have discussed the major causes of instability in frozen foods. Some of these are temperature dependent, some are dependent on temperature gradients/fluxuations and others are dependent on both of these. In the coming chapters we will discuss the ways in which food selection, formulation and treatment can be adapted to minimise these changes during distribution and retail.
Chapter 2
Factors affecting the quality of frozen fruit and vegetables

A. Maestrelli, D. Torreggiani, T. Lucas, A.L. Raoult-Wack, and J. Philippon

2.1 Introduction

Fruits and vegetables (F&V) are very sensitive to freezing damage. Chemical and physical actions of freezing (see chapter 1) are highly detrimental to F&V products since their texture is mainly ensured by turgor (apple, berries, peach, tomato, lettuce, spinach, etc.). Turgor is the ability to retain water inside the cells. Rupture of cell walls due to growth of ice crystals and/or enzymatic actions during freezing prevents a return to the initial state. The product will exhibit a loss of cellular structure, which can manifest itself in increased drip loss while thawing, loss of shape and a less defined texture.

Liquid water is the molecule most involved in deterioration reactions. It provides a medium for diffusion of all other molecules involved in deterioration reactions. Water can also participate in deterioration reactions directly. Deterioration reactions are many-fold and include:

- production of off-flavours
- production of toxic substances by micro organisms
- changes in colour due to enzymatic or non enzymatic reactions on pigments (especially browning).

As we have seen in Chapter 1, water can also migrate within food towards surfaces and then evaporate, re-crystallising as ice on cold outer surfaces. Food surfaces becomes dry, colour tarnishes. Even at -18°C, a fraction of food-constituent water remains liquid and free for these reactions. Water can also migrate from ice crystals present in food. A
food’s surface is the first affected since this is closest to the refrigerating medium (most often air).

If pre-freezing, freezing and storage operations are not conducted with an appreciation of the nature of the food, frozen products may resemble their fresh counterparts in name only.

2.2 How can the quality of frozen F & V be maximised?

There are several decisions that producers of frozen fruits and vegetables take which together determine the quality of the frozen product. The factors to take into count can be split chronologically into:

- Choice of product to freeze
- Freezing Technology
- Post-freezing factors.

2.3 How do you obtain F&V suitable for the freezing process?

2.3.1 Raw materials for frozen F&V

If the freezing process is correctly applied, it can at best produce products which approach that of the quality of the product prior to freezing and which will be capable being stored for several months. It cannot be expect to improve the quality of the raw ingredient. Put simply, “to obtain high quality frozen products, high quality raw materials have to be used”.

For this reason products rejected by the fresh market must not be used as raw material for freezing.

2.3.2 Cultivar selection

The word cultivar means “variety of cultivated agricultural produce”. For example, a cultivar can be obtained by naturally occurring or deliberate genetic crossing or by artificially induced mutation (genetic engineering). Throughout the world, there are many cultivars for every species of F&V, each with specific characteristics. For example, 2000
different cultivars of strawberries and hundreds of cultivars of apples, peaches, green beans, etc. are known.

**What makes a cultivar of F&V especially suitable for freezing?**

*a) agronomical factors*
Before a cultivar can be considered suitable for a specific area, the following factors should be considered:
- geographical conditions (altitude, exposure, hours of sunlight);
- soil (structure, fertility, available irrigation);
- climatic conditions (rain, temperature, prevailing winds).

A good cultivar should have:
- high yield / hectare;
- high resistance to parasites (insects, bacteria, fungi, virus). Physical damage to the plants means a decrease in the economic value. Pesticides, although required to protect the crop, may also contaminate the production if used excessively.

In order to have a continuous flow of the product to industry, the cultivar should be selected so as to provide early, regular and late ripening crops.

*b) technological factors*
To minimise labour costs, vegetables and some fruits (tomato, egg-plant, pepper, green bean, etc.) should be suitable for mechanical harvesting. For this reason it is important to consider:

- uniform ripening of the product
- carriage of the plant
- shape of the product
- how the product is distributed on the plant

F&V must be harvested when they reach the maximum sensory attributes level. If the product is frozen after this maximum level, many of the reactions that lead to reduced product quality will have begun. The result will be reduced storage life and/or poor sensory attributes in the frozen product.

If a product ripens non-uniformly, this causes difficulties in harvesting. If there is just one harvest, there is waste (size and colour differences), if there are successive harvests, the expenses are higher.

Cultivars should also be amenable to mechanical post harvest handling. This leads to reduced costs as a result of fewer manual workers. For this to be practical the cultivars must consistently have specific characteristics. For example:
• they should be easy to destalk (strawberry, apple, tomato, etc.)
• they should facilitate decoring (cauliflower should spontaneously separate, after decoring, into little florets of almost 25 g/each. This ensures that no manual cutting is needed and they are ready for blanching).
• simple calibration (green beans should be straight)

Tables 2.1 & 2.2 show the handling resistance of some common fruits and vegetables.

**Table 2.1 – Handling resistance of some fruits**

<table>
<thead>
<tr>
<th>Handling Resistance</th>
<th>Type of Fruit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistant</td>
<td>melon, kiwi, blueberry, chestnut, clingstone peach &amp; apple</td>
</tr>
<tr>
<td>Slightly Resistant</td>
<td>pear, peach &amp; apricot</td>
</tr>
<tr>
<td>Little Resistance</td>
<td>Strawberry, blackberry, raspberry &amp; redburrant</td>
</tr>
</tbody>
</table>

**Table 2.2 – Handling resistance of some vegetables**

<table>
<thead>
<tr>
<th>Handling Resistance</th>
<th>Type of Vegetable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistant</td>
<td>carrot, artichoke, onion, bean, potato, peas &amp; leek</td>
</tr>
<tr>
<td>Slightly Resistant</td>
<td>green beans, broad beans, fennel, pepper, parsley, celery &amp; squash</td>
</tr>
<tr>
<td>Little Resistance</td>
<td>asparagus, broccoli, cauliflower, mushroom, aubergine, tomato, spinach &amp; courgette</td>
</tr>
</tbody>
</table>

c) **sensory factors**

Colour, taste and texture of F&V are the most important elements both for farmers, industry and the consumer:

- Colour. A good cultivar should keep its original colour even after freezing. In some cases (e.g. strawberries and apricots) the original colour can be maintained using pre-freeze treatments (see chapter 4). Some vegetables (cauliflower and broccoli) have a violet or pink nuance (from anthocyanins pigments) this is not a defect and is eliminated by the blanching.

- Taste. Frozen F&V should not taste any differently from the original. The consumer can be very severe about the taste of frozen food, but this also depends on the culinary traditions of different countries. The frozen food industry should consider this important aspect, by selecting cultivars that respect the consumer’s preferences in various countries.

- Texture. Of the sensory attributes, texture is the most susceptible to negative modification after freezing. Selecting the correct harvesting period plays an important role in limiting the influence of the freezing process on the decrease in texture, which occurs during thawing. Vegetables are, usually, consumed cooked, so defects in texture are less evident. Furthermore lignin, fibre,
cellulose, starches and other polysaccharides protect the structure of most vegetables, with the exception of the leaves. Other products, such as precooked F&V or purees have already lost most of their texture during the heating stage. The final freezing operation will have no additional effect on texture. Fruits however, are mainly protected by pectins which are quite delicate and undergo irreversible biochemical modifications, after freezing and during storage. Cultivar selection plays an important role. For instance, the ‘Pavie’ peach, has thicker cellular wall and less active pectolytic enzymes, making it less easily damaged by freezing operations than other peaches. Osmotic pretreatments can also help, improving frozen fruit texture for specific food applications (see chapter 4).

d) nutritional factors
F&V cultivars to be used in a freezing process must start off with a high level of vitamins (especially the water soluble ones, like vitamin C) and mineral salt, to ensure that after the processing and consumption the nutritional value remains high. As we will see in chapter 4, there are pre-freeze treatments for some fruits that can enrich the product by adding sugars, vitamins and mineral salts. Vegetable cultivars, besides containing a high level of vitamins, should also be rich in fibre.

The cultivars behaviour must be stable in respect to the above mentioned factors. The quality attributes are measured by analysis of:

- Sensory characteristics: a small group of expert tasters can prepare a simple quality chart of the cultivars. The Quality Control group can organise a panel test which can evaluate the sensorial attributes by triangle test or multiple comparison test. From this latter test the panel can give information on intensity and acceptance of the different parameters (appearance, colour, taste, texture).

- Morphology: the size and average weight of certain number of samples can give an idea of the agronomic variability of the cultivars. It is useful to use home made callipers, as a grill (wood, metal or plastic) adapted for different products (strawberry, florets of cauliflower, asparagus), creating special windows with the dimension (diameter or length) of the most frequent size.

- Texture: using a manual dynamometer, the texture of fruit cultivar can be, more or less, correctly measured. The dynamometer can be equipped with different kinds of plugs (star, needle, cylindrical) or blades. The texture measurement can be repeated several times on a significant amount of sample, on the same part of the product and, for some fruit, such as kiwi or apple, after removing a thin area of skin. The measurements should be performed by the same operator applying the same manual force, at the same speed on the sample.

- Colour: using colorimetric chart (comparison), or using a color meter which gives a series of numbers corresponding to the colour characteristics, for example L (lightness), a* (red-green) and b* (yellow-blue) values. The colour measurements
have to be obtained by always putting the detector window on the same area of the product. When the product presents different colours (eg. half green half orange apricot, edible dark green leaves and light green florets of broccoli) an average of colour data can be estimate by pureeing the product.

- Refractometric index (°Bx): using optical refractometer the sugars content in the fruit can be approximately measured. The best accuracy of the measurements is only possible after the homogenisation of the sample. The °Bx index value must be the result of the average of several measurements, which can be made either by taking each fruit singularly (minimum 20 fruit) or by homogenising a lot of fruit.

- Photographic file: using slides and photos of the cultivar, always using the same camera, film, light and aperture diaphragm conditions, so creating a useful archive. The photographs of the cultivars must be made during the different physiological steps, with pictures of flowers, leaf profiles, and the axial section of a fruit or vegetable, at the correct ripening stage.

### 2.3.3 Setting of quality standard specifications for fruits and vegetables

A quality standard specification gives a range of values defining each quality factor of the F&V suitable for freezing e.g. sugar content, vitamin contents. Almost all the European Union countries are interested in creating official standards for F&V for freezing. Farmers, processors, researchers, distributors, retailers and consumer organisations are all involved in creating such standards.

### 2.4 Is there an optimum freezing rate for F&V?

It is often believed that the quicker food freezing is achieved, the better is frozen food quality, however this point should be qualified. To preserve frozen F&V texture as much as possible, too slow a freezing rate must obviously be avoided; slow freezing is unavoidable in a non ventilated cold room or in a freezer with low air velocity and poor temperature conditions. However most commercial freezing equipment (spiral belt-freezer, fluidized bed freezer, plate freezer, immersion freezer, etc.) can provide a freezing rate high enough to ensure good frozen food texture. For many F&V, texture might not be improved by further speeding up the freezing operation. However, for some F & V (e.g. strawberry, mushroom, melon, asparagus and green beans) higher freezing rates afforded by cryogenic tunnels for example result in improved texture retention. If too high a freezing rate is achieved, high internal mechanical stresses may be formed, leading to bursting of F&V products.
There are no absolute threshold values separating slow, quick and very quick-freezing, these must be determined for each product. We will illustrate this with results for frozen green beans in table 2.3. Thus, in the case of green beans, slow freezing is beyond 12 hrs, quick freezing is between 30 min and 12 hrs and very quick-freezing is within 30 min.
### Table 2.3 – Effect of freezing rate upon sensory properties of green beans

<table>
<thead>
<tr>
<th>Time for Core to Reach – 20°C</th>
<th>Sensory Characteristics of Cooked Product</th>
<th>Type of Freezing</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 30 minutes</td>
<td>No loss of firmness, colour and flavour preserved</td>
<td>Very Quick-Freezing</td>
</tr>
<tr>
<td>30 minutes – 12 hours</td>
<td>Loss of texture, colour and flavour unaltered</td>
<td>Quick-Freezing</td>
</tr>
<tr>
<td>&gt; 12 hours</td>
<td>Loss of texture, colour and flavour adversely affected</td>
<td>Slow Freezing</td>
</tr>
</tbody>
</table>

Colour and taste deterioration is mainly temperature-dependent, the lower the food temperature, the slower the evolution of food characteristics with respect to colour and taste. In particular, a delayed or long cooling stage increases the extent of deterioration reactions, especially changes in colour. For instance, mushroom slices will turn brown within 30 minutes. When cooling food below its freezing temperature, liquid water will solidify and will not be further available for reaction or diffusion. However, even at -18°C some food-constituent water remains liquid (usually between 1 and 5%) and available to take part in reactions, albeit at a slower rate.

#### 2.4.1 What benefits does a rapid crust freezing stage have?

Quick freezing of food surfaces can be considered as a surface protection and improves frozen food quality as it slows down phenomena of evaporation (water, volatile aromas).

#### 2.5 Where might further Technological developments be focused?

Because so many cultivars of F&V are available for selection each year, it is very difficult to identify those cultivars that are the most suitable for freezing. It follows that the breeder must work together with the industry to focus on specific cultivars that fulfill the requirements of the freezing process.

#### 2.5.1 How might genetic engineering affect the choice of F&V?

Clearly the advent of genetic engineering methods offer the opportunity to design desirable properties into F & V. These properties could include those that are desirable for good freezing properties as we have discussed in this chapter. Ultimately, consumer acceptability and economic factors will determine to what extent these technological innovations are commercialised.
One specific application may be the development, by traditional or genetic engineering techniques, of new cultivars with enzymatic compositions that require minimal or zero blanching.

### 2.5.2 Can surface pre-treatments help producers retain better colour and taste in frozen F&V?

Both cutting operations and freezing contribute to cell rupture on a food surface, interactions between previously partitioned substances then become possible. One common consequence is enzymatic browning. Different surface pretreatments or protections before freezing can avoid changes in colour and taste. Until now, browning and off-flavors have been successfully avoided for most products by blanching or chemical treatments before freezing (see chapter 4). However, heat treatments are known to be detrimental to a foods texture and nutritional quality. Chemical treatments should be used cautiously, because the absorption of high levels of some chemicals may generate well known health problems.

Today, immersion treatments in sugar solutions before freezing, open the way for protecting food items by other means. Immersion treatments in sugar solutions, additionally reduce evaporation phenomena and changes in texture throughout the cold chain.
3.1 What are we trying to achieve with this report?

This document has been produced to give those concerned with the manufacture of frozen meat and fish products, an easy-to-read guide to the factors, which affect frozen meat and fish quality. Readers seeking further details of the subject are directed to the bibliography at the end of this chapter.

3.2 What factors determine frozen meat quality?

The main factors determining frozen meat quality can be grouped into three sections: pre-freezing, the freezing process and frozen storage. Because of its importance packaging is the subject of a separate chapter.
3.3 How is Quality Affected by Pre-freezing Factors?

Computer programmers have an acronym GIGO (Garbage In, Garbage Out) which highlights the importance of ensuring that the input to any process is of sufficiently high quality. With frozen meats, the choice of breed and diet of the livestock affects the quality characteristics of the frozen products. Also important is the handling of the animals during transportation and the subsequent slaughter technique employed. Finally, post-mortem treatment of meat prior to freezing can significantly alter its subsequent storage properties. We will now give examples of each of these factors for several important meat products.

3.3.1 What is the Effect of Different Feeding Regimes?

The diet on which an animal is fed can influence its frozen storage life. Pork chops from pigs fed on household refuse are found to possess half the storage life than those from pig fed on milk/barley ration. Pigs fed on a diet of offal have also been found to produce pork with a reduced practical storage life.

In poultry the type of fatty acid composition of "depot fat" and its stability are directly
related to the composition of fats ingested. In particular, the feeding of fish oils or highly unsaturated oils (e.g. linseed) can lead to fishy flavours in the meat. Removal of these oils from the diet of poultry 8 weeks prior to slaughter can help to reduce the level of rancidity after frozen storage. Rapeseed oil in feeds has also been associated with the more rapid development of rancidity during frozen storage.

In general the instability of fats is found to be associated with higher linoleic and especially linolenic acids in the tissues of birds. A high linoleic acid level in other meats (Beef and Mutton) has also been found to correlate with the development of rancid odours and flavours in frozen storage. With pork the trend towards leaner pigs has led to a higher proportion of linoleic acid in their tissues. Therefore the practical storage life of pork may be less than has been found in older studies.

Because rancidity occurs as a result of the oxidation of fatty acids, an obvious approach to reduce its occurrence is to introduce dietary supplements of antioxidants. The use of vitamin E supplements reduces the levels of discolouration and lipid rancidity in frozen minced beef and lamb muscle. It was also found to improve the oxidative stability of turkey burgers.

3.3.2 Why is Handling and Transport Important in Determining Meat Quality?

The way animals are handled and transported before slaughter is known to affect meat quality and its storage life. The problem is most marked in pigs, in which increased stress or exhaustion can produce pale soft and exudative (PSE) meat. PSE is known to have genetic origins, at least two genes are known to be responsible. One is associated with sensitivity to the halothane anaesthetic, the other with an abnormally low pH in the post-mortem muscle. The first gene is common in the Pietrain breed, whereas the second gene is common in the Hampshire breed of pigs. Lamb and poultry have also been known to produce PSE meat if stressed excessively.

A condition known as dark, firm, dry meat (DFD) occurs in beef and lamb obtained from animals that have undergone long-term stress and/ or starvation. Post slaughter lactic acid levels are found to be low leading to a high pH. The meat is unsuitable for vacuum packed or chilled distribution, because the high pH does not inhibit growth of spoilage microorganisms.

3.3.3 How Does Chilling and Aging Affect Frozen Meat Quality?

Meat is not usually frozen until rigor is complete and a degree of conditioning has occurred, otherwise toughening and increased drip loss normally occurs. The length of storage prior to freezing affects the rate of deterioration during frozen storage. Frozen
Lamb and Pork both deteriorate at a faster rate under storage if they are stored for a period at 0°C prior to freezing rather than being frozen immediately after accelerated conditioning.

Therefore techniques which accelerate the conditioning of meats can be used to allow meats to be frozen sooner after slaughter, producing a more stable frozen product. Accelerated conditioning has been demonstrated commercially using high voltage electrical stimulation of lamb carcasses that were frozen pre-rigor. Another possibility for accelerated conditioning of meat involves the use of very fast chilling (VFC). A number of studies have demonstrated that the VFC of meats reduces the toughening effect normally associated with fast chilling.

3.3.4 How can Pre-freezing Processing Affect Storage Life?

Processing of meat prior to freezing can either increase or decrease storage when compared to the unprocessed material.

**Factors which increase storage life.**
Cooking of meat can result in longer storage life of the product. This is probably due to enzyme and microbial inactivation in a similar way that blanching of vegetables prior to freezing optimises their storage life.

Since many of the reactions leading to rancidity are oxidative the addition of antioxidants can improve storage times. Many herb and spice seasonings contain substances which help control rancidity in meats.

Smoking meats has a beneficial effect upon storage life. This is due in part to the antioxidant properties of the chemicals in the smoke and in part to the smoke masking off-flavours.

**Factors that reduce storage life.**
The first rule of thumb is that meat cut into domestic portions deteriorates faster than meat left in carcases or primal joints. Mincing meat increases the rate at which oxidation can occur by increasing the surface area and distributing fat throughout the meat sample. Increasing the fat content of meat products in decreases their storage life. The incorporation of mechanically recovered meat (MRM) in meat products also shortens storage life as a result of the high fat content of MRM.

Other treatments, which increase the fat content of the meat product such as frying, can lead to increased off-flavours during storage.

Salt can reduce frozen storage life due to increasing the rate of processes leading to rancidity. This effect leads to the anomalous frozen characteristics of bacon, which shows accelerated rancidity as the temperature is lowered.
3.4 What is the Best Means of Freezing Meat Products?

Whilst freezing undoubtedly causes changes to components of meat such as muscle fibres, lipids and proteins, there is little scientific evidence to substantiate the belief by consumers that commercially frozen meats are inferior to their fresh counterparts. The question of the optimum method by which meat should be frozen is the subject of many studies. In particular the relative merits of cryogenic and blast freezing. Slightly superior chemical and sensory attributes have been found in cryogenically frozen meat. The main advantages relate to moisture retention, ice crystal location and reduced protein denaturation. Moisture retention in cryogenically frozen meats is greater than that achieved using blast and domestic freezers. During storage, drip losses for all frozen meat samples increase. This is probably as a result of disruption of meat structure by growing ice crystals. However the difference in drip loss between cryogenically and air frozen meat samples diminishes over long storage periods.

The method of freezing can significantly affect the appearance of meat products. Faster freezing results in smaller ice crystals being formed which scatter light more effectively than larger crystals resulting in a lighter coloured product surface. For poultry this enhances the surface appearance, although it should be noted that this advantage will easily be lost if the surface is subjected to temperature fluctuations during storage.

Currently, there seems to be little evidence that the method of freezing affects flavour or aroma greatly although brine freezing reduces storage life, possibly due to the salt diffusing into the meat.
3.5 How Can Storage Conditions Affect Frozen Meat Quality?

The main factors during storage that influence frozen storage life are:

1. the storage temperature;
2. degree of fluctuation in the storage temperature;
3. the type of packaging.

In this section we concentrate on temperature related effects. Martin George will describe factors influencing the choice of packaging in chapter 5.

### 3.5.1 The Effect of Storage Temperature

<table>
<thead>
<tr>
<th>Product</th>
<th>-12°C</th>
<th>-18°C</th>
<th>-24°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beef carcasses</td>
<td>8</td>
<td>15</td>
<td>24</td>
</tr>
<tr>
<td>Beef steaks/cuts</td>
<td>8</td>
<td>18</td>
<td>24</td>
</tr>
<tr>
<td>Ground beef</td>
<td>6</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>Veal carcass</td>
<td>6</td>
<td>12</td>
<td>15</td>
</tr>
<tr>
<td>Veal steaks/cuts</td>
<td>6</td>
<td>12</td>
<td>15</td>
</tr>
<tr>
<td>Lamb carcasses</td>
<td>18</td>
<td>24</td>
<td>&gt;24</td>
</tr>
<tr>
<td>Lamb steaks</td>
<td>12</td>
<td>18</td>
<td>24</td>
</tr>
<tr>
<td>Pork carcasses</td>
<td>6</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>Pork steaks/cuts</td>
<td>6</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>Sliced bacon (vac.)</td>
<td>12</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>Chicken, whole</td>
<td>9</td>
<td>18</td>
<td>&gt;24</td>
</tr>
<tr>
<td>Chicken parts/cuts</td>
<td>9</td>
<td>18</td>
<td>&gt;24</td>
</tr>
<tr>
<td>Turkey, whole</td>
<td>8</td>
<td>15</td>
<td>&gt;24</td>
</tr>
<tr>
<td>Ducks, Geese, whole</td>
<td>6</td>
<td>12</td>
<td>18</td>
</tr>
<tr>
<td>Liver</td>
<td>4</td>
<td>12</td>
<td>18</td>
</tr>
</tbody>
</table>
In general the lower the storage temperature of a meat product, the longer the storage life. The most important exception to this rule is that of bacon, which shows accelerated rancidity as the temperature is lowered in permeable packs. Other cured products may also show abnormal temperature behaviour. Table 3.1 details practical storage life for a range of meat products (Source: International Institute of Refrigeration (IIR) red book). Whilst these figures give guidance of storage life, the literature shows that there is wide animal-to-animal and study-to-study variation. Therefore care should be exercised in adopting storage guidance based on this data.

Most studies have found that the relationship between temperature and storage life is not a linear one over a wide temperature range. Greater temperature dependencies for quality parameters are found at higher temperatures > -18 °C than lower ones.

### 3.5.2 The Effects of Temperature Fluctuations

It is generally accepted that temperature fluctuations are detrimental to the storage of foods. The quality of frozen foods can be adversely affected by temperature fluctuations in a variety of ways. Temperature abuses that result in the product undergoing a freeze-thaw cycle are only the most obvious way in which product quality can be affected.

Much smaller fluctuations in temperature can, and do, lead to quality changes providing a driver for moisture migration as described in chapter one. In meat products this results in crystal growth within the product leading to increased drip on thawing and to a partial dehydration of surface and in extreme cases freezer burn.

### 3.7 Introduction to Fish Freezing

In the previous section we have described the factors which determine the quality of frozen meat. There are both similarities and differences between fish and mammalian muscle at all levels from the gross to the micro-structural level. There are also many different types of fish products that have no direct equivalents in the meat field and vice versa. In our description of this topic we will concentrate on the factors in the frozen fish processing which differ significantly from that of meat.

### 3.7.1 What are the Principle Differences Between Fish and Meat?

Perhaps the most fundamental difference between fish and meat is that whereas red meats in particular benefit from a degree of post-mortem ageing, fish begins to decline in quality very soon post-mortem. There are two main processes that contribute to the deterioration of unfrozen fish stored on ice. These are:
• chemical and enzymatic autolytic processes which remove the characteristic flavours of fresh fish;
• products of autolysis are then used as substrates for bacteria leading to the unpleasant flavours and eventually putrefaction.

A guide to how fresh fish stored over ice deteriorates with time is shown in figure 3.2. From this it is clear that freezing effectively prevents the growth of bacteria during storage thus preventing the build up of unpleasant flavours that render fish unacceptable.

![Figure 3.2 – Decrease of Freshness Scores with Storage Time](Adapted from Chilled Food – The State of the Art Ed: T.R. Gormley)

Fish muscle is a very palatable food and a major part of its attractiveness is due to the nature of the proteins and their effects on consistency and texture of the flesh and its structural and functional properties.

The texture of meat also improves post-mortem, as it becomes more tender. Fish is tender to start with and becomes even softer during storage. There is greater proteolytic activity in fish muscle. The collagen of fish is less tough, less cross-linked and has a lower melting temperature than that of meat. Only rarely does collagen in cooked fish contribute significantly to toughness, although it can be a very important contributor to other textural attributes such as mouth feel, stickiness and succulence.

As lipids are important membrane components in meat and fish, lipolysis and oxidation, (both chemical and enzymatic) play a role in product instability leading to rancidity if uncontrolled.

A further difference between meat and fish is the variation in properties with age and season. This is more pronounced with fish e.g. fatty fish such as Herring has a flesh fat content of between 5% and 30% depending on the season.
3.8 What factors affect the quality of frozen fish?

3.8.1 Species Variability and Handling

Fish type
Many parameters affect the shelf life of fish and therefore fish of different types spoil at different rates (table 3.2). In general it can be stated that larger fish spoil more slowly than small fish, flat fish keep better than round fish, lean fish keep longer than fatty fish under aerobic storage and bony fish are edible longer than cartilaginous fish.

Handling
Rough handling will result in a faster spoilage rate. This is due to the physical damage to the fish, resulting in easy access for enzymes and spoilage bacteria. Post mortem pH varies between species and is higher than in meat from warm-blooded animals. If fish are kept alive in containers until processing and freezing microbial spoilage is avoided. The fish is, however, starved under these conditions and uses up glycogen.

3.8.2 What is the Importance of Chilling Fish Rapidly Prior to Freezing?

The post-catch and post-mortem handling of fish is different to that of meat, even though they are both usually chilled. Fish temperature reduction to about 0°C is by far the most important factor for the quality of fish. This should be achieved as rapidly as possible. The first sensory changes during storage of fish are those that concern appearance and texture. The most dramatic change is the onset of rigor mortis. The rate in onset and resolution of rigor varies from species to species and is affected by temperature, handling, size and physical condition of the fish.

When the temperature is high, the time from death to onset of rigor is short and vice versa. In the case of cod, high storage temperatures result in a fast and very strong rigor mortis. This should be avoided because the strong rigor tensions can cause gaping i.e. weakening of the connective tissue and rupture of the fillet.

The technological significance of rigor mortis is of major importance when the fish is filleted before or in rigor. In rigor the fish body will be completely stiff and the filleting yield will be very poor and rough handling can cause gaping. If the fillets are removed from the bone pre rigor the muscle can contract freely and the fillets will shorten following the onset of rigor. Dark muscle may shrink up to 52% and white muscle up to 15% of the original length.

When pre-rigor fillets are cooked they can shrink about 50%, loosing fluid and getting a rubbery texture. If the fish is cooked pre rigor the texture will be very soft and pasty.
Cooking in rigor results in flesh which is tough but not dry. Post rigor the cooked flesh will become firm, succulent and elastic.

Whole fish and fillets frozen pre rigor can give good products if they are carefully thawed at a low temperature in order to give rigor-mortis time to pass while the muscle is still frozen.

3.8.3 How can Pre-freezing Processing Affect Storage Life?

Factors that increase storage life.
Cryoprotectants as carbohydrates (used in Japanese surimi) and polyphosphates (only allowed in some countries) can be used to minimize the disruption to textural properties caused by the freezing process.

Factors that reduce storage life.
Product preparation has a considerable effect on quality. Whole and eviscerated fish have longer shelf stability than fillets, while minces can usually be stored for a still shorter period of time. These characteristics, which are more apparent in white fish, probably result from the release of salts and enzymes due to tissue damage that leads to more rapid deterioration.

Mixing of red and white muscle (red muscle containing more fat and more hemoglobin) may also result in the dispersion of lipids and enzymes leading to more deteriorative changes. The procedures used to gut fish are an important determinant of shelf life for fish. The complete removal of gut tissues and enzymes reduces gut enzyme activity, which would otherwise lead to reduction in the quality characteristic of the fish. Incomplete or careless gutting, which leads to the spreading of gut material onto the prime fish tissue, is worse than no gutting at all.

3.8.4 How does the frozen storage temperature affect quality?
There is a great difference between practical storage life (PSL) and storage life with high quality (HQL - High Quality Life). HQL is, as a rule, 3 – 5 days less than PSL and an increase in HQL will give higher prices and a better quality to the consumer. Using freezing in an optimal way can be considered as “minimal processing” and is then the preservation form that results in minimum changes, compared to chilled food.
Table 4.2 Practical storage life (months) at different storage temperatures

<table>
<thead>
<tr>
<th>Product</th>
<th>-12°C</th>
<th>-18°C</th>
<th>-24°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lean Fish</td>
<td>-</td>
<td>7</td>
<td>12</td>
</tr>
<tr>
<td>Fatty Fish</td>
<td>-</td>
<td>7</td>
<td>18</td>
</tr>
<tr>
<td>Fatty Fish (small)</td>
<td>-</td>
<td>5</td>
<td>10</td>
</tr>
</tbody>
</table>

3.8.5 Is the method of thawing important?

Before further processing frozen fish must be thawed in a way that maintains the properties. Often a formation of thaw drip becomes apparent, leaching out dissolved materials (protein, vitamins and minerals). Fish frozen pre-rigor enter a very strong rigor mortis when thawed at high temperatures resulting in gaping (breaking of connective tissue between the muscle segments) and loss of drip. Therefore a controlled slow thawing is recommended. However for fish frozen post-rigor the thawing should be as rapid as possible.

3. 9 Conclusions

The preparation of high quality frozen meat products requires care to be exercised before, during and after the freezing process. Particular emphasis should be paid to:

- livestock selection, handling and preparation of meats prior to freezing;
- moisture retention during the freezing process;
- storage temperature and size of temperature fluctuations.

Freezing is an excellent means of ensuring a consistently acceptable supply of fish with a useful shelf life. Many of the factors which affect the quality of frozen meat, also apply to frozen fish, for example:

- moisture retention during the freezing process;
- storage temperature and size of temperature fluctuations.

However, the imperative for rapid chilling followed by freezing at the earliest stage practical is the most important factor determining the quality of frozen fish.

If fish are frozen pre-rigor, as may be the case with farmed fish or fish frozen on board processing ships, thawing at a slow and controlled rate is necessary to prevent a very strong rigor.
Chapter 4
Using Pre-treatments to Improve the Quality of Frozen Foods

D. Torreggiani, T. Lucas, G. Blond and A.L. Raoult-Wack

4.1 Introduction
Chapter 1 deals with physical and biochemical changes occurring during frozen food storage. In this chapter, we discuss the ways in which pre-treatments, in particular formulation, can be used to maximise the stability of frozen foods.

4.2 What pre-treatments can be used to "prepare" foods for freezing?

4.2.1 Washing
The washing of fruits and vegetables is important to remove soil and other contaminants. Washing plays an important role in reducing the microbial load on fresh produce.

4.2.2 Heat treatments
The two main heat treatments are:

- blanching (for most fruits and vegetables)
- pasteurisation (to reduce levels of pathogens)
- cooking (for lobsters, crabs and shrimps).
**Blanching**

Blanching is a surface heat pretreatment commonly used for most vegetables that are to be frozen and ultimately cooked before use. The imposed temperature is close to 100°C. The aim of blanching is to inactivate enzymes responsible for deterioration in food. Inactivation is achieved by denaturing the proteins that would otherwise take part in reactions leading to deterioration.

There are however, certain drawbacks due to blanching. Cellular tissues are also affected by high temperature, and effects similar to those caused by freezing may be observed. These include loss of texture and an increased risk of microbial contamination due to the removal of the foods natural microbial flora.

Minimization of quality loss through blanching can be achieved by preferring short time exposure at high temperature to longer times at relatively lower temperatures.

Blanching can be achieved by immersion or steaming. Blanching by steam has the advantage of minimising the leaching out of soluble materials. This factor is becoming increasingly important as environmental regulations regarding wastewater are tightened. At present, blanching is responsible for 60 to 70 % of organic pollution in food industry water outputs from plants employing blanching in their process.

From this point-of-view, blanching by steam is to be preferred, provided that the cooling stage is not achieved by immersion. This is especially the case for finely chopped foods (e.g. carrot slices).

However for the same operating temperature, blanching by steam is 20 to 40 % longer than blanching by immersion because of poorer thermal exchange. The advantages and disadvantages of immersion blanching over steam blanching are summarised in Table 4.1.

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. decreased pesticide or nitrate levels (in spinach, carrots...)</td>
<td>Leads to the greater death of cellular tissue with</td>
</tr>
<tr>
<td>2. specific applications :</td>
<td>high possible deterioration of texture</td>
</tr>
<tr>
<td>✫ reduces bitter taste of cabbage</td>
<td>✫ higher sensitiveness to microbial growth afterwards</td>
</tr>
<tr>
<td>✫ adjusts sugar content in potato pieces, reduces frying time and improves product texture.</td>
<td>✫ greater loss of solutes integral to food e.g. vitamins, with resulting pollution of the blanching bath</td>
</tr>
<tr>
<td></td>
<td>✫ higher absorption of water by food and modification of yield</td>
</tr>
</tbody>
</table>
Table 4.1: Advantages and disadvantages of immersion blanching compared to steam blanching.

Are there any treatments that improve blanching?
Immersion of foods in aqueous solutions containing specific molecules can complement blanching. For instance, addition of citric acid (0.5 %) to the immersion bath decreases pH and thus the threshold of thermal denaturation of enzymes. This technique is used when processing artichokes. When combined to blanching, it reduces blanching operation by 20 to 30 %. Addition of sodium bisulfite (0.5 %) avoids mushroom browning and yellowing of cauliflower may be avoided by metabisulfite. The addition of chemicals to the immersion bath that can enhance frozen food quality e.g. CaCl₂ used to enhance food texture is attractive, but the quantities permissible to add are often legally regulated.

A cooling stage between blanching and freezing processes is highly recommended. It helps to stop and thus to control in duration the food exposure to high temperature. Rapid cooling avoids microbial growth on the by now exposed surfaces. When choosing between different possible treatments, higher food yields have been obtained when combining immersion blanching with air blast chilling (with use of fog). The duration of cooling stage should be at least as long as duration of the blanching stage.

4.2.3 What other pre-treatments may enhance food quality?

Presentation
Presentational pre-treatments such as comminuting, coating, grinding and packaging may be useful in helping to create a stable frozen product.

Formulation
The design of a food’s formulation may be tailored to improve its freezing qualities. Examples of this include:
- adjusting the physico-chemical composition of the food by reducing water content
- incorporating ingredients or additives with antioxidant or other preservative properties (herbs, spices, sugars, ascorbic acid, sulphur dioxide etc.)
- the addition of solutes of nutritional or organoleptical interest.

4.2.4 Why is there so much interest in formulation pre-freeze treatments?
Frozen foods may undergo quality changes during storage, and also texture degradation, structural collapse, and drip losses while thawing.
The application of pre-freeze formulation treatments can reduce these problems. For instance, partial water removal (up to at least 50% of the original content) from the fruit prior to the freezing process has the following effects:

- the concentration of cytoplasmatic components within cells
- the reduction of free water content (Figure 4.1)
- depression of the freezing point
- increased undercooling.

The process is termed “dehydrofreezing” and has been known for 50 years ago. It leads to a reduction in the total latent heat of freezing, a lower energy demand and a higher freezing rate (Figure 4.2). It also results in the formation of less large crystals within the food. A consequence of this is a reduction of structural and sensorial modifications due to the freezing process. Moreover the refrigeration load is reduced and there are savings in packaging and distribution costs.

At present there is a renewal of interest for implementing “formulation” stages, either utilising partial dehydration, or solute incorporation, or both, prior to freezing. The reason for this renewed interest is the versatility of the technique, which makes it possible to reduce water load to freezing and/or improve quality and/or develop new products.

**4.2.5 How can you achieve formulation pre-freeze treatments?**

There are various techniques, depending on the food to be transformed and on the final utilisation of the product. Three different formulation techniques are now described. These techniques can be used alone or in combination prior to freezing.

*Partial air drying*
As described above has proved to be effective for apple, pear and clingstone peach.

*Dewatering and Impregnation Soaking (DIS) or Osmotic Dehydration*
This involves soaking a foodstuff in concentrated aqueous solutions mainly comprising salts, sugars, and additives (e.g. ascorbic acid), at concentration level from 30 to 70g solute per 100g solution.

The concentration difference between the solution and the food leads to mass exchanges between food and solution: the food dehydrates and simultaneously impregnates (it may gain up to 30-40g solute per kg of initial material, it may loose up to 80g per 100g initial material). Some of the solute may not migrate into the cells but simply penetrate into the intercellular spaces. This is because of the wide variation in permeability and selectivity
of the tissue structures, which is dependent upon maturity, storage conditions, heat and chemical pre-treatments of the raw materials.

**Immersion chilling and freezing in concentrated aqueous solutions (ICF)**

As in the case of DIS, the food is immersed in a solution. As the name of this technique implies, the solution is chilled to sub-zero temperatures. The function of the added solutes in the immersion solution is twofold. The concentration of solution provokes mass transfer, but at lower rates than are achieved using DIS (3-4% w/w water loss, 10% w/w solute gain). However, the solutes also depress the freezing point of the solution and hence make it possible to use as an effective freezing medium. Typical heat transfer coefficients are 4 to 10 times higher than those achieved with air-blast freezing. ICF treatments therefore allow slight surface formulation and individual quick freezing, prior to air-blast freezing and cold storage.

### 4.2.6 Examples of the application of formulation pretreatments prior to the freezing of fruits

The advantages of substituting conventional air drying with DIS or combining air drying with DIS have been explored. The rationale for this approach is to:

- modify the nutritional and functional properties of the food
- reduce energy costs
- reduce or eliminate antioxidant pretreatments such as blanching or SO₂.

By modifying both the dehydration level and the dehydration methods, the functional properties of the dehydrofrozen fruit can be adapted to formulate new fruit products suitable for various industrial uses.

**High and reduced moisture fruit ingredients**

Using partial air drying alone, fruit ingredients of high water activity \( (a_w > 0.96) \) are generally obtained, since water removal is limited to 50-60% of the original content. To avoid browning during air drying, blanching could be applied. Other treatments such as dipping in antioxidant solutions of ascorbic acid and sodium chloride or citric acid can help to reduce the tissue damage caused by blanching.

To optimise these reformulation systems, both the cultivar selection (see chapter 2) and the dehydration technique are important. A limited but uniform dehydration of the individual pieces is required, together with “free flowing” properties for the bulk product, for continuous in line operations. These requirements are not satisfied by conventional drying techniques on a static bed. Using this technique an even dehydration is reached only in the last stages of the process and the process is hindered by particle
agglomeration. The use of fluidized bed drying has proved to be very useful in overcoming these problems: evenness of dehydration of the individual pieces can be achieved even with high product loads, provided that good fluidization is maintained.

The colour of certain fruits (strawberry, kiwifruit etc) is susceptible to being modified by heat. For example, kiwifruit when air dehydrated to 50% weight reduction, show a definite yellowing of the typical green colour even at 45°C. For these fruits, air drying has to be replaced by DIS, which is effective even at room temperature. The incorporation of different sugars into kiwifruit slices through DIS modifies their low-temperature phase transitions and significantly influences chlorophyll stability during storage at -10°C (Figure 4.3). The chlorophyll content of kiwifruit which has undergone osmotic dehydration in maltose, and thus having the highest Tg’ value, shows the highest stability. It should be noted from this example that these storage improvements have been gained even though the fruit juices were all stored at temperatures above Tg’. However as we will discuss in greater depth later, not all solutes affect a food’s storage stability above Tg’ in a way that may be predicted from their effect upon its Tg’. Greater knowledge about the physico-chemical parameters that affect reaction kinetics above Tg’ are being seen as the key to understanding and utilising product formulation.

Dehydrofrozen products with high water activity obtained utilising both partial air drying and DIS have resulted in a commercial frozen fruit salad, which is available in the French market. These fruits can also be used for pies and tarts, so avoiding the soggy pastry common in such productions.

**Intermediate moisture fruit ingredients**

A combination of air drying and DIS makes it possible to produce fruit ingredients at reduced water activity (0.7-0.9) called “frozen intermediate moisture fruits”. The specific role of osmosis is in the enrichment of soluble solids, rather than the removal of water. In this way, a lowering of water activity, which is dependent on soluble solids concentration, is obtained with only a limited decrease in the water content and thus a limited increase in textural consistency. Compared to simple air drying, a softer dried product is obtained (Figure 4.4), more pleasant to eat as a snack item or to incorporate in products such as pastry and ice creams. Fruits that have been successfully pretreated in this way include apple, pear, sweet cherry, clingstone peach and apricot.

If a concentrated fruit juice is used as osmotic solution, an even softer product is obtained (Figure 4.4) because of the higher content of monosaccharides in fruit juices compared to that of syrups from starch hydrolysis. This results in fruit juices possessing higher water contents for a given water activity. The product is totally of fruit origin, which is an important market consideration. If sorbitol is present as a component in the fructose syrup even softer products can be obtained. The process has also been applied to vegetables. Red pepper cubes have been osmodehydrated in a new type of osmotic solution (H.L.S.) from cheese whey ultrafiltration permeate. The addition of sorbitol leads to a softer consistency and provides a specific protective effect during the air drying step.
4.3 What is the Glassy State?

The physical properties of food products determine their behaviour during processing and storage. These properties change dramatically depending on water availability and temperature. Amorphous and partially amorphous structures in foods are formed in various processes such as baking, drying and freezing. The removal of water, by evaporation or separation as ice, produces supersaturated states of dissolved substances. Depending on temperature and water content, these unfrozen fractions can be in either a glassy or rubbery state.

4.3.1 Why is the Glassy State Important in Understanding Storage Stability?

The major assumption relating to shelf life and quality of foods is that stability is maintained in the glassy state. Furthermore that, changes occur above the glass transition with kinetics that are determined by the difference between the storage and the glass transition temperatures.

Stability of frozen foods strongly depends upon the storage temperature. The deterioration rate may be multiplied by a factor of between 2 and 30 for an increase of the storage temperature by 10°C. This strong temperature dependence is due to the drastic decrease in viscosity at T>Tg’, which is a result of both a direct temperature effect and the melting of ice. It is obvious that Tg’ is a temperature limit, since below this temperature the freeze-concentrated fraction is a glass and thus long-term stability may be expected. Table 4.2 shows the Tg’ of various food products.

<table>
<thead>
<tr>
<th>Food Product</th>
<th>T_g’ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>orange juice</td>
<td>-30</td>
</tr>
<tr>
<td>raspberry juice</td>
<td>-37, -40</td>
</tr>
<tr>
<td>strawberry</td>
<td>-43</td>
</tr>
<tr>
<td>apple</td>
<td>-37</td>
</tr>
<tr>
<td>tomato</td>
<td>-21</td>
</tr>
<tr>
<td>carrot</td>
<td>-32</td>
</tr>
<tr>
<td>egg white</td>
<td>-38</td>
</tr>
<tr>
<td>egg yolk</td>
<td>-32</td>
</tr>
<tr>
<td>beef muscle</td>
<td>-80/ -35</td>
</tr>
<tr>
<td>ice creams</td>
<td>-34</td>
</tr>
</tbody>
</table>

From table 4.2 it is clear that the glassy state is only readily attainable for a limited number of frozen food systems at temperatures commonly employed in the distribution chain. This leads to the question as to what is the appropriate glass transition temperature for predicting the stability of frozen foods at temperatures above Tg’?
Can Glass Transitions tell us about Product Stability above Tgi?

It was tempting to explain the drastic effect of temperature above Tg’ by Williams-Landel-Ferry (WLF) kinetics. This equation specifies a much greater dependence temperature of molecular mobility than the Arrhenius equation. However, this model fits rather badly the experimental data of ice crystal growth in ice creams as a function of \( T_{\text{storage}} - Tg' \), and cannot explain the influence of stabilisers which do not influence Tg’.

The rates of degradation in foods generally appear to be less dependent upon temperature than predicted by the WLF equation with Tg’ as reference. If the reference glass transition temperature used in the WLF equation is that of the unfrozen fraction at the storage temperature, an improved fit is observed. At the storage temperature, the unfrozen phase is less concentrated and if cooled rapidly enough to prevent crystallisation processes would lead to a formation of a glass at Tg < Tg’. This Tg value predicts the enzymatic reaction rates in sucrose solutions better than Tg’ (Champion et al 1997).

For ice creams, the Tg’ value is close to -34°C, if the storage temperature \( T_s \) is -18°C, the freeze-concentrated fraction is a liquid with a \( C_s \) concentration. Because its melting curve can be compared with that of sucrose (Blond et al 1997), the Tg reference to consider for stability studies can be estimated to be around -75°C (Tg), i.e. the temperature at which the liquid phase would turn into a glass if it could be cooled without further crystallisation.

Further investigations must be, and are being, carried out in more complex systems with experimental measurements of the viscosity and diffusivity. Tg’ and even actual Tg values do not allow us to explain the practical effect arising from the addition of low concentrations (0.3-0.5%) of polysaccharides of the type used in ice creams as stabilisers. These improve texture and decrease ice crystal growth during storage without modifying the Tg’ of the products. The kinetics of changes depend on the difference between the Tg
reference temperature and the storage temperature but also on other factors such as pH, and specific solute interactions.

In practice this makes it difficult, at present, to give ready-made recipes to improve the quality of frozen products by reformulation based on a single physico-chemical parameter e.g. Tg’. However, as has been shown by the work on fruit juices and ice creams, understanding mobility of reactive species in foods as a function of temperature and formulation is central to understanding frozen food stability.

4.4 Future and prospects

A wide range of water and soluble solid contents in final products can be achieved to prepare food ingredients with functional properties suitable for specific food applications. Partially dehydrated fruit pieces could be useful, for example, to avoid whey separation in yogurts containing fruits. For different fruit species “functional compatibility maps” (Figure 4.5), which describe the extent to which functional properties can be modified by proper processing, have been developed. These maps could represent, for the food industry, an effective and useful tool for formulating new fruit ingredients so improving quality of frozen fruit.

Apart from fruits, formulation processes can be used for many kinds of products (vegetables, fish and meat, dairy products), in various applications (smoked foods, intermediate moisture foods, marinades). To date, formulation pretreatment strategies prior to freezing have been investigated most extensively for fruits. However it is likely that recent advances in formulation pre-freeze treatments, mainly obtained for fruit, could benefit to other types of materials such as frozen vegetables, frozen aromatic herbs (already on the market), or frozen pieces of meat and fish generally used in frozen cooked dishes.

Bibliography


5.1 Introduction

Packaging plays an important role in the preservation of quality of frozen foods, protecting the food product from contamination by external sources and from damage during its passage from the food producer to the consumer. Although the type of packaging selected by the food producer will depend upon the particular product, a well designed and a consumer-appealing frozen food package will help to portray an image of high quality and responsible food production to the frozen food consumer.

However, the food processor’s choice of packaging is also often dictated by other factors, such as the availability of packaging equipment, the cost of the package, legislative requirements, the company’s packaging philosophy, and consumer demands. This chapter reviews the current state of the art in frozen food packaging, highlighting recent advances in packaging technologies that allow greater control of food quality in the frozen food chain. Trends in environmental issues that may affect choice of packaging are also discussed.
5.2 What are the General Requirements of Frozen Food Packaging?

The primary function of food packaging is to protect the food from external hazards. Similarly, the packaging material itself should not affect the food in any way. The package material chosen should comply with the relevant legislation, such as that in the UK under the “Materials and Articles in Contact with Food Regulations 1987”. These regulations dictate that the packaging materials and articles do not transfer their constituents to food in quantities that could: (a) endanger human health, or (b) bring about a deterioration in the sensory characteristics of such food or an unacceptable change in its nature, substance or quality. There are also EC directives relevant to food packaging, covering e.g. permitted material composition, chemical migration limits (from the packaging to the food) and methods of testing for migration.

In addition to the above, packaging materials intended for frozen food applications should meet other minimum requirements, many of which have a direct influence on the quality of the frozen food.

5.2.1 We require temperature stability

The package material should be physically and chemically stable over a wide temperature range, extending from freezer temperatures (-40°C and above) to normal ambient temperatures. If the food product is to be reheated or cooked in the package, the packaging material should also be capable of withstanding temperatures up to 250°C. Temperature also plays an important role in defining the other package characteristics quoted below. Consequently, the design and selection of a frozen food package should consider packaging material properties over the intended temperature range of application.

5.2.2 We require barrier properties

Barrier properties should prevent moisture loss from the food which may lead to dehydration and weight loss. However, moisture migration may still take place from the centre to the surface of the food, which can result in frost formation between the food product and the package and possible desiccation and development of off-flavours at the food surface. This can be remedied by designing the food package to be a close fit around the food. The design of frozen food packaging also needs to consider the permeability to gas, light and water vapour, which can result in deterioration of colours, lipids, proteins and sensory qualities.

Gas permeability influences the atmosphere within the food package. The exclusion of oxygen from the frozen food markedly reduces the oxidative reactions which lead to
rancidity and off-flavours; packaging materials with low oxygen permeability can therefore increase the product shelf life. A low oxygen permeability also reduces other detrimental reactions, including the formation of thiobarbituric acid (TBA), which is a measure of lipid oxidation, and the destruction of carotenoids and ascorbic acid, which are key descriptors of many oxygen-sensitive frozen foods. However, it should be noted that in some foods the anaerobic conditions formed within a frozen food package possessing low oxygen permeability, may lead to tissue breakdown and development of off-flavours. In such cases, the package micro-environment may need to be controlled, e.g. by modified atmosphere or controlled atmosphere packaging (MAP or CAP).

Package permeability to water vapour is dependent upon material permeability, surface area and temperature. Packaging materials with high water permeability may cause acceleration of protein denaturation and lipid oxidation, with resultant increases in rancidity and off-flavour development. Also, dehydration-induced quality losses can be minimised by appropriate water vapour permeability properties.

The package should also provide a light barrier to inhibit light-induced oxidation of pigments and unsaturated fats within the food. Thus, packaging materials which incorporate light-impermeable materials or ultra violet (UV) light absorbers will improve the surface colour retention of many frozen foods and help to prevent lipid and pigment oxidation.

In addition to the above, the package should be resistant to staining from the components within the food, e.g. water and grease. These components can penetrate the package fibres and lead to loss of physical stability and a poor package appearance.

5.2.3 Good insulation properties are desirable

For specific food products, the packaging material may also be required to possess some degree of thermal insulation, to help maintain the low temperature of the food during periods outside the freezer or to help minimise the effects of temperature fluctuations within the frozen food chain. Such packages may be constructed of thermally insulating materials (e.g. polystyrene foam) or by packages formed by coupling layers of stagnant air within the packaging material. The need for well-insulated packaging increases as the mass of the frozen food portion decreases. The susceptibility of the product to temperature abuse and the amount of value added to the product will determine whether or not this is economically feasible.

5.2.4 We want good compatibility with packaging machinery

The choice of packaging material will also be dictated by its ease of use with mechanical machinery systems. This is particularly important for high speed automated packing lines, where the package will require tightly-controlled tolerance on properties such as
frictional characteristics, stiffness, crush resistance, sealability, ease of separation, and cutting and folding characteristics, to ensure that the operation of packaging machines is not compromised. The choice of the frozen food package is, therefore, also dictated by the access to food packaging machinery and/or the cost of new food packaging equipment, including conveying systems, filling lines, and package-forming and sealing systems.

5.2.5 Consumer appeal is very important

It is vital that the frozen food package presents the food product to the consumer in an appealing manner. A key factor is the ability to print onto the package surface. This can be described in terms of surface smoothness, gloss, absorbency, wettability, and resistance to the appropriate ink medium. Finally, the material must be capable of surviving the ink-drying process.

Presentation of the food product to the consumer is also very important. Advances in high barrier, antifog, shrink-wrap films are involving combining good gas barrier properties with high package transparency and gloss to ensure added merchandising and consumer appeal. New developments in packaging technology which remedy the colour deterioration of frozen meats (notably red meats and poultry) are also emerging. A process which entails placing the portioned meat in a high pressure pure oxygen atmosphere, which restores the oxygen content of the meat to pre-slaughter levels, has recently been reported. Red meats retain their colour ('bloom') during frozen storage.

An emerging issue is the ability of the package to indicate tampering of the enclosed food and much development work on tamper-evident packages is in progress. Also, new developments in the field of active packaging are currently being promoted, including the use of temperature and time-temperature indicators, oxygen or other gas scavengers, moisture absorbers and light and UV filters. The frozen food package must also comply with the relevant food labelling regulations and provide the necessary product information, e.g., ingredients, weight and nutritional content.

5.3 Which materials are suitable for frozen food packaging?

A wide variety of materials have been used for the packaging of frozen foods, including plastics, metals and paperboard. Advances in materials technologies, together with new techniques, such as MAP and dual-ovenable packaging, have revolutionised frozen food packaging and now provide the frozen food producer with a wide choice. The following section represents the major materials currently used.
5.3.1 Plastic packaging materials

2 Polyethylene (PE) low density (LDPE)
These materials are used for vegetable bags. Heat sealability is good while the film is relatively inexpensive. High density polyethylene (HDPE) is used in certain ‘boil in the bag’ applications.

3 Polyester terephthalate (PET)
These films can withstand high temperatures and are resilient to grease and water vapour. PET and crystallised polyester terephthalate (cPET) form a large and growing sector of packaging materials used in the prepared foods market. The trays are suitable for reheating in both conventional and microwave ovens, with stability at temperatures in excess of 250°C.

4 Polystyrene (PS)
PS is a general plastic for frozen food applications. It has a high resistance to breakage at freezing temperatures but is relatively expensive and has relatively high transmission of water vapour and oxygen.

5 Polyvinyl chloride (PVC)
This is generally used for rigid containers. It is cheaper than PS and has a much lower permeability to water vapour. However, PVC possesses less impact resistance than PS and other plastics.

6 Polyamide (PA)
PA forms a plastic with good strength and moulding characteristics. It is suitable for thermoforming laminations, commonly used in ‘boil in the bag’ applications.

7 Polypropylene (PP)
Modified films have found a niche for certain products and are becoming more widely used as a flow wrap film.

8 Laminates and co-extrusions
By combining films of plastics with different properties it is possible to optimise the material to gain the specific properties required.

5.3.2 Metal packaging materials

Aluminium’s compatibility with foods contributes to its utility as a packaging material. Aluminium foil is used for trays and may also be laminated to plastic films and paper and board to provide specific additional requirements. Aluminium foil is an excellent light and moisture barrier for frozen foods.

Aluminium is also used in microwave susceptor boards for certain frozen foods (e.g. pizzas and pies). Susceptor boards consist of a thin PET film, which is very lightly
vacuum metallised with aluminium. During microwave heating, the aluminium layer can reach a temperature of 240°C, facilitating browning and crisping of foods in contact with this hot surface.

5.3.3 Paper and card packaging materials

Paperboard materials used in frozen food packaging are usually considered in three groups:

(a) paper (thickness up to 3mm)
(b) board (thickness between 3-11mm)
(c) fibreboard.

All are made from wood pulp which is manufactured from virgin pulp or recycled waste paper. Paper is also used as a surface coating to provide a smooth surface for high quality printing.

Board is used to produce both folding and rigid cartons. Board often consists of plies made from different materials; e.g. white lined chipboard (Dulex) has a white surface on one side made from a bleached virgin pulp, with the bulk being composed of “chip” which is usually grey and made from a high proportion of waste paper. Fibreboard is used in the production of outer cases.

Paper and board can be laminated with PE or waxed to provide moisture barriers, while the use of varnishes can protect the packaging from ingress of moisture. PET coated paper and board is used for dual ovenable trays.

5.4 What packaging systems are available?

The choice of a frozen food package will also depend upon the availability of packaging machinery, which usually forms part of an integrated production line. The following systems list (not exhaustive) are commonly used for packaging frozen foods:

9Form, fill and seal (FFS)

These machines form pouch or tray shaped packages from sealable films. The packages are formed and filled in the machine simultaneously or consecutively. They generally work in a vertical plane for “loose” products, e.g. vegetables, and in a horizontal plane for “wet” products, e.g. ready meals, ice cream, etc.
**10 Cartoning Systems**
Cartons can be top filled (generally irregular products), end filled (small regular products), or side filled (large regular products). Machines generally perform the operations of erecting, filling and sealing at speeds of between 50 and 400 cartons per minute.

**11 Shrink and stretch film wrapping**
These machines apply material from rolls around a given number of consumer-portion sized packages.

**12 Vacuum packaging and gas flushing**
Certain products need an oxygen free atmosphere to enable long shelf life to be achieved. Partial vacuum or gas flushing of sealed packs are used in such cases.

### 5.5 What environment issues will affect the choice of packaging?

The environmental aspects of packaging and the responsibility imposed upon the food producer by European directives need careful consideration.

Directive 94/62/EC on Packaging and Packaging Waste has major implications for all sectors of the food chain. The aim of the directive is to diminish the impact of packaging and packaging waste on the environment and to limit the consumption of energy and raw materials. The directive sets EC member states targets for recovery and recycling to be reached by the year 2001. These targets are: 50% - 60% packaging waste must be recovered, within this 25% - 45% must be recycled, and a minimum of 15% by weight of each packaging material must be recycled. The means by which member states achieve these targets is directed by individual states.

The broad definition of packaging - ‘products made of material of any nature to be used for the containment, protection, handling, delivery and presentation of goods’ means that the food industry will have to take some responsibility for ensuring that these targets are met. This will force the industry to take a closer look at its current methods of waste disposal and its use of packaging. By the year 1999, packaging may only be placed on the market if it complies with certain criteria, which includes ensuring that pack volume and weight is limited to the minimum necessary to maintain safety, hygiene and product acceptability. Thus, even at the packaging design stage it will be necessary to take into account the environmental impact of the package.
5.6 Summary

Packaging plays an important role in preserving the quality of frozen food during the journey from food producer to consumer. Careful consideration of the technical aspects of packaging materials and applications provides the food producer with a means of minimising the undesirable physical, chemical, biochemical and sensory changes which occur during storage. However, it is likely that future improvements in frozen food packaging will be dictated as much by changing consumer demands as by further technological developments. Ultimately, packaging has a key role in determining the consumer’s acceptance of the frozen food product.

Bibliography


There is also a monthly alerting service on food and environment law via the CCFRA Foodlaw Alert Bulletin. This is available to CCFRA members in the legislation section of the CCFRA website at the address: http://www.campden.co.uk
Chapter 6

Future Possibilities for Frozen Foods

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6.1 Introduction

Compared to technological innovation in other areas, few new developments in the domain of food freezing have emerged from research in the last years. However, some promising novel ideas have been discovered recently and are heading for patent applications and development.

In a more general sense, handling of frozen goods will profit from development of new temperature recording devices. They will allow the monitoring of temperatures on-line in goods, packaging and in freezers through the entire distribution chain. Additionally, re-designing retail display will limit temperature fluctuation, considered as a major cause of ice crystal growth in frozen products.

The above measures focus upon improving the existing cold chain. A more radical approach might be to change the cold chain itself. Advances in information technology and telecommunications offer the potential for the different delivery systems.

6.1 Increased use of high freezing rates

A large part of quality deterioration of frozen food during storage can be attributed to temperature abuse. Most of the damage during freezing and frozen storage is caused by growth of ice crystals. It is the consequence of thermodynamics, so we cannot avoid it but we may try to slow it down. Other deterioration, like damage of texture by mechanical means, will not be considered here.
It is well known that high freezing rates are beneficial for most frozen food. Rapid freezing limits growth of individual ice crystals and cools frozen foods quickly to sufficiently low core temperatures. Re-crystallisation of ice is very limited in this case and damage to the product can be largely avoided. Such products are already on the market as IQF (individually quick-frozen) products.

For optimal use of rapid freezing, smaller size of pieces need to be prepared. In larger pieces, much more time is required for core temperatures to be reduced below the freezing point. As a result the product will benefit less from rapid or ultra rapid freezing because of the insulation effect of ice. Most recent equipment uses liquid nitrogen for rapid cooling and this may still imply increased freezing costs.

Products produced using such techniques are likely to give improved sensory qualities, whilst retaining the benefit of a long shelf life. The increasing use of such products either as semi-prepared or ready to serve meals in the foodservice sector is widely forecast.
6.2 Controlling ice nucleation

6.2.1 Using biological means

Some biological agents have the special feature of initiating ice formation in aqueous solutions. These so called ice nucleation agents are involved in the forming of an ice crystal in slightly supercooled water at temperatures of −2 to −5°C. They are thought to possess proteins which act as template for solvating water molecules. These water molecules are ordered in such a way that the addition of further water molecules will create an ice-like structure. When this assembly of water molecules is big enough, it is called an ice embryo, this will grow to give a microscopic ice crystal. Because ice nucleators limit supercooling of liquids, they help to ensure freezing of a product and would be useful for food that is generally difficult to freeze. The successful use of biological ice nucleation agents in the freeze concentration of difficult to concentrate lemon and strawberry juices has been demonstrated.

Figure 6.1 Showing the growth and merging of ice embryos to for ice crystals

Nucleation of ice is important for freezing when no initial ice is present. In most cases ice crystals should be small and the number of ice crystals should be as high as possible. The advantage of many and small crystals is obvious.

By providing a large number of nucleation sites at higher temperatures, ice nucleation agents could encourage the formation of a larger number of ice crystals. This type of freezing technique should result in smaller average crystal size at the end of the freezing period. However such freezing systems will need sufficient heat transfer during freezing to rapidly remove the latent heat of fusion for an optimal effect.
Biological ice nucleators must be food grade and permitted as food ingredients. The most common nucleators however are plant-pathogenic bacteria. They nucleate water at –2°C., however, these microorganisms are not food-grade and will probably not be allowed in food within the next few years. Though non-plant-pathogenic strains of the genus *Xanthomonas*, which is permitted for food use, have been found to be active ice-nucleators. Although most ice-nucleation proteins are membrane-bound, some bacteria have been found which shed vesicles formed from the ice nucleating proteins. One possibility lies in harvesting these vesicles and using them in foods.

Another source of ice nucleators can be found in plants. The berries of the Sea buckthorn, a plant common in some European countries, have ice nucleators that act at –5°C. Extracts of this plant can easily be added to many types of food before freezing. Only very low quantities are needed, and no alteration of taste is detected. Additionally, such nucleation agents are not very expensive.

6.2.2 Using non-biological means

As well as the biological ice nucleators described above, a variety of methods of nucleating supercooled water exist which use physical stimuli. These stimuli include:

- ultrasound;
- shockwaves;
- friction;
- electrostatic forces.

In each case it is thought that the mechanism responsible involve acoustic cavitation. Acoustic cavitation is the formation of pockets of gas in a liquid. This gas may be formed from previously dissolved gas or water vapour when the local pressure in the liquid is reduced below the tensile strength of the liquid. If the bubbles of gas are unstable they will collapse leading to a micro-region of very high pressure in the water. How this can induce nucleation can be understood by reference to the phase diagram of water. By increasing the pressure of the water ahead of the collapsing interface, the water is moved from a point in the liquid region to one in the solid region of the diagram. This produces a localised region of the liquid sample in which the water molecules are forming an ice-structure. Once this ice embryo grows to a critical size nucleation occurs.
Figure 6.2 – Showing a simplified PT phase diagram for water

Because ultrasound can penetrate deep into aqueous samples this offers the potential for increasing the number of nucleation sites in a sample to be frozen. Once again heat transfer must be high if latent heat is to be dissipated quickly enough to prevent ice crystals growing.

6.3 Controlling ice crystal growth

As well as improving ice nucleation rates by the addition of ice nucleators, ice crystal growth can be influenced. Many sugars and mainly polysaccharides are known to inhibit ice crystal growth, as water activity of unfrozen water is reduced during freezing. These agents act in a colligative way and growth rate is determined by the concentrations of the different sugars. In complex food, emulsifiers could also play a major role.

Some proteins that are found in food-grade Arctic and Antarctic fish are called Antifreeze proteins (AFP). They protect these animals from freezing. In ice-laden seawater, temperatures are below the freezing point of the fish. These proteins of different sizes (5 to 25 kDa) are able to separate melting point from freezing point of water, points that are usually identical. As a consequence, a solution containing these proteins will not freeze in-between this temperature range and ice crystals present will not grow but may change to spike-like bipyramidal forms. The freezing behaviour of
such a liquid is called thermal hysteresis and the proteins are sometimes called thermal hysteresis proteins (THP).

Thermal hysteresis is measured as the difference between melting and apparent freezing temperature and depends on concentration of AFP. Freezing in the presence of a high concentration of AFP’s results in many very small ice crystals. At low concentrations, ice crystal growth is very much inhibited. This inhibition is also concentration dependent and gets null at a given threshold concentration. Efficiency of AFP however is about 100x higher than polysaccharides.

When used in food, AFP inhibits ice crystal growth from the very beginning of freezing wherever it is in contact with water or ice. The protective effect to food remains intact throughout the entire distribution chain. This protection however is not complete and ice crystal growth will still increase under severe temperature abuse, though less rapidly than without AFP.

Today these agents are still very expensive. For large-scale production of frozen food, AFP is not commercially available yet. Cheap production in very large quantities may get interesting when produced by genetically modified micro-organisms. Alternative sources for AFP are not fully satisfactory at present.

6.4 Direct shopping – an opportunity to improve frozen foods?

Predicting the uptake of new technology is notoriously difficult, however, few commentators doubt that Direct Shopping is likely to increase in importance in the future. Driving forces for this transition include environmental concerns over car usage, an increase in one-person households and wider uptake of home computing and access to digital telecommunications. Pressure on suppliers to find delivery systems that fit in with the busy modern lifestyles of consumers is unlikely to diminish. Already many financial services have seen successful entrants using modern telecommunications and IT systems.

Wider consumer acceptance of Direct Shopping could offer an opportunity for the frozen food industry to take control of the weakest links in the cold chain. Retail display cabinets and in-store and store-to-home journeys offer the most serious challenges to the cold chain’s integrity. By delivering direct from a supermarket cold store to the consumer in refrigerated transport it should be possible to reduce the incidence of temperature abuse experienced by frozen foods. In the UK, one specialist frozen food retailer is currently offering delivery of produce in temperature controlled vehicles and several of the major supermarket chains are experimenting with Internet shopping and home delivery.
6.5 Conclusions

In this chapter we have outlined some of approaches which the food industry is exploring to improve the quality of frozen foods. Methods of initiating and controlling the freezing process involving the use of biological and non-biological ice nucleating agents have been described along with use of high freezing rates. The potential of antifreeze proteins in the control of ice crystal formation and growth is discussed.

These technological innovations are put into the context of an industry that is seeking to improve the temperature stability of the cold chain. Telemetric time-temperature recording devices are being developed which allow real-time monitoring of the cold chain.

Finally, we have described the significant opportunity for improvement in the integrity of the cold chain that is afforded by Direct Shopping.