Course Manual on

Shrimp Processing and Quality Assurance for Export

AU-Avanti Aquaculture Skill Development Centre
(AU-Avanti ASDC)
Established by Avanti Foundation
New Building, MLR Department, Andhra University
Visakhapatnam, Andhra Pradesh

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Freezing Technology in Shrimp Processing

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Freezing of food involves the removal of heat from the food, thereby diminishing the kinetic energy of that food material. Thus, it reduces the temperature of foods to below their freezing point, which cause a proportion of water in the food to undergo a change in state leading to the formation of ice crystals. The immobilization of water as ice and resulting concentration of dissolved solutes in unfrozen water, lowers the water activity (a_w) of the food. Preservation of food is achieved by a combination of low temperatures that reduce biochemical changes, enzymic and microbial activity as well as by reduced water activity, while causing no significant changes in their sensory qualities and nutritional values. Freshness of fish can be maintained only for limited period and quality deterioration take place quickly in the iced and chilled fish. In thermal processing, foods are exposed to elevated temperature leading to thermal shock to the food, loss of nutrients, changes in flavor and texture etc. Freezing has distinct advantages over other preservation techniques such as canning and drying in terms of nutritional properties, high quality and freshness. It also considered as a superior preservation process with the potential to deliver food with improved microbial safety, nutritional profile, organoleptic quality and convenience. However, the condition of food prior to freezing, postharvest management and freezing techniques employed are the main factors which determine the quality of food that has been frozen. Distribution of frozen foods has a relatively high cost, due to the need to maintain a constant low temperature throughout the cold chain. Thus, successful freezing technology depends on delivering superior quality products to the consumers at reasonable cost.

Frozen foods are considered to be the next generation of convenience foods, since the global market is expected to reached USD 307.33 billion by 2020. The growing world market for frozen food products, attract innovative freezing techniques shifting from bulk freezing to convenient and consumer friendly individual quick freezing (IQF) and other novel freezing technologies mainly high pressure freezing (HPF), electrically and magnetically assisted freezing (EF & MF), ultrasound assisted freezing (UAF), antifreeze protein (AFP), etc.

PRINCIPLES OF FREEZING TECHNIQUES

Freezing curve

Freezing process causes phase transitions of water and in some cases, solute components. The freezing involves the removal of sensible heat and latent heat which is associated with the reducing temperature and phase changes, respectively. The mechanism of ice crystallization consists of two processes, namely nucleation and growth. The latent heat associated with phase change is much larger than that of sensible heat and is need to be removed so that the ice can form. Moreover, solutes must also be eliminated from the growing ice surface as ice tends to form pure crystals.

The time-temperature record during freezing process or so called "freezing curve"; "freezing profile" are shown in (Fig. 1A & 1B) for pure water and food system, respectively. The removal of sensible heat (4.18 kJ/kg°C) reduces temperature of the food systems from initial temperature (point A) to just below 0°C without the formation of ice crystals. Once the critical mass of nuclei is reached, the system nucleates (point B) and releases its

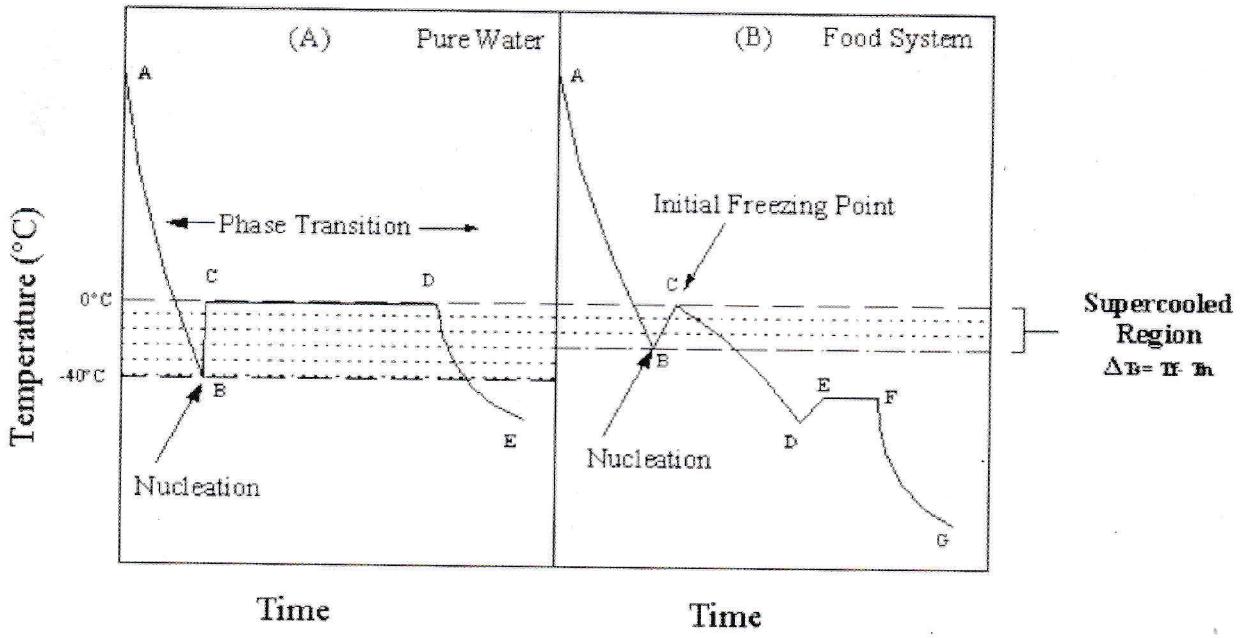


Fig 1. Typical freezing profile of frozen pure water and food system.

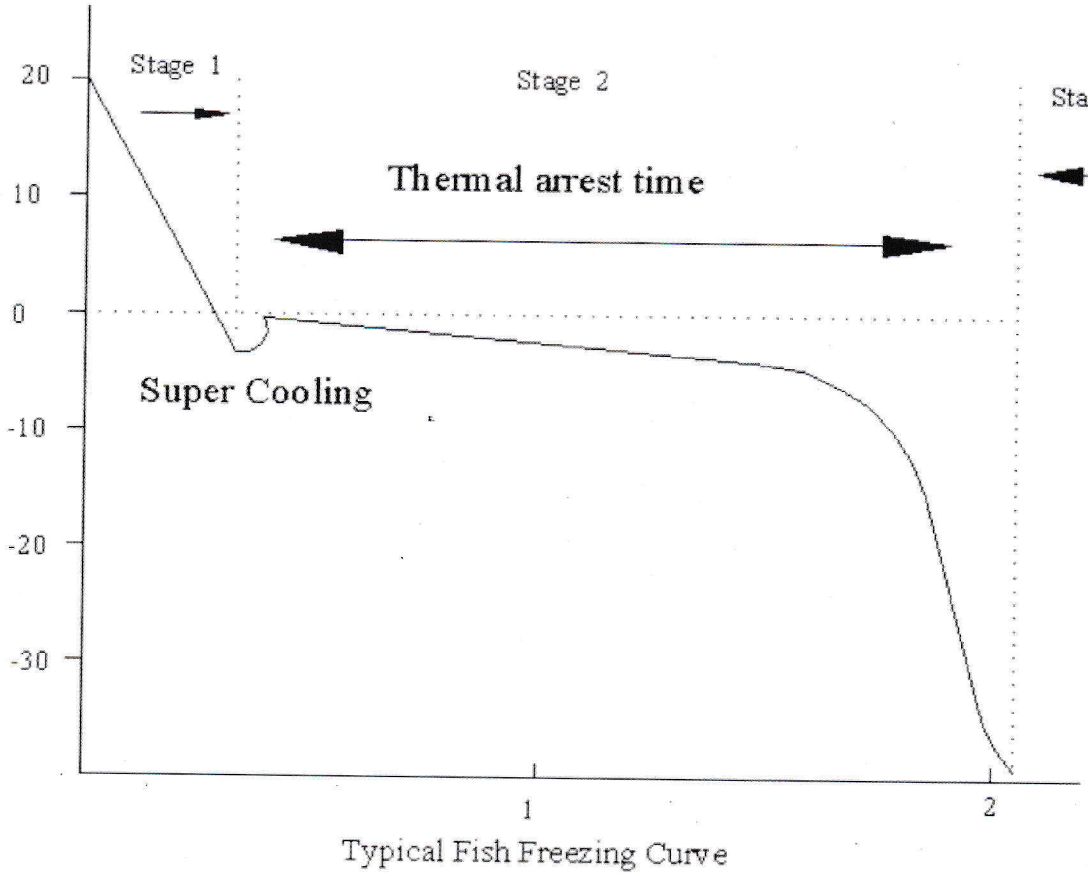


Fig. 2. Typical fish freezing curve

latent heat (335 kJ/kg at 0°C) showing the abrupt increase in temperature (point B–C) which represents the onset of ice crystallization. The lowering of temperature below the normal freezing point of materials without any formation of ice is called supercooling. The supercooling is generally lower in aqueous solutions than in pure water because the presence of solute promotes heterogeneous nucleation which accelerates the nucleation.

The highlighted area shows the supercooled region in which the systems remain liquid below their freezing point. ΔT_s: degree of supercooling; T_f: initial/equilibrium freezing temperature; T_n: nucleation temperature. (Zaritzky, 2012)

When crystallization begins, the temperature reaches point C, the freezing point, which is 0°C for pure water and below 0°C for solution and food systems. The further cooling causes ice formation and reduced amount of liquid water. In pure water system, the liquid–solid transition of water takes place at an identical temperature. Conversely, the increased concentration of unfrozen phase causes instant decrease in freezing point due to the colligative effect as water forms ice. Upon solidification, further removal of heat decreases temperature of the systems toward freezer temperature (point E in pure water system). The decreased temperature can cause solute supersaturation and crystallization at point D and the crystallization of solute releases latent heat of fusion raising the temperature to eutectic equilibrium point that remains constant during eutectic solidification (point E–F). Subsequently, the further cooling to freezer temperature (point G) is achieved after the solidification (crystallization and vitrification) is completed.

During crystallization stage, the bulk of the water changes to ice and therefore the temperature remains more or less constant at -1°C to -5°C and this period is known as "thermal arrest time" (Stage 2, Fig. 2). During the early stage of thermal arrest time water separate as pure ice crystals and at later stage eutectic mixtures and other complex solids may form. At the end of the thermal arrest time the food system will contain much less freezable water. Therefore, removal of relatively smaller amount of heat energy will cause a much greater reduction in the temperature (Stage 3). Crystallization of water in fish commences when the temperature is around -1°C. The percentage of water frozen at different freezing temperature ranges are given in table 1. Largest portion of water freezes between -1°C to -5°C and this temperature zone which also corresponds to the thermal arrest time is called the zone of maximum crystallization.

Table 1. Percentage of water frozen at different temperature ranges in a typical fish and fishery product with 80% water

Temperature (°C)	**Frozen water (%)**
0	0
-1	10 (crystallization begins)
-2	55
-3	69
-4	76
-5	80
-10	80
-20	91
-30	92
-50 to -60	Almost all

Freezing time

Freezing time is the most critical factor associated with the selection of a freezing system to ensure optimum product quality. The freezing time is defined as the time required to lower the temperature of the product to an equalization temperature of -18°Cunder adiabatic conditions. Freezing time in the freezing process can be calculated based on analytically derived equations or based on numerical simulation. The first and most popular equation for predicting freezing time was proposed by Plank in 1913 and adapted to food by Ede in 1949. The Plank's equation was based on the assumptions that the entire foodstuff is initially at freezing temperature, the thermophysical properties are independent of temperature, and the volume change is negligible during freezing. Plank's equation can be used to determine the freezing time; however, due to assumptions involved in the calculation, it is mainly useful for obtaining an approximate freezing time (t). The general form of Plank's equation used for calculating freezing time is given below:

$$t=\frac{\lambda\rho}{\Delta\theta}\left[\frac{ax}{h}+\frac{bx^2}{k}\right] \qquad \text{...........(1.1)}$$

Where,

$\Delta\Theta$= the temperature the temperature difference between the freezing point of the food and the freezing medium;

λ = the latent heat of the food product,

ρ= the density of the product, kg.m^{-3}

h = convective heat transfer coefficient in the air-ice interface, $W.m^{-2}.K^{-1}$

k = thermal conductivity of the frozen phase, $W.m^{-1}.K^{-1}$

a and b are shape-specific constants

As the Plank's equation ignores the sensible heat and the gradual phase change, various researchers modified the Plank equation to introduce the effect of sensible heat above and below the freezing point. One of the most recommended equations for predicting the freezing time of one-dimensional foodstuffs by means of a mean freezing temperature is given by Pham and is given bellow,

$$t = \frac{d_c}{E_f h}\left[\frac{\Delta H_1}{\Delta T_1} + \frac{\Delta H_2}{\Delta T_2}\right]\left(1 + \frac{N_{Bi}}{2}\right) \quad \text{..........} \ (1.2)$$

where,

dc= a characteristic dimension, either shortest distance to the center, or radius (m),

h = the convective heat transfer coefficient (W/ [m2 K]),

= the shape factor, an equivalent heat transfer dimension.

= Biot number

ΔH1and ΔT1are the specific enthalpy (J/m3) change and temperature difference, respectively, for the precooling period, and ΔH2and ΔT2those for the combined freezing-post-cooling period, calculated from:

$$\Delta H_1 = p_u c_u (T_i - T_{fm}) \text{.........} \quad (1.3)$$

Where,

is the density of unfrozen material (Kg/m3).

is the specific heat for the unfrozen material (J/[kg K]),

is the initial temperature of the material (°C).

$$\Delta H_2 = p_F[L_f - c_f(T_{fm} - T_c)] \text{.......} \quad (1.4)$$

Where,

cf is the specific heat for the frozen material (J/[kg K]),

Lf is the latent heat of fusion of food (J/kg), and

is the density of frozenmaterial.

The temperature gradients ΔT1 and ΔT2 are obtained from following equations:

$$\Delta T_1 = \left(\frac{T_i + T_{fm}}{2}\right) - T_a \quad \text{..............} \ (1.5)$$

$$\Delta T_2 = T_{fm} - T_a \quad \text{...........} \ (1.6)$$

Tfm is the 'mean freezing temperature' and the following empirical equation is probably valid for most water-rich biological materials:

Tfm = 1.8 + 0.263Tc + 0.105Ta .... (1.7)

Where,

Tc is the final center temperature (°C).

Ta is freezing medium temperature (°C).

Pham's procedure involves first calculating various factors given in Equation (1.7) and Equations (1.3) to (1.6) and then substituting in Equation (1.2) to obtain freezing time. Note that, depending upon the factor Ef, the equation is useful in determining freezing time for an infinite slab, infinite cylinder, or a sphere shape.

Crystallization

Crystallization during freezing is the formation of a systematically organized solid phase from a solution or liquid. It an important thermo-physical phenomenon through which a substance precipitates due to supercooling or supersaturation. This phenomenon consists of two stages, i.e., nucleation and crystal growth. The nucleation step is defined as the formation of a new crystal and happens either in a crystal-free solution, which is then called primary nucleation, or at the presence of formerly created crystals, which is defined as secondary nucleation. The main driving force for the deposition formation of a solid crystalline phase from liquid and solutions is the supersaturation or supercooling achieved in the system. After the formation of the nuclei, the next step of crystallization process is crystal growth. When the size is not sufficient for the growth is called embryo. During crystal growth an enlargement of nucleus takes place by an orderly addition of water molecules. The cooling rate influences the rate of nucleation and crystal growth and consequently the ice crystal size and distribution. However, the size and shape of the ice crystals formed are not stable and they can change during long storage. The process by which the number, size, shape, and orientation of crystals are changing during storage after freezing is known collectively as recrystallization. The microstructure and quality of frozen foods are strongly influenced by the processes of ice crystal formation and subsequent changes.

Nucleation

Nucleation is the first step in ice formation and it critically affects the crystal size and shape during crystallization. Nucleation starts with a microscopic particle called the nucleus, which can induce the formation and growth of ice crystals. Once a nucleus is in place, other molecules align themselves at the solid-liquid interphase of the nucleation sites. This stage is called crystal growth, in which ice crystals start to mature gradually to a larger diameter by consuming unfrozen water. A nucleus can be created by three ways,

I) Seeding: It is the simplest way to form a nucleus. When a suspension of the small crystals is added to a supersaturated solution, the solution generally loses its supersaturation and ice crystals are formed around the nuclei and grow in time.

ii) Heterogeneous nucleation: Some impurities or different components in a solution, such as biochemicals, starch and protein etc. have similar surface properties. Thus, if some particles are present in an unpurified or complex solution, other molecules that have similar surface properties may adsorb on their surface to form a layer to start crystallization.

iii) Homogeneous nucleation: Homogeneous nucleation can occurs spontaneously without a preferential nucleation site and can be observed in a very pure system with superheating or supercooling phenomena.

Ice nucleation appears to be a key parameter for the optimization of industrial processes related to freezing. However, ice nucleation occurs spontaneously and stochastically and is affected by several factors such as impurities, asperities, surface properties, etc. that in general cannot be easily monitored and manipulated.

Ice crystal growth

The second phase of crystallization consists of crystal growth. It requires a lower degree of supercooling (usually less than -1°C) than does the nucleation process. The crystal growth occurs by the systematic addition of molecules to the crystal surface. There are two factors affecting the rate of ice crystal growth: heat transfer and mass transfer. During ice crystallization, latent heat is released, leading to a decrease in the free energy of solid liquid interface and the formation of a supercoiling degree. After stable nucleus formed, molecules greater than the critical size all aggregate into crystals of visible size, which is the process of ice crystal growth.

Fast and slow freezing

Generally, in food freezing the temperature of the food is reduced from some initial value above the freezing temperature to some value much below the initial freezing temperature. In this process, a temperature range of 0°C to -5°C is known as the critical zone. The time taken by a food product to pass through the critical zone determines the number and size of ice crystals that are formed. The freezing rate is the most important factor influencing the size and location of ice crystals in a frozen system. A fast freezing rate causes a large number of small ice crystals homogeneously distributed throughout the food, whereas slow freezing rate causes a small number of large ice crystals. Slow freezing keeps the product in the critical zone for a longer time when compared with fast freezing. High heat transfer rates lead to high rate of freezing and form many small ice crystals, whereas slow freezing gives a small number of large ice crystals. Slow freezing gives more time for the water molecules to migrate to the growing nuclei giving large size crystals. On the other hand, if the food is rapidly cooled to a temperature well below its freezing point (fast freezing), then this results in high degree of supercooling and results in a large number of small ice crystals.

In the slow freezing, the movement of the freezing front is generally at a rate of 0.1 to 0.2 cm/h and it may take as long as 20 h for the product to be completely frozen. In case of fast freezing, the freezing front travels at a rate as fast as 5 cm/h. the translocation of water from the interior to the exterior region of the cell is less during quick freezing, resulting in minimal changes to the native structure of myofibrils. The fine crystal formed during fast freezing cause only negligible cellular damage. Therefore, in terms of quality, fast freezing provides a product that is juicier, better texture and less drip loss when thawed. Generally, for fast freezing, the material is exposed to a temperature of about -40°C and the freezing is completed with in 1 to 2 h. in case of IQF, the time might be as short as 3 to 20 min depending on the equipment and temperature.

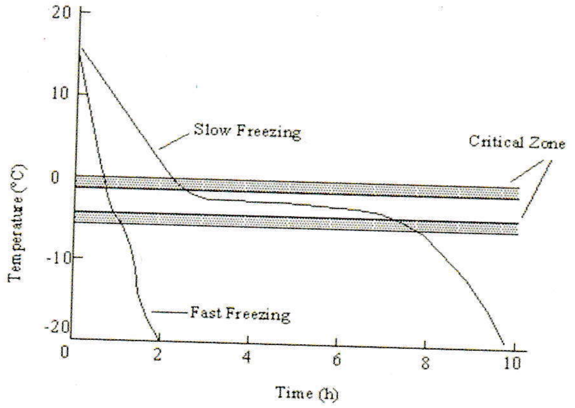


Fig 3. Schematic of rate of freezing on residence time of fish in the critical zone.

FREEZING TECHNIQUES

The freezing process can be accomplished by using either indirect or direct contact systems. Most often, the type of system used will depend on the product characteristics, both before and after freezing is completed. There are a variety of circumstances where direct contact between the product and refrigerant is not possible. The freezing equipment can be classified according to the temperature applied (above or below -40°C), the processed product (solid and liquid), the freezing medium (air, cold surface and liquid), and the way of processing (continuous and batch). There are number of methods by which fish can be frozen and freezing methods can be broadly classified as,

- Immersion freezing
- Indirect contact freezing
- Air blast freezing and
- Cryogenic freezing

Freezers can also be grouped according to the rate of movement of the ice front:

- slow freezers and sharp freezers (0.2 cm h-1) - still-air freezers and cold stores;
- quick freezers (0.5±3 cm h-1) - air-blast and plate freezers;
- rapid freezers (5±10 cm h-1) - fluidised-bed freezers; and
- ultra rapid freezers (10±100 cm h-1) - cryogenic freezers.

Air freezing

Air is by far the most widely used method of freezing food as it is economical, hygienic and relatively non-corrosive to equipment. The big advantages of air systems are their cost and versatility, especially when there is a requirement to cool a variety of irregularly shaped products. Air freezing systems are of two types: still air freezing and forced air freezing. In forced air freezing, air is blown horizontally or vertically to the fish product depending on the freezing method.

Still Air Freezers

Still air freezers are relatively large and serve the purpose of freezing as well as the storage of the product like cold store. Freezer consist of insulated room or a cabinet maintained at temperature -28 to -45°C and air flow with very low velocities. Fish, packed or otherwise, placed in metal trays are kept on the shelves made of pipes or coils through which refrigerant is circulated. Refrigerant coils are generally located at one side of the room or cabinet. The convective heat transfer coefficients are very low and the time taken for freezing may be requires longer time (12 hours or more). The slow freezing may lead to quality damage to the product because of formation of large ice crystals. Freezing time is influenced by various factors such as temperature and load of the freezer, shape and size of the fish, presence and absence of packaging and arrangement of fish in the freezer. Weight loss of the fish, especially unwrapped products, will be more as the fish is in contact with the air for a longer time. Freezing in still air is still popular because of cost effectiveness and applicability to a wide range of products, however, this conventional freezing system is the slowest method as well.

Air blast freezers

Air blast freezer operate by blasting refrigerated air over a fish product to remove heat. Air blast freezers consists of an insulated small rooms or tunnels in which cold air is circulated by fans through the finned cooling coil of the refrigeration system. This cold air then passes over the product which needs to be frozen, picks up heat from the product and the walls of the freezer and returns to the evaporator reduction of temperature. Since, the cold air comes into direct contact with the surface of the fish product, hence improves the heat transfer and freezing rate. Most freezers of this type operate at air temperature of -40°c. The air moves in a direction opposite to the product at the velocity varies between 5 to 10 m/sec to give most economic freezing. This type of freezer is economical and is capable of accommodating products of different size and shape. Packaging is recommended to prevent excessive dehydration and weight loss in the product during freezing.

Types of air blast freezer:

Depending on their mode of operation, air blast freezer can be divided into batch type, semicontinuous, or continuous modes.

1. Batch freezers

Fish placed on shelves or trays of racks/trolleys, multipass conveyor belts or hung from hooks on slide rails are manually loaded into the batch air-blast freezer. When the freezer is switched on, fans blow low-temperature air at high flow rates from the evaporator(s) over the fish and back again to the evaporator(s). Thus, the fan-driven circulating low-temperature air comes in direct contact with fish. The air flow arrangement can be horizontal or vertical in relation to the fish product. Fish trolleys are kept inside the freezer for the required time and when fully frozen the first batch is removed for cold storage and another batch is loaded into the freezing compartment. The freezing time required depends on the temperature and velocity of air, size and shape of fish, types of packaging and the extent of contact between individual fish and the refrigerating air. Small and uniform size fish is required short freezing time and adequate product quality can be achieved. The freezer is run until the fish is frozen to the required temperature and then switched off for manual unloading.

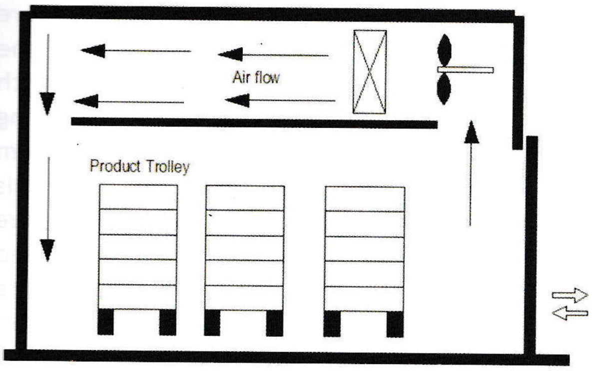


Fig 4. Batch air blast freezers

2. Tunnel air-blast freezers without conveyor belts

This freezer consists of an insulated chamber/cabinet of considerable length and limited width, where loading and unloading occur at the same end or at opposite ends. Refrigerated air is vigorously circulated by means of fans from the evaporator over the fish with air flowing parallel to the direction of movement ("cocurrent and countercurrent") or perpendicular to it ("cross-flow"). Fish products are usually placed on trays or trolleys which pass through the tunnel. The trolleys are moved in and out of the freezer by manually or mechanically at the same end or a chain drive (carrier tunnel freezer) at opposite ends. Unlike loading and unloading at the same end, which allows semi-continuous freezing operations, charging and discharging of fish at opposite ends permit continuous freezing.

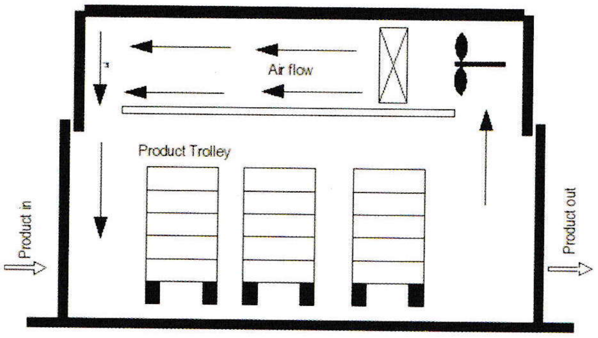


Fig 5. Continuous air blast freezers

3. Tunnel air-blast freezers with conveyor belt

In a conventional tunnel air-blast freezer with conveyor belts, fish are distributed uniformly with sufficient intervals onto a long single-meshed conveyor belt. Conveyor belts takes the fish through the tunnel freezer from one to the other end of the freezer. Refrigerated air is blown top-down through the conveyor belt. By moving the conveyor belt forward and backward, the product is kept in continuous motion until the product surface is frozen and at the same time prevents sticking.

4. Spiral belt air blast freezers

Spiral belt air-blast freezers have a meshed spiral conveyor belt, conveying the fish from bottom to top along a helical path. The design consists of a self-staking and self-enclosing spiral belt for compactness and better control of airflow. The number of tiers in the belt can be varied to accommodate different capacities and line layouts.

The belt is continuous and moves around a cylindrical drum giving up to 50 rounds. The products are placed on the belt outside the freezer and subjected to a horizontal and vertical airflow of refrigerated air. Spiral freezing (Fig.6) is one of the most currently used methods in the freezing industry for large production due to its convenience, reduced floor space, flexibility and efficiency. This type of freezer is well suited for products require longer freezing times, packaged and unpackaged products and bigger size products.

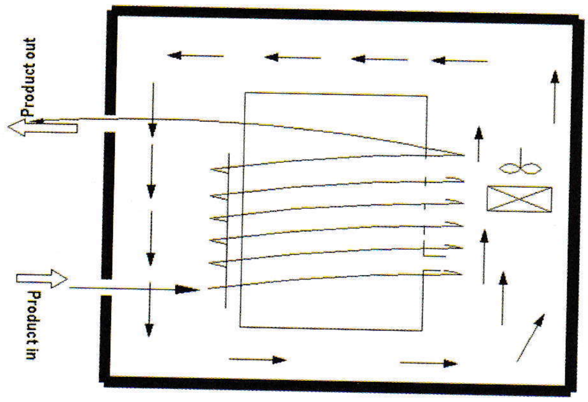


Fig 6. Spiral belt freezers

5. Fluidized bed tunnel freezers

Small size shrimp, fish and fish fillets can be fluidized on the perforated metal belt through which chilled air is pumped upwards at the rate sufficient to partially lift or suspend the products. Each product is separated from the others, free to move and surrounded by low temperature air which evokes very high convective heat transfer coefficients on the product surface, resulting in short freezing times. An air velocity of least 2 m/sec or more is necessary to fluidized the product and air temperature of -35°C to -40°C is commonly employed. Some fluidized bed freezers involve of two stage freezing techniques, wherein the first stage consists of an ordinary air blast freezing to set the surface of the product and second stage consists of fluidized bed freezing. Fluidized bed freezers are very suitable for individual quick freezing (IQF) of small foods or food particles such as shrimp. IQF leads to the rapid formation of a solid crust on the product surface, which prevents the delicate foods from sticking together in large lumps. In fluidized beds the moisture loss will be in the order of 2%. Fluidized-bed freezing is limited to small, uniform size and shape product particles, as maintaining larger product particles in a fluidized state requires much more energy and is therefore not always practically possible.

6. Impingement Freezer

In a conventional air blast freezer, a stagnant boundary layer of air surrounding the product offers high resistance to heat transfer, resulting poor convective heat transfer. Hence, coefficient freezing rates are low and large ice crystals will be form leading to poor quality of the product. In an impingement freezer, cold air at very high velocity is impinged perpendicularly using nozzles against the food surface. The impingement breaks up the boundary layer of air surrounding the product and increases heat transfer by three to five times that of conventional tunnel freezers. Nozzles used in impingement freezers have a great influence on air flow and may be single hole, orifices or jet tubes. The advantage of an impingement freezers is it require low freezing times and low product weight loss. This type of freezing technique is being used in freezing onboard freezing of fish fillets.

Indirect Contact Freezing

In indirect contact freezing, fish products are kept in contact with a metal surface which is cooled by the refrigerant. In this system the refrigerant does not come into direct contact with the material being frozen. It is only circulated through hollow plates which are refrigerated and absorb heat from the fish product placed on it either directly or in metal trays. These types of freezer are called contact plate freezer and are commonly used in the fishing industry for the production of blocks of fish or other seafood. The two main types of plate freezers are horizontal plate freezer and vertical Plate freezer. When the plates are arranged horizontally to form a series of shelves and as the arrangement suggests, they are called horizontal plate freezers. While plate freezers can be arranged with the plates vertical to form a series of bins are called vertical plate freezers. In both types, the products are brought into close contact with aluminium alloy plates which contain circulating refrigerant. All plate freezers have hydraulic system which move the plates closer or further apart. This allows the products to be compacted so they freeze more quickly by closer contact, and are released more quickly after freezing. Double contact plate freezers are commonly used for freezing blocks of fish and shrimp (Fig 6A). Recently, plate freezers with carbon dioxide as the natural refrigerant in place of conventional ammonia has been developed. The advantages are better product quality, safety, less space requirements and no negative impact on environment.

1. Horizontal Plate Freezers

These freezers (Fig.7) consist of a horizontal series of hollow plates, through which refrigerant is pumped at -40°C temperature. Generally, these freezers have 15-20 plates. The fish products to be frozen contained in a metal freezing trays before freezing are loaded between freezing plates. The hydraulic system positions the plates in close contact with the top and bottom of the trays to ensure maximum heat exchange. The freezing trays may either be lined with polyethylene sheet prior to packing or fish can be held in cardboard cartoons as well. Depending on the product, the trays may divide into compartments to give uniform block sizes, which may also have tightly fitting lids, which will help to provide adequate contact with freezing plates at the top. Trays and cartons should be filled to the top to ensure good contact with both plates.

Horizontal plate freezers are used mainly in shore-based fish freezing plants, although they are sometimes installed on board ships for freezing prawns at sea. Freezing time depends on the thickness of the product between the shelves. Typically, 2 to 2½ hours are required to freeze a 6 cm thick block of fish to a core temperature of -18°C, with plate temperature at -35°C to -40°C.

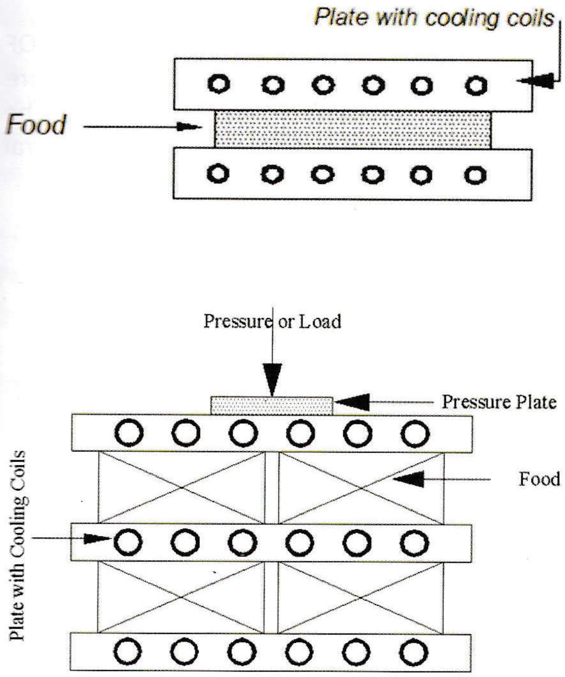


Fig 7. Plate freezers:

(A) double plate and

(B) horizontal plate with press.

2. Vertical plate freezers

The main advantage of vertical freezer (Fig.8) is that fish can be frozen in bulk without the requirement to package or arrange on trays. The plates form what is in effect a bin with an open top and fish are loaded directly into this space. This type of freezer is therefore particularly suitable for bulk freezing and it has been extensively used for freezing whole fish at sea. The freezer consists of a series of vertical metal alloy that form partitions in a container and the spaces between the plate are known as stations. Vertical plate equipment usually has 12-16 plates, lying 5 to 9.5 cm apart. Temperature is maintained between -30°C and -40°C when in operation. Fish are dropped between the plates until each station is full. The plates are then closed together to form the fish into blocks and the refrigerant flowing through the plates then freezes the fish. Uniform sizes of fish should be packed into each block because non-uniform sizes will lead to uneven freezing rates and may damage smaller fish.

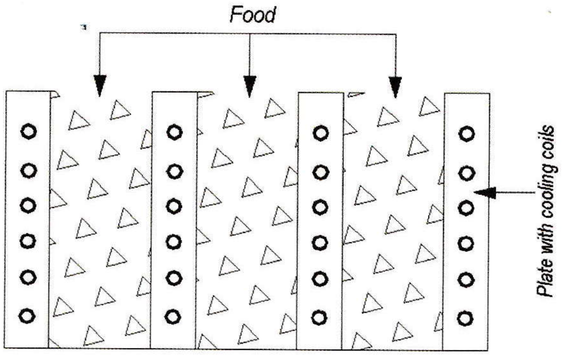


Fig 8. Vertical Plate freezers

Liquid immersion freezing

In this system glycol or brine, water solute mixtures such as sugar alcohol, propylene glycolwater mixtures are used as coolants. Generally, packaged products are frozen in immersion systems. Freezing with this system is fast and efficient because of very low temperatures of freezing media and all the surfaces of the product come in direct contact with the freezing media. Liquid foods can also be frozen in these systems, in which case the belt conveyor used will have long corrugations and the product is placed in the corrugations. The coolant is sprayed from the bottom of the belt. There is no direct contact between the food and the cooling medium. Alternatively, the corrugated belt can be arranged to pass through a bath of freezing medium giving immersion type of arrangement. However, the top of the corrugation is above the coolant surface thereby preventing direct contact between the product and the coolant. Careful consideration should be given to the safety of the product while choosing the freezing media and the product should be heavier than the freezing fluid. These systems are not commonly used nowadays.

Cryogenic Freezers

Cryogenic freezing came into existence in the 1960s with the introduction of cryogens such as liquid nitrogen and carbon dioxide. Cryogenic liquids have very low boiling points. The boiling points of liquid nitrogen and liquid carbon dioxide are -196°C and -79°C, respectively. Cryogens are colorless, odorless, and chemically inert. They give very large temperature differences and high heat transfer rates.

A cryogenic freezer comprises of an insulated cabinet in which a metallic perforated belt moves continuously. The belt is loaded with the fish at one end and frozen fish are unloaded at the other end. The entire belt length can be subdivided into several sections: a precooling section, spray or immersion section and equilibrating section. The precooling section helps in reducing the product temperature close to -70°C. This assistances in preventing freeze cracking damage to the fish product when exposed to direct contact with the cooling medium in the subsequent immersion or spray section. In the immersion/spray section, the fish comes in contact with liquid nitrogen giving a product temperature in the order of -190°C. Attaining such a low temperature is possible because the evaporating liquid nitrogen gives very high convective heat transfer coefficients.

In case of freezing with liquid CO_2, when high-pressure liquid CO_2 is released to atmosphere it forms vapor and dry ice. Conversion of liquid CO2 to vapor requires some time for sublimation and hence spray of coolant is done close to the entrance of the freezer. When combined with air impingement, these freezers are referred to as cryogenic impingement freezers. The high velocity air jets decrease the surface heat transfer resistance by disrupting the relatively stable boundary layer of gas surrounding the product.

Individual Quick Freezing (IQF):

Consumer demand for easy to prepare convenient seafood is shifting focus from traditional bulk freezing to IQF and value added fishery products. The global demand for quality seafood in competitive market is the driving force behind the demand of IQF products. IQF is defined by the international Institute of Refrigeration as the freezing of individually separated food units of small sizes such as berries, peas, shrimp etc. The IQF process allows the processor to supply customer with seafood in small, ready to cook quantities instead of large solid blocks, which have to be cut or thawed prior to packaging or use. In IQF, individual piece of shrimp is frozen separately either in a mechanical or cryogenic freezer. During IQF, smaller ice crystals are formed in shrimp due to quick freezing that ultimately results in a higher quality of the food product. High value products like shrimp and certain seafood such as fish fillets, squid, squid tubes, squid fillet, squid ring, cuttlefish fillets, lobster etc. are favourite raw material for this technology. Freezing times and production capacity differ with the nature of the material. The various preprocessing steps prior to freezing of the shellfish including cleaning, beheading, peeling, cooking, icing and dip treatment in preservative solutions such as bisulphate. Shrimp for freezing may be prepared in different forms as whole head on, headless shell on (HL), peeled and undeveined (PUD), peeling and deveined (PD), fan tail / butterfly, centred peeled, cooked, peeled and deveined (CPD) and peeled, deveined and cooked (PDC).

There are two major freezing methods for IQF shrimp. For small shrimp, fluidized bed freezers are normally used, where fluidization assurances the full IQF product with negligible loss in weight. Spiral

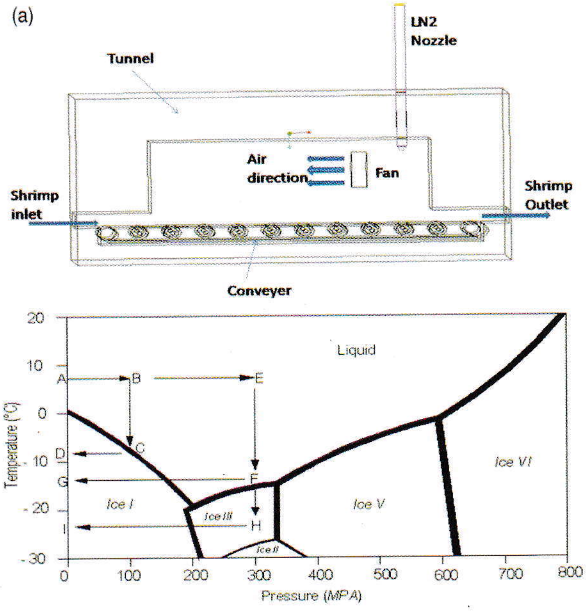


Fig 9. Tunnel type cryogenic IQF freezer

belt freezers are commonly used for large shrimps. As the belt speed is variable, optimum holding times can be set for each product. The controlled counter flow air distribution system keeps weight loss down to a minimum.

In the cryogenic freezer, minimal defects (cracking and break down), lower dehydration and drip losses, and shorter freezing time is reported compared to its mechanical counterpart. Additionally, increased production capacity and longer shelf life of food were other advantages of the cryogenic freezer. Although the setup cost of a cryogenic freezing unit is approximately one-fourth of the cost of traditional mechanical freezers, operating costs are approximately eight times higher. The majority of operating cost is due to cryogens such as liquid nitrogen (LN2). In a cryogenic freezer, the cooling capacity of LN2 is utilized to extract heat from the food product. A cryogenic freezer is probably the simplest IQF device as far as the operation is concerned. However, the inefficient utilization of cryogen and handling issues results in a higher cost of frozen food products. Thus, an insight into heat transfer phenomena in the cryogenic freezer may lead to an improvement in design, efficient utilization of cryogen, reduction of freezing time, and improvement in overall product quality.

Glazing:

Weight loss by dehydration during freezing and storage is directly proportional to the exposed surface area and can be reduced by two methods: covering the surface with packaging material, and surrounding the product with a thin layer of ice. As soon as seafood is removed from a freezer, they should be glazed and immediately transferred to a low temperature store to rapidly refreeze and to preserve taste, smell and texture as well as to minimize thaw drip loss. Ice glazing applies a protective layer of ice on the frozen seafood product, preventing air from penetrating the product's surface. The shrimp glazing process is carried out by dipping or spraying the product with water (which is most common, but also salt-sugar solutions are used) to apply a thin layer of ice or packaging only (Table 3). The aim of this process is to reduce the impact on quality resulting from cold storage deterioration and another argument for implementing glazing is that if the product is subject to inadequate cold storage, the glaze will evaporate instead of the tissue water itself. Glazing is just a form to assure the moisture loss by sublimation during the frozen storage which becomes an important quality and economic factor in the seafood industry. In order to form a complete and uniform glaze on the surface of the seafood, the glazing process requires to be closely controlled. The level of glaze that is typically applied should be from 4% to 10%, with the final amount of glaze applied depending on the following factors:

- The glazing times
- The seafood temperature
- The water temperature
- The size, shape and surface area of the product

Table 2: Comparison of Bulk frozen shrimp and IQF shrimp

Parameter	**Bulk frozen product**	**IQF product**
Freezing machinery	Conventional contact plate freezer using ammonia as coolant	Belt or cryogenic freezer using liquid nitrogen or carbon dioxide as coolant
Product size	Usually 2 kg	Individual shrimp
Glazing	Amount of glaze employed varies.	Uniform coating of the product by the glaze. Usually water without any additive is used as glaze
Freezing times	3 to 6 h	15 to 30 min depending upon the product size, belt speed and ambient temperature
Price	Determined by drained weight	Price not determined by drained weight
Sensitivity to temperature fluctuation	Low	High
Retention of water from glaze	Uneven gathering of water	Uniform
Consumer acceptability	Poor due to difficulties in handling	High, easy to handle

Flow Chart in IQF:


Raw Material
↓
Grading & Receiving
↓
Be-heading
↓
Wash & Chill Room
↓
Export Grading
↓
Pressure Wash
↓
Weighing
↓
IQF Freezer
↓
Glazing & Hardening
↓
Weighing
↓
Packing & labeling
↓
Frozen Storage
↓
Export

Codex (www.codexalimentarius.org) requires that the water used for glazing is of potable quality. Standards of potability should not be less than those contained in the latest edition of the World Health Organisation's "International Guidelines for Drinking Water Quality".

Emerging freezing technologies

Freezing rate of established freezing methods include air blast freezing, cryogenic freezing and plate contact freezing is normally low due to the low thermal conductivity of foods. Low freezing rate generally produces large, irregular and unevenly distributed ice crystals, causing severe damage of muscle tissue. This kind of damage of cell structure caused by ice crystals during freezing and frozen storage may induce an increase of thawing drip loss, denaturation of certain proteins and some other quality losses. Therefore, novel freezing technologies have been developed to overcome these disadvantages. These technologies mainly include High Pressure Freezing (HPF), Electrically and Magnetically assisted Freezing (EF & MF), Ultrasound Assisted Freezing (UAF), Antifreeze Protein (AFP) etc. and principle of novel freezing techniques are discussed. Some of these novel freezing technologies are aimed at increasing the rate of heat removal from the food while others change the physical/chemical structure of the product.

High pressure freezing (HPF)

High pressure freezing (HPF) is the process of cooling food under pressure up to its phase change temperature at the applied pressure, i.e., the freezing takes place under a constant pressure. HPF utilizes different states of water under pressure in the range of 100-400 MPa. When water is frozen at atmospheric pressure, its volume increases which causes tissue damage in foods. Under high pressures and different temperatures, water

Table 3: Glazing Methods

Method	Description	Advantages	Disadvantages
Dipping	Placing the frozen product in a tank of water for a period of time	Cost-effective Low capital costs Relatively simple	Inconsistent glaze coverage. Uncontrolled Seafood can be left too long or 'soaking' . Many need repeat applications
Spraying	Typically involves purpose designed equipment to spray water over a product	Controlled Consistent glaze coverage	Capital costs
Packaging only	Involves packaging the seafood in plastic packaging (e.g. film or bags) or vacuum packing	Can be simple Semi-controlled	Can be difficult to exclude packs. Many only suitable for oxygen from non vacuum short periods Packaging costs

Table 4. Principle and objective of novel freezing techniques

Novel techniques	Objective	Principle
Hydrofluidization freezing	To improve heat transfer rates to enable rapid freezing	Circulation system creating agitating jets to form a fluidized bed of highly turbulent liquid and moving products
Pressure-assisted freezing	To control the way ice is formed in the food during freezing, or after	Application of high pressures (typically of 200–400 Mpa)
Ultrasound-assisted freezing	Controlling ice nucleation and fragmentation of ice crystals already present into smaller crystals. Accelerate convective heat transfer in the cooling media	Application of low frequency (20 to 100 kHz) and high intensity (generally higher than 1 W cm-2)
Magnetic resonance assisted freezing	Disruption of ice-crystal nucleation by magnetically induced mechanical oscillation	Application of permanent magnets and induction coils to produce a weak oscillating magnetic field within the freezing chamber
Electrostatic assisted freezing	Controlling supercooling and ice crystallization	Application of high voltage electric field to a food will orientate the polar molecules (e.g., water)
Microwave-assisted freezing	Disruption of ice nucleation and formation during freezing	Application of microwave energy along with a cryogen (e.g., liquid nitrogen) to exploit water dipole rotation induced by microwaves
Radio frequency–assisted freezing	Disruption of ice nucleation and formation during freezing	RF waves energy along with cryogen (e.g., liquid nitrogen)

usually form multiple kinds of ice (I-VI) by different phases with greater density than water and does not expand in volume during formation and exists in a 'vitreous' non-crystaline state, which may reduce tissue damage (Fig. 10). Therefore, HPF can be classified into three types: high pressure induced freezing (HPIF, ABEFHI in Fig. 10), high pressure shift freezing (HPSF, ABEFG in Fig. 10) and high pressure assisted freezing (HPAF, ABCD in Fig. 10), with HPSF being the most common option.

With PSF the food is cooled under high pressure to subzero temperatures but does not undergo a phase change and freeze until the pressure is released. When the pressure is released, theoretically, rapid nucleation takes place throughout the food resulting in small, uniform, homogenously distributed ice crystals. This should result in a reduced duration of the phase transition, less mechanical stress during formation of the ice crystals, and smaller ice crystals with a uniform distribution throughout the food.

Ultrasound-assisted Freezing (UAF)

Ultrasound-assisted thawing has been a proven process for a relatively long time, while its use to assist freezing is more recent. Ultrasound can be divided into low frequency diagnosis ultrasound (>1 MHz) and high intensity power ultrasound (20-100 kHz). The medium is not affected by the sound wave propagation under low power ultrasound, and therefore in the food industry, power ultrasound is used for enhancing food processing including freezing. Ultrasound assisted freezing is mainly based on the cavitation and micro-streaming effects generated by the ultrasound. The ultrasound creates cavitation bubbles throughout the product, enhancing the mass and heat transfer and promoting more even ice nucleation and fragmenting large ice crystals. Although studies show that, ultrasound as a potential tool can be used to make ice crystals in model foods, applications of ultrasound assisted freezing are still limited, in particular few investigations are focused on meat freezing.

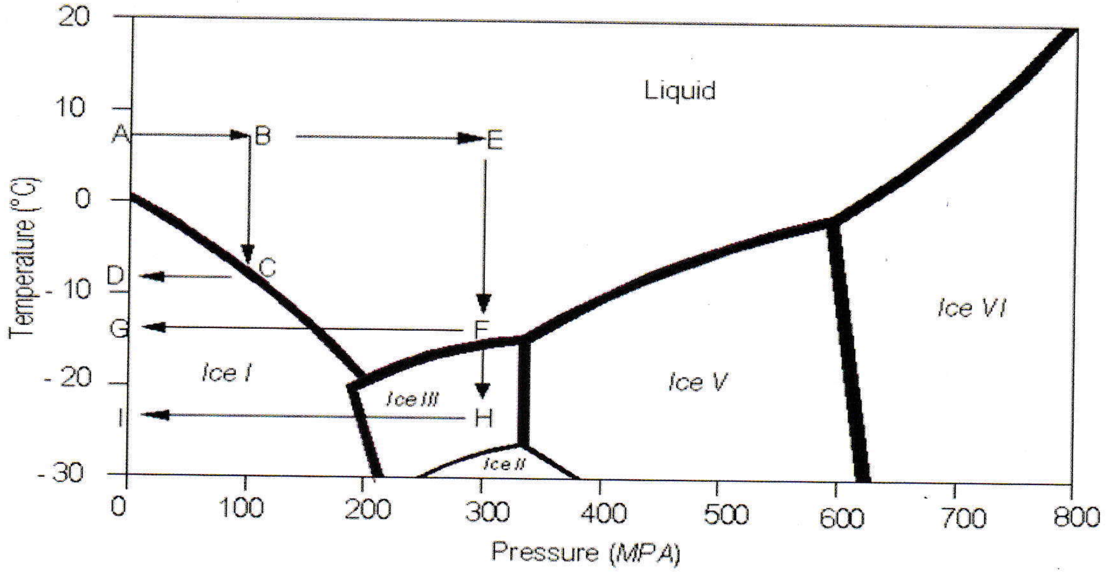


Fig 10. Phase diagram of water (ABCD for pressure assisted freezing, ABEFG for pressure shift freezing, and ABEFHI for pressure induced freezing) (Cheng et al., 2015).

Table 5. Use of pressure shift freezing (PSF) for freezing fish

Food	**Conditions**	**Conclusion**	**Reference**
Salmon	PSF at 100 MPa (−8.4 °C), 150 Mpa (−14 °C) and 200 MPa (−20 °C)	Smaller ice crystals; more homogenous structure and distribution	Zhu et al. 2003
Carp	PSF up to 140 MPa (−14 °C)	No significant effect on texture; lower total drip losses after cooking; smaller, more regular, intracellular ice crystals	Sequeira-Munoz et al. 2005
Salmon	PSF at 100 MPa (−10 °C) and 200 MPa (−18 °C)	Smaller ice crystals; more homogenous structure and distribution; reduced thawing drip	Alizadeh et al. 2007a, b, 2009
Sea bass	PSF up to 200 MPa (−18 °C)	Improvement on the cellular integrity of the tissue	Tironi et al. 2007, 2009, 2010
Shrimp	PSF up to 100 MPa (−8.4 °C), 150 MPa (−14 °C) and 200 MPa (−20 °C)	Smaller, regular, more homogeneously distributed ice crystals	Su et al. 2014a, b

Microwave assisted Freezing

The proposed principle behind microwave-assisted freezing is to exploit water dipole rotation induced by microwaves to disrupt ice nucleation, formation and growth during freezing. At present, microwave-assisted freezing (in common with radiofrequency-assisted freezing) is at an early research and development stage and studies on real food have been published, therefore further studies should be conducted for possible industrial applications.

Magnetic Resonance-assisted Freezing (MRAF)

With the freezing rates that are provided by conventional freezing methods, the migration of water molecules cannot be prevented and thus the undesirable mass transfer within the food product under freezing. This phenomenon may result in cellular dehydration, loss in tissue integrity, texture and shape of the food product after freezing. The magnetic resonance freezing process includes subjecting the product to continuous magnetic vibrations while freezing for a specific time followed by abrupt removal of magnetic field.

Table 6. Studies on the use of magnetic resonance-assisted freezing for fish

Food	Conditions	Conclusion	Reference
Bigeye tuna and yellowtail tuna	−35°C, 3.4 ms−1, field intensity 0to 100 G	No apparent effect on degree of supercooling, equilibrium freezing temperature, or freezing duration	Watanabe et al., 2011

There is evidence that water, being a diamagnetic material, can be magnetised in a magnetic field and freezing water under the influence of a magnetic field can change the freezing characteristics.

Quality changes during storage:

Although freezing is an effective method of preserving foods, however, some deterioration in frozen food quality occurs during storage. The extent of quality loss depends on many factors, including the rate of freezing and thawing, storage temperature, temperature fluctuations, freeze-thaw abuse during storage, transportation, retail display and consumption.

During frozen storage of shrimp and other shellfish products, the quality changes caused by oxidation, denaturation of proteins, sublimation and recrystallization of ice crystals are predominant. These can result in off-flavors, rancidity, dehydration, weight loss, loss of juiciness, drip loss and toughening, as well as microbial spoilage and autolysis.

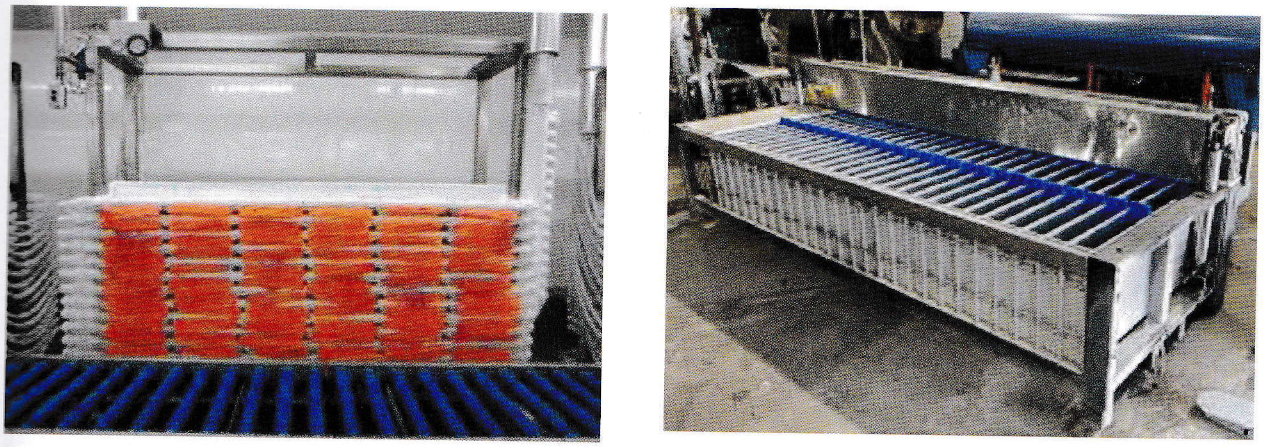


Fig.11. Horizontal Freezer & Vertical Freezer

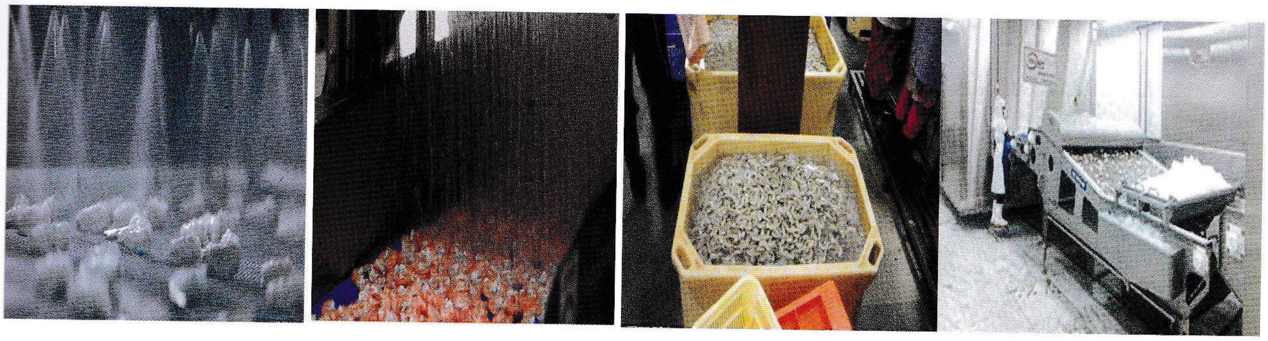
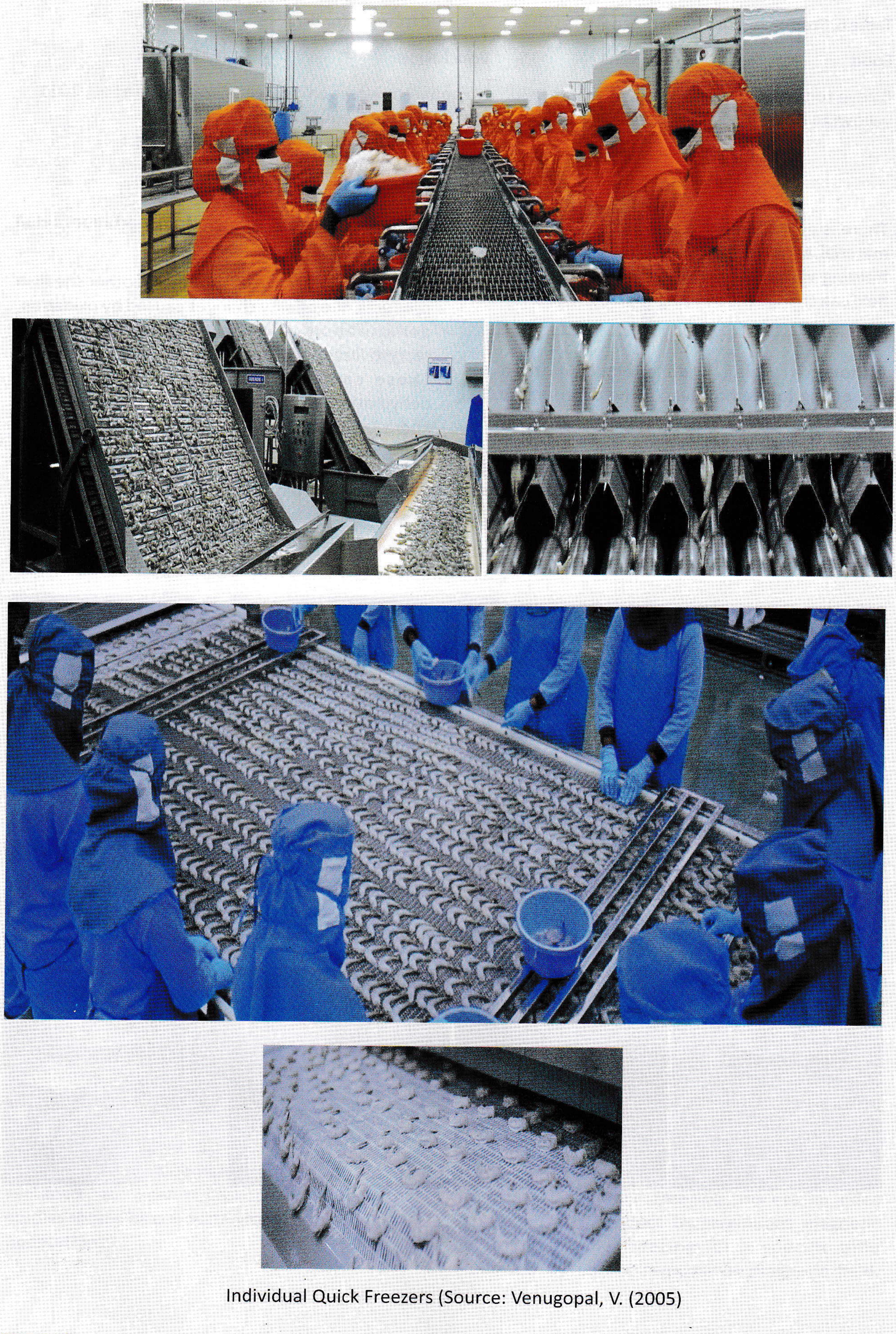


Fig.12. Glazing of shrimp (Source: Seafish)



Individual Quick Freezers (Source: Venugopal, V. (2005)