# Chapter 5 Handling, Chilling and Freezing of Fishery Products

**Dr. George Ninan** Principal scientist, ICAR-Central Institute of Fisheries Technology Cochin-682029, Kerala, India

George.Ninan@icar.gov.in

Maintaining the quality of fish begins with harvest and carries through the harvest -toconsumption chain. Careful handling of fish and shellfish while harvesting and during transport to the processing plant is critical if the high quality of the product is to be maintained. There are, however, several constraints on handling the fish; the important among them are the bacteriological, chemical and physical processes that cause degradation of fish. The surface of dead fish is an ideal growth habitat for bacteria and the end result of such activity is spoiled fish. Reduction of temperature can prevent the growth of many bacteria that cause the spoilage. Chemical breakdown due to oxidative and enzymatic reactions can lead to off odors and flavors and rancidity. Digestive enzymes can initiate decomposition in the dead fish. Physical factors can enhance the bacteriological or chemical processes: bruising, tearing, cutting etc. can expose fish muscle to more rapid bacteriological growth, cause internal bleeding which darkens the fillets and expose greater surface area for chemical oxidation.

Since fish is a highly perishable item of food, it has to be immediately processed to various products to preserve the quality and to increase the shelf life. Fish requires proper handling and preservation to increase its shelf life and retain its quality and nutritional attributes. The objective of handling, processing and preservation is to control or reduce the spoilage process so that the final product is wholesome and safe for the consumer. Fish and fishery products brought to market in a well-preserved condition will generally command higher prices, both at wholesale and retail levels, and thus give better returns to the fishing operation.

# Handling

The earliest practice of fish handling in many parts of the world to avoid spoilage and loss of quality is to keep caught fish alive until cooking and consumption, particularly in China where live carp trade has been practiced for more than three thousand years. Till date, this remains to be one of the common fish-handling practices. A large number of fish species are usually kept alive in holding basins, floating cages, wells and fish yards. Holding basins, normally associated with fish culture companies, can be equipped with oxygen control, water filtering and circulation and temperature control. Simpler methods are also used viz., keeping fish in floating cages in rivers or simple fish yards constructed in backwaters. Also, the transportation of live fish ranges from very sophisticated systems installed on trucks that

regulate temperature, filter and recycle water and add oxygen, to very simple artisanal systems of transporting fish in plastic bags with an atmosphere supersaturated with oxygen.

For harvested fish, the general handling operations after capture are: Transferring catch from gear to vessel, holding of catch before handling, sorting/grading, Bleeding/gutting/washing, Chilling, Chilled storage and unloading. These operations range from manual methods to fully automated operations. The number of operations and the order in which they are performed depend on the fish species, the gear used, vessel size, duration of the voyage and the market to be supplied. It is crucial to provide a continuous flow in handling and to avoid any accumulation of unchilled fish, thereby bringing the important time-temperature phase under complete control. Icing is the oldest method of preserving fish freshness by chilling and it is widely used. Mechanical refrigeration makes ice readily and cheaply available. In addition, ice keeps fish moist, has a large cooling capacity, is safe, and is a portable cooling method that can be easily stored, transported and used by distributing it uniformly around fish. Block ice is used in crushed form to chill fish. The use of ice at various stages of handling and processing require suitable insulated containers. These containers are designed and constructed locally, using natural or artificial insulating materials, with enough handling flexibility.

The most important factors to be considered in the initial handling and transport are the temperature, duration of storage/transport and the hygiene in all respects including that of the handlers. The important requirements are cleaning the fish from dirt and debris, chilling it immediately to prevent its temperature from rising and maintaining high standards of cleanliness at all stages. Fish, which has struggled for long in the net or onboard, is likely to spoil more quickly than a fish, which dies instantaneously or is killed quickly. Similarly, fish with its stomach full while catching, will spoil more quickly and fish, which is bruised while catching or handling, will spoil more quickly than a physically sound fish.

# Washing and sorting of fish

The harvested fish should be washed well with potable water to free it from dirt and other extraneous matter. Water chlorinated at 10 ppm level is ideal for initial cleaning. Most of the surface bacterial load is cleared by washing. In some freshwater species viz., eel carp and trout, slime constitutes 2-3% of the body weight (Venugopal,2006) The excretion of slime which stops before rigor, creates a perfect environment for bacterial growth. Hence the carcass has to be thoroughly washed to remove slime. After washing the catch should be sorted species – wise and size – wise. Bruised, damaged and decomposed fish shall be separated from the catch during sorting.

# Dressing

It is desirable to avoid the struggling of large fish by instant killing. The more the fish struggles, the faster will be the fall of pH after death. A pH of 6.0 encourages protein denaturation of muscle during frozen storage (Robb, 2001). The dressing operations of the catch include heading, bleeding and gutting have to be carried out as fast as possible without significant bacterial contamination. Gills and viscera harbor several spoilage bacteria in large numbers. Partially digested food in the viscera may become sour or putrid due to bacterial action. The powerful digestive enzymes in the viscera can bring about accelerated spoilage of fish. Therefore, wherever possible, it is advisable to remove the gills and viscera before the fish is preserved and stored. Gutting or evisceration should not cause any bruise on the exposed belly portion. Retention of any visceral parts can easily contaminate the soft belly and bruises can cause accelerated spoilage by permitting easy penetration of bacteria. The

fish should be washed thoroughly after each operation. The larger fish are gutted by hand, washed and iced. Gutting helps to remove digestive enzymes and foul-smelling compounds associated with gut. It also prevents accumulation of bloodstains and control haemoglobin catalyzed lipid oxidation in the fillets (Hultin, 1992).

The blood in the fish can clot and turn black or brown in colour adversely affecting the colour and appearance of the meat. Therefore, bleeding is done to preserve the quality of the meat. Bleeding and evisceration can be done only to fish of reasonably large size. Slitting the throat followed by hanging the fish by tail or slitting the throat and immersing in cold water are the methods for bleeding.

#### **Good Handling Practices**

The type of handling the fish receive on land during preprocessing and processing will determine the quality of the final product. Every stage from capture, handling and processing, and eventually to sale, to the consumer, involves some loss of quality. Different raw material specifications are used for each product. For example, chilled fish for immediate sale on the local market may not be perfectly fresh but may still be acceptable to the consumer. But in the case of a product such as frozen fillets, fresh raw material will be required as it will have to withstand the rigors of the freezing process and extended cold storage before it reaches the consumer. Hence during pre-processing stage raw material is graded according to the suitability for various processing methods. Handling the fish (raw material) during processing varies with type of the fish, the processing methods and the intended final product. However, there are some important good practices to be followed in general, which are described below:

- As far as possible, every precaution should be taken to avoid the warming of fish, as this will favour the action of enzymes and bacteria.
- Avoid mishandling of the fish. This will damage the skin and flesh and accelerate the process of bacterial contamination and enzymatic action.
- Cool the fish as quickly as possible by any convenient method. Whatever be the method, it is important to cool the entire fish.
- The fish, which are caught at different times, have to be kept apart since they will be at different stages of spoilage.
- Small fishes have to be kept separately from large fishes, as they tend to spoil more rapidly than the latter.
- Soft-bellied fishes are to be kept separately and if the guts are being removed or the belly has burst, the body cavity has to be washed to remove any traces of the gut.
- The containers used for the transportation of fish should be cleaned after every use. Chlorinated water should be used, whenever possible for every fish washing operation.
- Do not put fish on the ground; it can be kept on simple concrete / wooden platforms, which, if frequently cleaned, will reduce contamination.
- Fish handlers at every pre-processing and processing stage should learn about and adopt good hygienic practices.

Low temperature preservation by chilling and freezing methods are widely practiced to maintain the quality and freshness of fish and fish products. Chilled storage method, i.e., keeping the fish in the unfrozen condition has only limited shelf life and it will vary between 4 and 20 days depending on the condition and species of fish. In frozen storage also, the shelf life is restricted but it varies from few weeks to years. The various factors that affect the

frozen storage shelf lives are condition of fish at the time of catch, handling, processing and product development, packaging and glazing of the product, freezing method adopted, frozen storage temperature, stacking methods and transportation techniques. These factors can be put together and can be termed as 'Product, Processing and Packaging' (PPP) and 'Time Temperature Tolerance' factors (TTT).

# **Chilled** storage

Chilling is an effective way of reducing spoilage in fish if it is done quickly and if the fish are kept chilled and handled carefully and hygienically. Immediate chilling of fish ensures high quality products (Connel, 1995: Huss, 1995). For every 10  $^{0}$ C reduction in temperature, the rate of deterioration decreases by a factor of 2-3 (Hardy,1986). The objective of chilling is to cool the fish as quickly as possible to as low a temperature as possible without freezing. Chilling cannot prevent the spoilage together but in general, the colder the fish, the greater the reduction in bacterial and enzyme activity.

The important chilling methods of fish and fish products at non-freezing temperature are:

- ✤ Iced storage.
- ✤ Chilled seawater (CSW) storage.
- Chilled freshwater (CFW) storage.
- ✤ Mechanically Refrigerated seawater (RSW) storage.
- ✤ Cold air storage.

The most common means of chilling is by the use of ice. Although ice can preserve fish for some time, it is still a relatively short-term means of preservation when compared to freezing, canning, salting or drying, for instance. When used properly it can keep fish fresh so that it is attractive in the market place.

Ice is available in several forms such as blocks, plates, tubes, shells, soft and flakes. Of these, flake ice is the most popular form for industrial use because of its cooling efficiency. It is also relatively dry and will not stick together to form clumps when stored. Cooling capacity is more for flake ice due to a large surface area for heat exchange. It also causes minimum damage to the flesh. To ensure maximum contact of ice with the fish, proper selection of the size of ice particles and good stowage practices are needed. The rate of chilling is governed by:

- The size, shape and thickness of fish;
- The method of stowage;
- Adequate mixing of ice, water and fish (in ice slurries);
- Adequate contact of ice with the fish;
- The size of the ice particles.

Icing is widely employed for chilled storage of freshwater fish in the country. The dressed and cleaned fish is kept in a chill store in insulated boxes with proper icing prior to preprocessing. The major advantage of using ice for chilling the fish is that it has a high latent heat of fusion so that it is capable of removing large amount of heat as it melts without changing the temperature at 0  $^{0}$ C. During transition from ice to water 1 kg of ice absorbs 80 k cal of heat and this will be sufficient to cool about 3 kg of fish from 30  $^{0}$ C to 0  $^{0}$ C. Hence

theoretically about 30 % of ice is needed to bring down the temperature from ambient conditions to  $0^{0}$ C. However, ice is needed to maintain the temperature as well as to accommodate the heat from the environment. Hence in tropical conditions a 1: 1 fish to ice ratio is ideal for ice storage. Fish of the same size and species are placed in the same boxes. It is always recommended to add about 12-20% extra ice to the fish in order to compensate for water loss from melting and bad handling (Zugarramurdi, et. al,1995). The effectiveness of chilling by temperature exchange depends on the thickness of the layers of fish and the distribution of ice. The rates of cooling of fish are given in Table 1.

Distance to centre of fish/fish layer (cm)	Time to cool from 25 $^{0}$ C to 1 $^{0}$ C (hours)
1	0.33
2	1.25
4	5.00
10	31.25
20	125.00
40	500.00

\*Clucas, I.J. and Ward, A.R.(1996) Post – harvest Fisheries Development: A Guide to Handling, Preservation, Processing and Quality. Natural Resources Institute, Chatham, Maritime, Kent ME4 4TB, UK pp 73 – 141.

# Chilling versus freezing of fish

There are many factors to be considered when considering the differences between chilling and freezing of fish products for various markets. Both chilling and freezing operations can produce stable products and the choice of one or the other depends on many factors.

Table 2 lists some of the advantages and disadvantages of the two methods. It can be used to help decide whether freezing or chilling is the option most appropriate to a particular situation.

Chilling	Freezing		
Short-term storage (up to one month maximum for some species, only a few days for others)	Long-term storage (a year or more for some species)		
Storage temperature 0 °C	Storage temperature well below zero, e.g30 °C		
Relatively cheap	Relatively costly		
Product resembles fresh fish	If poorly done can badly affect quality		
Relatively low-tech	Relatively high tech		
Low skills required	High skills required		
Portable refrigeration	Generally static operations		

Table	2. Advantages and	disadvantages of	f chilling and freezing *

\* Shawyer, M.; Medina Pizzali, A.F. (2003) The use of ice on small fishing vessels. FAO Fisheries Technical Paper. No. 436. Rome, FAO, 108 p.

#### Determination of spoilage rates

Spoilage of fish is linearly related to storage temperature since the enzymatic and microbial activities are directly related to temperature. If the shelf life of a fish at 0  $^{0}$  C and at another temperature (t  $^{0}$  C) are known, their ratio gives the relative rate of spoilage (RRS) at t  $^{0}$  C. The RRS for tropical fish are more than twice as estimated for temperate fish species.

Relative rate of spoilage (RRS) at t $^{\circ}C =$	shelf life at 0 °C
	shelf life at t 0 °C

# Factors affecting the rate of spoilage in chilled fish

The main factors that affect the rate of spoilage in chilled fish are:

- Temperature
- Physical damage
- Intrinsic factors

#### *Temperature*

It is well known that high temperatures increase the rate of fish spoilage and low temperatures slow it down. Therefore, if the temperature of fresh fish is low, then quality is lost slowly. The faster a lower temperature is attained during fish chilling, the more effectively the spoilage activity is inhibited. Generally, the rate at which fish loses quality when stored in ice (0 °C) is used as the baseline when comparisons are made regarding shelf-life at different storage temperatures. The effect of temperature reduction on the rate of spoilage and shelf life of fish is given in Table 3.

Reduction in Temperature (0 <sup>0</sup> C)	Rate of spoilage (%)	Extension of shelf life
0	100	-
5	50	× 2
10	25	× 4
15	12.5	× 8
20	6.25	× 16

 Table 3. Effect of temperature reduction on fish spoilage \*

\*Clucas, I.J. and Ward, A.R.(1996) Post – harvest Fisheries Development: A Guide to Handling, Preservation, Processing and Quality. Natural Resources Institute, Chatham, Maritime, Kent ME4 4TB, UK pp 73 – 141.

#### Physical damage

Fish is soft and easily damaged; therefore rough handling and bruising result in contamination of fish flesh with bacteria and allow releases of enzymes, speeding up the rate of spoilage. In addition, careless handling can burst the guts and spread the contents into the fish flesh.

# Intrinsic factors

The intrinsic factors affecting the spoilage rate of chilled fish are shown in Table 4.

Intrinsic factors	Relative spoilage rate of fish stored in ice			
	Slow rate	Fast rate		
Shape	Flat fish	Round fish		
Size	Large fish Small fish			
Fat content in the flesh	Lean species	Fatty species		
Skin characteristics	Thick skin	Thin skin		

# Table 4. Intrinsic factors affecting the spoilage rate of chilled fish\*

\*Huss, H.H (1995) Quality and quality changes in fresh fish, FAO Fisheries Technical Paper No. 348. Rome. 195 p.

# Shelf life of iced fish

Shelf life can be defined as the maximal period of time during which the predetermined attributes of the food are retained (Daun, 1993). The different expressions of shelf life related to the product, process and context is given as Annexure 1.

The chilled storage life of fish is primarily determined by sensory evaluation. Apart from the factors discussed in the previous session, chilled storage life of fish depends on several factors such as composition, microbial contamination and the type of microflora present in the fish (Venugopal,2006). The fish spoilage pattern is similar for all species, with four phases of spoilage as outlined in Table 5.

# Table 5. The four phases of fish spoilage\*

Phase I (Autolytic changes, caused mainly by enzymes)	Fish just caught is very fresh and has a sweet, seaweedy and delicate taste. There is very little deterioration, with slight loss of the characteristic odour and flavour. In some tropical species this period can last for about 1 to 2 days or more after catching.
Phase II (Autolytic changes, caused mainly by enzymes)	There is a significant loss of the natural flavour and odour of fish. The flesh becomes neutral but has no off- flavours, the texture is still pleasant.
Phase III (Bacteriological changes, caused mainly by bacteria)	The fish begins to show signs of spoilage. There are strong off-flavours and stale to unpleasant smells. Texture changes are significant, flesh becoming either soft and watery or tough and dry.
Phase IV (Bacteriological changes, caused mainly by bacteria)	Fish is spoiled and putrid, becoming inedible.

\* Shawyer, M.; Medina Pizzali, A.F. (2003) The use of ice on small fishing vessels. FAO Fisheries Technical Paper. No. 436. Rome, FAO, 108 p.

There have been many research studies regarding the shelf-life of fish stored in ice. Based on these studies, it is generally accepted that some tropical fish species can keep for longer periods in comparison to fish from temperate or colder waters. The normal life of coldwater fish chilled to 00C immediately postmortem is 1-2 weeks, while fish from tropical waters remain in good condition for longer periods (Venugopal, 2006). This can be attributed to differences in the bacterial growth rates, with a 1-2 week slow growth phase (or period of adaptation to chilled temperatures) in tropical fish stored in ice. However, due to differences in the criteria used to define the limit of shelf-life, and methodologies used, comparison between shelf-life of fish from tropical and temperate waters is still difficult. Up to 35% yield of high value products can be expected from fish processed within 5 days of storage in ice, after which a progressive decrease in the utility was observed with increase in storage days and beyond 9 days of ice storage no high value products could be processed (Venugopal and Shahidi, 1998). Delay in icing also can adversely affect the shelf life (Table 6). The shelf-life of several fresh water fish species stored in ice is summarized in Table 7.

Species	Delay (Hours)	Storage life in ice (days)
Mackerel (Rastrelliger spp.)	0	9
	3	7
	6	4
	9	≈1
Tilapia (Oreochromis spp.)	0	16
	4	13
	8	5
	12	< 1
Milk fish (Chanos chanos)	0	14
	4	12
	8	6
	12	≈1
$O!1 = o!1 = (C + 1) + 1 + \cdots + N = o$	0	7
Oil sardine (Sardinella longicepes) Nov-	0	7
Dec. period	3	5
	6	1
Farmed white prawn (Fenneropenaeus	0	16
indicus)	3	14
	6	9
	9	4

Table 6. Effect of delayed icing on the storage life of some tropical species \*

\* Ninan, G. (2003) Handling and Chilled Storage of Fish In: Product development and seafood safety. Central Institute of Fisheries Technology, Cochin, India, pp 43-58.

Species	Shelf-life (days in ice)		References	
	Temperate	Tropical waters		
	waters			
Catfish (Lean)	12-13	15-27	(Huss, 1995)	
Trout (Lean)	9-11	16-24	(Huss, 1995)	
Rohu, Mrigal & Catla		15 - 18	(Joseph et.al.,(1990)	
(Lean)				
Labeo sps. (Medium)		9-18	Bandhopadhyay et. al., (1985)	
Clarias sps. (Medium)		10 -15	Bhattacharya et.al.,(1990)	
Channa sps. (Lean)		8-9	Perigreen, et. al., (1987)	
Tilapia (Lean)		10-27	(Santos Lima Dos et. al., 1981)	
Common carp (Medium)		24-25	Santos Lima Dos et. al.,	
Enclassication processor (Loop)		10.12	(1981) Ninon et. el. (2002)	
Freshwater prawn (Lean)		10 - 12	Ninan et. al.,(2003)	

Table 7. Shelf-life of freshwater fish & shell fish species stored in ice\*

\* Fat content and shelf-life are subject to seasonal variations.

# Requirement of ice during handling and transportation

The weight of ice needed to chill 1 kg fish  $(0^{\circ}C)$  can be calculated theoretically as shown below in Table 8.(in practice some more ice will be needed).

# Table 8. Theoretical weight of ice needed to chill 10 kg of fish to 0 °C from various ambient temperatures \*

Starting temperature of fish (°C)	Weight of ice needed (kg)		
30°	3.4		
25°	2.8		
20°	2.3		
15°	1.7		
10°	1.2		
5°	0.6		

\*FAO (1984). Planning and engineering data 4. Containers for fish handling, J. Brox, M. Kristiansen, A. Myrseth & Per W. Aasheim (Eds.) Fisheries Circular No. 773. Rome, Italy, 53 p.

The necessary quantity of ice required to maintain the fish chilled will depend upon the ambient temperature, the insulative properties of the container, the place of the individual box within the load and the length of the storage. The following table (Table 9) gives an example of ice requirements to chill and maintain the chill condition of fish held in individual boxes and within a stack of boxes.

	Melting of ice per box of 50 kg fish					
	1 box			3	35 boxes	
Surrounding temperature (°C)	+30	+20	+10	+30	+20	+10
Chilling fish (kg)	21	14	7	21	14	7
Keeping chilled (kg/h)	3	2	1	1	0.7	0.3

# Table 9. Ice requirements for chilling and storage of fish\*

\*FAO (1984). Planning and engineering data 4. Containers for fish handling, J. Brox, M. Kristiansen, A. Myrseth & Per W. Aasheim(Eds.) Fisheries Circular No. 773. Rome, Italy, 53 p.

For practical purposes the following rules of thumb can be given to calculate ice requirements:

l. Fish boxes: Ice to fish ratio in tropics are 1 kg ice to 1 kg fish, and ice to fish ratio in temperate climate and in insulated van are 1 kg ice to 2 kg fish.

2. Insulated tanks: Water to ice to fish ratio in tropics are 1 kg water to 2 kg ice to 6 kg fish and in temperate climate 1 kg water to 1 kg ice to 4 kg fish.

Necessary volume of ice to chill the fish down to a temperature of  $0^{\circ}C$  is included in the above mentioned rules. If the fish is already chilled the volume of ice can be reduced accordingly.

The fish carrying capacities of various boxes and containers depend on the density of the mixture of ice and fish. Table 10 shows the densities of different types of ice.

Type of ice	Bulk weight kg/dm <sup>3</sup> = l	Specific volume m <sup>3</sup> /ton
Crushed block	0.690	1.45
Tube	0.565	1.80
Plate	0.570	1.75
Flake	0.445	2.25

# Table 10. Density of different types of ice\*

\*FAO (1984). Planning and engineering data 4. Containers for fish handling, J. Brox, M. Kristiansen, A. Myrseth & Per W. Aasheim(Eds.) Fisheries Circular No. 773. Rome, Italy, 53 p.

# Disadvantages of icing

Icing in the conventional method using crushed ice can bruise the flesh which results in leaching of flavour compounds and water-soluble proteins. Prolonged ice storage can cause changes in the texture of the muscle, particularly the reduction in breaking strength and hardness of fillets. Muscle proteases including cathepsin D and cathepsin L, calcium activated proteases (calpains), trypsin, chymotrypsin, alkaline proteases and collaginases are involved in softening of fish tissue during storage (Bremner, 2000)

Ice storage has been found to adversely influence protein stability and water holding capacity in salmon and cod fillets\*. Icing cannot completely arrest the activities of psychrotrophic organisms in fish, which is a quality problem in refrigerated food (Olssen, 2003).

# Transportation of Chilled fish

Land transportation of chilled fish is carried out in insulated or mechanically refrigerated vehicles. The refrigerated vehicle used for chilled fish transportation should have a minimum inside temperature of 7  $^{0}$  C (Venugopal, 2006). Boxes for land transportation are made of wood, aluminium, high density polyethylene, expanded polystyrene or polyurethane. The ideal fish transportation box should be light weight yet strong enough to withstand the combined weight of fish, ice and stacking and should have good insulating properties. The boxes should be easy to clean. Boxes are usually made of double bottom to collect the melt water. Containers used for air transportation of chilled fish should be water tight.

Air shipment of chilled fish requires a lightweight and protective container. Modern insulated containers are made of high-density polypropylene with polyurethane insulation sandwiched between the inner and outer walls of the double walled container. Instead of ice, pads of nonwoven fabric encapsulating synthetic absorbent powder are used for chilling of air shipped fish. These pads could be soaked in water and deep frozen for use (Venugopal, 2006). Special thermal barrier films are used in combination with the pads to protect fish containers from heat (Subsinghe, 1996)

# Freezing

Freezing is the most accepted method for long term preservation of fish and fishery products. Freezing reduces the spoilage activity and extends the shelf life of the product. Freezing represents the main method of processing fish for human consumption, and it accounted for 55.2 % of total processed fish for human consumption and 25.3 % of total fish production in 2010. (Anon.2012). Freezing involves the cooling down of materials from ambient temperature conditions to a temperature below the freezing point. Generally, the freezing process has three stages; in the first stage (pre-freezing stage) corresponds to removal of heat from the food, when the temperature is reduced to freezing point. The second stage (freezing stage) is the period of transformation of water to ice through the whole mass of food. Between the first and second stages there is a transitory super cooling period when the temperature falls below the freezing point which is not observed in some cases. In the third stage nearly 75% of the water in the muscle turns into ice which leads to further rapid drop in temperature, as the thermal diffusivity of ice being much higher than water. Bound water, which forms the integral part of the tissue will be frozen at extremely low temperature of about -55  $^{0}$  C.

As the water in fish freezes out as pure crystals of ice, the remaining unfrozen water contains higher concentration of salts and other compounds which are naturally present in the fish muscle. The increasing concentration of the salts will depress the freezing point of the unfrozen water. Hence unlike pure water, conversion to ice will not occur at 0  $^{0}$  C but proceeds over a range of temperature. Thus, even at -30  $^{0}$  C, a portion of water in the fish muscle will remain in unfrozen state. Slow freezing produce ice crystals of comparatively larger size and few in numbers which may cause rupture of the cell walls and result in fluid loss and textural changes on defrosting. In contrast fast freezing produce large number of small crystals, thus reducing the possibility of shrinkage or rupture. In fish, however, the cell may be considered sufficiently elastic to withstand excessive damage from the growth of large crystals, therefore this does not account for the drip loss on thawing the frozen fish (Garthwaite, 1997). The drip loss on thawing of fish occur mainly due to denaturation of protein during freezing which result in the loss of water binding capacity of the protein. The optimum range of temperature for denaturation is -1  $^{0}$  C to -2  $^{0}$  C; thus, in order to reduce the thaw drip to minimum the time spent in this temperature zone should be minimum.

Quick freezing is a general term applied to most of the freezing processes which result 'Individual Quick Frozen' product. If the temperature of fish/fishery product is reduced from  $0^{\circ}$  C to  $-5^{\circ}$ C in 2 hours or less, then it can be termed as a quick frozen product. During freezing process, the temperature of the fish should be lowered to  $-30^{\circ}$ C before it is transferred to the cold store. Most of the commercial freezers operate at temperatures of  $-40^{\circ}$  C to  $-35^{\circ}$  C. The thermal centre of the fish should attain  $-20^{\circ}$  C prior to its removal from the freezer. The time taken to lower the temperature of the thermal centre to  $-20^{\circ}$  C is termed as the freezing time.

#### Freezing systems

There are three basic methods for freezing fish. These are:

Air blast freezing: Where a continuous stream of cold air is passed over the product.

*Plate or contact freezing*: where the product is placed in direct contact with hollow, metal, freezer plates, through which a cold fluid is passed.

*Spray or Immersion freezing*: where the product is placed in direct contact with fluid refrigerant.

#### Air blast freezing

Circulating cold air at high speed enables freezing to proceed at a moderately rapid rate and this method is referred to as air-blast freezing. Air-blast freezing is usually accomplished by placing the products on a mesh belt and passing it slowly through an insulated tunnel containing air at-18 to -34°C or lower, moving counter current to the product at a speed of I to 20 meter/sec. Air at -29°C and at a speed of 10-12 meter/sec, is often satisfactory, although lower temperatures are preferred. Air blast freezing is economical and is capable of accommodating products of different sizes and shapes. It can result in (1) excessive dehydration of unpackaged products if conditions are not carefully controlled, and this in turn necessitates frequent defrosting of equipment and (2) undesirable bulging of packaged products which are not confined between flat rigid plates during freezing.

# Spiral Belt Freezer

Modern designs of belt freezers are mostly based in the spiral belt freezer concept. In these freezers a conveyor belt that can be bent laterally is used. The present design consists of a self-staking and self-enclosing belt for compactness and improved air flow control. The number of tiers in the belt stack can be varied to accommodate different capacities and line layouts. The belt is continuous. The products are placed on the belt outside the freezer where it can be supervised. As the belt is continuous it is easy for proper cleaning. Both unpacked and packed products are frozen and the freezer gives a large flexibility both with regard to product and freezing time. Both horizontal and vertical air flow can be used. Vertical airflow is more efficient.

#### Carton freezer

This freezer consists of a number of carrier shelves which are automatically moved through the section of the unit. The operations are carried out hydraulic power with mechanical linkage to coordinate different movements. The boxes are fed automatically into the freezer on a feeding conveyor.

# Fluidized Bed Freezing

Marine products of small size like prawns can be fluidized by forming a bed of prawns on a mesh belt and then forcing air upward through the bed at a rate sufficient to partially lift or suspend the particles. If the air used for fluidization is sufficiently cooled, freezing can be achieved at a rapid rate. An air velocity of at least 2 meter/sec. or more is necessary to fluidize the particles and an air temperature of - 35°C is common. The bed depth depends on ease of fluidization and this in turn depends on size, shape and uniformity of the particles. A bed depth of slightly more than 3 cm is suitable for small prawns where as a depth of 20 to 25 cm can be used for non-fluidizable products such as fillets. Fluidized bed freezing has proven successful for many kinds and sizes of products. The best results are obtained with products that are relatively small and uniform in size. Some fluidized-bed freezing to set the surface of the product and the second stage consists of fluidized bed freezing.

The advantages of fluidized bed freezing are (1) more efficient heat transfer and more rapid rates of freezing and (2) less product dehydration and less frequent defrosting of the equipment. Dehydration loses of about 1% have been reported during fluidized bed freezing of prawns. The short freezing time is apparently responsible for the small loss of moisture. The major disadvantage of fluidized-bed freezing is that large or non-uniform products cannot be fluidized at reasonable air velocities.

#### Contact Plate Freezing

Fish products can be frozen by placing them in contact with a metal surface cooled by expanding refrigerants. Double contact plate freezers are commonly used for freezing fish/prawn blocks. This equipment consists of a stack of horizontal cold plates with intervening spaces to accommodate single layers of packaged product. The filled unit appears like a multi layered sandwich containing cold plates and products in alternating layers. When closed, the plates make firm contact with the two major surfaces of the packages, thereby facilitating heat transfer and assuring that the major surfaces of the packages do not bulge during freezing. Vertical plate freezers are also in use especially onboard fishing vessels. Contact plate freezing is an economical method that minimises problems of product dehydration, defrosting of equipment and package bulging. In this method the packages must be of uniform thickness. A packaged product of 3 to 4 cm thickness can be frozen in I to 1.5 hour when cooled by plates at -35°C. Freezing times are extended considerably when the package contains a significant volume of void spaces.

#### Liquid Immersion Freezing

Liquid immersion freezing or direct immersion freezing is accomplished when a product is frozen by immersing or by spraying with a freezant that remains liquid throughout the process. This technique is occasionally used for fish and prawns. Liquid immersion freezing can result in moderately rapid freezing. Freezants used for liquid immersion freezing should be non-toxic, inexpensive, stable, reasonably inert, and should have a low viscosity, low vapour pressure and freezing point and reasonably high values for thermal conductivity. Freezants should have a low tendency to penetrate the product, little or no undesirable effects on organoleptic properties and require little effort to maintain desired standards for sanitation and composition. Aqueous solutions of propylene glycol, glycerol, sodium chloride, calcium chloride and mixtures of sugars and salt have been used as freezant.

#### Cryogenic Freezing

Cryogenic freezing refers to very rapid freezing by exposing food products to an extremely cold freezant undergoing change of state. The fact that heat removal is accomplished during a change of state by the freezant is used to distinguish cryogenic freezing from liquid immersion freezing. The most common food grade cryogenic freezants are boiling nitrogen and boiling or subliming carbon dioxide. Boiling nitrous oxide also has been considered, but at present it is not being used commercially. The rate of freezing obtained with cryogenic methods is much greater than that obtained with conventional airblast freezing or plate freezing, but is only moderately greater than that obtained with fluidized bed or liquid immersion freezing. For example, shrimp freeze in about 9 min in a commercial liquid nitrogen freezer and in about 12 min in a fluidized bed freezer. Currently liquid nitrogen is used in most of the cryogenic food freezers. Usually liquid nitrogen is sprayed or dribbled on the product or alternatively very cold gaseous nitrogen is brought into contact with the product. Freezing with carbon dioxide usually involves tumbling the product in the presence of powdered or liquid carbon dioxide. Carbon dioxide is absorbed or entrained by the product in this method. This entrapped  $CO_2$  should be removed before it is packaged in an impervious material.

# Crusto Freezer

This is a combination of cryogenic freezing system and air blast freezing system. The equipment utilizes the possibility of a fast and efficient crust freezing of extremely wet, sticky products which can then be easily handled in a spiral belt freezer or a fluidized bed freezer without deformation or breakage.

#### Individually Quick-Frozen Products (IQF)

Lobster, squid, cuttlefish, different varieties of finfish etc. are processed in the individually quick-frozen style. IQF products fetch better price than conventional block frozen products. However, for the production of IQF products raw-materials of very high quality need to be used, as also the processing has to be carried out under strict hygienic conditions. The products have to be packed in attractive moisture-proof containers and stored at  $-30^{\circ}$ C or below without fluctuation in storage temperature. Thermoform moulded trays have become accepted containers for IQF products in western countries. Utmost care is needed during the transportation of IQF products, as rise in temperature may cause surface melting of the individual pieces causing them to stick together forming lumps. Desiccation leading to weight loss and surface dehydration is other serious problem met with during storage of IQF products.

Some of the IQF products in demand are prawn in different forms such as whole, peeled and de-veined, cooked, headless shell-on, butterfly fan tail and round tail-on, whole cooked lobster, lobster tails, lobster meat, cuttlefish fillets, squid tubes, squid rings, boiled clam meat and skinless and boneless fillets of white lean fish. IQF products can be easily marketed as consumer packs, which is not possible with block frozen products. This is a distinct advantage in marketing.

# Pre-freezing and Freezing Considerations

The quality of frozen-thawed cooked fish is influenced by a number of factors including species, composition, size, how and where caught, elapsed time between harvest and freezing, the state of rigor and quality when frozen and the details of freezing process and frozen storage.

The major problems encountered during the freeze-processing of fish are oxidative deterioration, dehydration, toughening, loss of juiciness, and excessive drip. Effective pre-freezing and freezing techniques are available for controlling many of these problems except toughening and loss of juiciness. Reasonable control of toughening and loss of juiciness can be accomplished only by storing fish for a minimal time and / or at temperatures at  $-18^{\circ}$ C or lower. Undesirable oxidative changes in fish can be minimized by (1) eliminating oxygen (2) avoiding contamination with heavy metals (oxidative catalysts) (3) adding antioxidants and (4) by using low storage temperature. Dehydration can be avoided by applying glaze and suitable protective coatings. Most foods expand on freezing but to a lesser extent than pure water. The various factors that contribute to volume change upon freezing of food are:

- > Cooling of specimen prior to freezing causes contraction
- ➢ Ice formation during freezing causes expansion
- Cooling of ice crystals causes contraction
- Solute crystallization causes contraction or expansion depending on the type of solutes.
- > Cooling of solute crystals present in eutectics causes contraction.
- > Solidification and cooling of non-solutes such as fat causes contraction.

The effect of ice formation predominates during freezing. A consequence of the increase in volume during freezing of food is the development of mechanical stress and hence freezing damage to food. The dislocation of water that accompanies slow freezing and re-crystallization may also cause mechanical stress. Mechanical damage to the texture of tissues during freezing is marginal in muscles because of its pliable consistency and parallel arrangement of cells. Sample size, freezing rate and final temperature of the tissue appear to influence the intensity of stress. In large tissues, outer surface freezes to solid before freezing commences in inner areas. On further freezing, the inner areas get frozen leading to considerable internal stress. The rate of freezing also influences the severity of stress. Slow freezing results in unusually great damage due to detrimental size and location of ice crystals. Rapid freezing coupled with low temperature will result in severe cracking of tissues containing large percentage of water.

During freezing of tissues, nearly all the non-aqueous constituents concentrate in a diminished quantity of unfrozen water. The extent of concentration is influenced

mainly by the final temperature, and to a lesser extent by the eutectic temperatures of the solutes present, agitation and rate of cooling. Agitation of the fluid phase during freezing aids in the formation of pure ice crystals by minimizing accumulation of solutes at the solid liquid interface. Slow removal of heat results in a smooth, continuous solid liquid interface, maximum crystal purity and concentration of solutes in the unfrozen phase. Rapid freezing results in an irregular and discontinuous interface, considerable entrapment of solutes by growing crystals and less than maximum concentration of solutes in the unfrozen phase. During freezing, the unfrozen phase changes significantly in properties such as pH, acidity, ionic strength, viscosity, freezing point, surface tension, interfacial tension, and oxidation reduction potential. Freezing forces the macromolecules like proteins to come closer making interactions between molecules more probable. The pH changes occur because of increasing concentration of solutes in the unfrozen phase during freezing. The effect of eutectics on pH is governed by the type of solutes that crystallize during freezing.

The freezing process is considered complete when most of the water at the center of the food product has been converted into ice. At  $-15^{\circ}$ C, more than 80% of total water is transformed into ice. The system is segregated into a crystalline phase of pure water and an amorphous domain, which contains solutes and residual water. As the temperature decreases, the viscosity of the interstitial fluid increases rapidly as a result of both increase in concentration and decrease in temperature. When the viscosity reaches a very high value (~1011 – 1012 PaS), solidification (vitrification) occurs, and the concentrated phase surrounding the ice crystals becomes a glass. The temperature of the maximally freeze concentrated system. The freezing of water is stopped at this temperature; water still unfrozen is often called "un-freezable water".

#### Physical changes during frozen storage

The major physical changes during frozen storage of fish are freezer burn and recrystallization. Freezer burn is a surface phenomenon which occurs in improperly packed products. Freezer burn appears as an opaque dehydrated surface. It is caused by the sublimation of ice on the surface of the muscle. The sublimation takes place when the vapour pressure of ice on the surface of fish muscle is higher than the vapour pressure of the cold store. Other factors contributing to freezer burn are air velocity in the cold store, cold storage temperature and post mortem condition of the muscle. It can be prevented or reduced by glazing the product in chilled water and air tight packaging with water impermeable packaging materials.

The ice crystals in the frozen muscle undergo transformations during frozen storage causing changes in number, size and shape. This phenomenon is called re-crystallization. During frozen storage, the ice crystals in rapidly frozen samples are found to grow slowly. The sizes of the ice crystals between rapidly frozen and slow frozen samples have almost the same size after a long storage. There are many reasons for the changes in size and shape. During storage, the reorientation of the ice crystals takes place to give a stable shape with a compact structure having smaller surface to volume ratio and lower surface energy. In frozen products, the large ice crystals may grow at the expense of small crystals. This may be caused by melting-diffusion-refreezing or sublimation-diffusion- refreezing. The net result is an increase in average crystal size, decrease in the number of crystals and decrease

in surface energy of the crystalline phase. Fluctuating temperature and associated vapour pressure gradients enhance this type of re-crystallization. Also contacting crystals fuse together resulting in an increasing crystal size, decrease in number of crystals and decrease in surface energy. Each frozen product exhibits a critical temperature below which re-crystallization does not occur at a significant rate. Low and uniform temperature of frozen storage can minimize re-crystallization.

#### Drip

Drip is the exudates coming out from a frozen product on thawing. Fish after freezing, frozen storage and thawing often exudates a considerable amount of drip. Drip may amount to 1 to 5% or much more. Drip loss may cause sizable financial On thawing, if the drip loss is high, the frozen products appear somewhat dry loss. and stringy. However, the relationship between texture and drip loss need not be linear up to moderate drip loss, but at high drip loss, the loss of texture is directly related. Though factors like internal pressure developed during freezing, freezing rate, size and location of ice crystals may influence thaw drip, the major factors are the quality of the raw material, abuse of frozen storage and the extent of resultant denaturation. When the quality is poor and the frozen product is stored especially at a higher frozen storage temperature for a long duration the amount of drip is found high and is almost proportional to the storage period. Very slow freezing and the development of large extracellular ice crystals also have some influence. quick freezing the cell dehydration during freezing is minimum due to the formation of uniform intracellular and extracellular ice crystals. This causes minimum damage to the cell and consequently expects a low drip.

# Temperature Fluctuation

In good cold storage it is rare that temperature fluctuation in storage rooms exceed more than  $\pm 2^{\circ}$ C. Temperature fluctuation has little effect on quality when the storage temperature is below -18°C. Very high temperature fluctuation may have an adverse effect on product quality.

# Quality Changes

Most of the quality changes normally attributed to the freezing process are indeed unrelated to that process. In fact, except for cases where texture is adversely affected by freezing, the frozen product is often practically indistinguishable from the fresh product when thawed immediately. However, after few months of storage, depending on product, process, packaging and storage temperature, changes are noticed. These changes are due to changes during frozen storage. The drip is very much increased by warm freezer storage temperatures. The explanation generally offered is that the high ionic strength of the solution causes rapid denaturation of proteins with poor binding of water as a consequence. This effect is not pronounced at colder freezer storage temperature because of reduced reaction rates. The most important adverse effect on freezing and frozen storage on nutritive value may be a loss of vitamins, mostly the more labile ones such as ascorbic acid, thiamin and riboflavin vitamins are water soluble and hence some losses occur in the drip.

#### *Time Temperature Tolerance*

Longer keeping times are recorded at colder temperatures in frozen storage shelf life studies. Many chemical reactions such as lipid oxidation, lipid hydrolysis and

protein denaturation and the resultant sensory changes in texture and flavor are temperature dependent. Time temperature tolerance studies for quality changes during frozen storage showed a logarithmic relationship of storage time vs. temperature of the storage. Various studies indicated that the frozen storage temperature has pronounced influence on quality and shelf life. In general, the retention of the qualities will be better at lower temperatures and an inversely proportional shelf life.

## Freeze/Thaw Stability

Most frozen food will suffer some physical deterioration if they are subjected to thawing and refreezing. There are often textural changes brought about by the formation and reformation of ice crystals. Fish and meat both suffer under these circumstances and cause protein denaturation. It is possible to give some protection against damage from freeze/thaw cycles by using certain stabilizers. Polysaccharides such as sucrose, sorbitol, carrageenan and modified starches exhibit such cryoprotective properties.

#### References

- Anon. (2012) The State of World Fisheries and Aquaculture 2012 Part I World Review of Fisheries and Aquaculture pp 63.
- Bandhopadhyay,J.K, Chattopadhyay,A.K and Bhattacharya, S.K (1985) Studies on the ice storage characteristics of commercially important freshwater fishes In: Harvest and Post –harvest Technology of Fish , Society of Fisheries Technologists (India), Cochin, pp 381-385.
- Bhattacharya, S.K and Choudhuri, D.R (1990) Studies on Storage Characteristics of Clarias batrachus at Different Temperatures. Fish Technol. 27, pp 127-129.
- Bremner,H.A (2000) A critical look at whether "freshness" can be determined. J.Aquat.Food Prod. Technol., 9, pp 5-25.
- Connel, J.J (1995) *Control of Fish Quality*. Fishing News Books, London, England p 245.
- Daun,H.(1993) Introduction, In *Shelf Life Studies of Foods and Beverages Chemical, Biological, Physical and Nutritional Aspects*, Charalambous, G., Ed. Elsevier Science Amsterdam, pp ix-x.
- Garthwaite G.A(1997)Chilling and Freezing of Fish. In: *Fish Processing Technology* 2<sup>nd</sup> Edition (Ed.Hall G.M), Springer (India) Pvt.Ltd, New Delhi, pp 98-108.
- Hardy, R (1986) Fish processing, Proc. R. Soc. Edinburg, 87B, 201.
- Hultin, H.O (1992) Control of lipid oxidation processes in minced fatty fish In Seafood Science and Technology, Bligh, E.G., Ed. Fishing News Books, Oxford, England p 93.
- Huss, H.H (1995) *Quality and quality changes in fresh fish*, FAO Fisheries Technical Paper No. 348. Rome. 195 p.
- Joseph J, Perigreen, P.A, Surendran, P.K and Gopakumar, K (1990) Iced storage characteristics of cultured major carps of India. I.I.F, I.I.R, Commission C2, Aberdeen (UK) pp 117 -121
- Ninan, G., Bindu, J, Ashok Kumar, K and Jose Joseph (2003) Biochemical changes during chilled storage of M.rosenbergii (De man, 1879) In: Freshwater Prawns – Advances, Biology, Aquaculture and marketing (C.M Nair & D.D Namboodiri Eds.), Allied Publishers, New Delhi, pp 625-632.

- Olssen, G.B (2003) *Changes in water holding capacity of halibut muscle during cold storage*, Lebensm. Wiss. Technol., 36, p 771.
- Perigreen, P.A, Jose Joseph, Surendran, P.K and Gopakumar, K (1987) Studies on Iced Storage of Common Murrel (Channa striatus), Fish Technol. 24(2), pp 99-102.
- Robb, D.H.F (2001) The relationship between killing methods and quality, In Farmed Fish Quality, Kestin, S.C and Warris, P.D., Eds. Fishing News Books, Oxford, England p 220.
- Santos Lima Dos, C.A.M (1981) The storage of tropical fish in ice- A review.Trop. Sci. 23,pp 97-127
- Subsinghe, S (1996) Handling and marketing of aquacultured fish, Infofish Int., 3, p 44.
- Venugopal, V. and Shahidi, F (1998) Food Rev. Int. 14.p 35.
- Venugopal, V.(2006) Bulk handling and Chilling, In *Seafood Processing: Adding value through quick freezing, retortable packaging and quick chilling,* CRC Press, Taylor & Francis Group, Boca Raton, FL., p 485
- Zugarramurdi, A., Parin, M.A., and Lupin, H.M (1995) Economic engineering applied to the fishery industry. FAO Fisheries Technical Paper No.351, FAO, Rome, Italy.

# Annexure 1

Context	Meaning	Measurement	Product	References
Commercial shelf life	Period fish can be offered for sale	Sensory (Consumer acceptability)	Whole and gutted fish, cooked fillets,	Gelman(1990)
Maximum shelf life	Up to inedibility of fish	Sensory	Whole and gutted fish, cooked fillets,	Gelman(1990)
Predict shelf life	Based on microbial count	Pseudomonas, Schewanella and Photobacterium counts.	Lightly preserved fish products	Gram, and Huss (1996)
Remaining shelf life	Sensory properties	Quality Index Method	Whole fish	Branch and Vail (1985)
Total shelf life	Until sensory rejection for any food use	Sensory evaluation	Fish	Gelman(1990)
True shelf life	Microbial rejection	Microbial count, mathematical prediction	Fish and other foods	Fu and Labuzza (1997)
Maximum storage time	Sensory (whole and cooked), chemical, scoring texture, odour and flavour	Freshness score, K-value, TVB, TMA	Albacore	Perez-Villarreal and Pozo (1990)
Keeping quality, storage life	Rejection mainly by sensory characteristics.	Water binding capacity, texture measure, sensory tables, sensory panel (for raw and cooked)	Fish in general	Santos Lima Dos (1981)