Low Temperature Preservation of Seafoods: A Review

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Introduction
Because of their ease of digestibility and the nature of the microbial and systemic enzymes that cause their spoilage, seafoods are among the most perishable of foods (Bramsnaes, 1957). The seafood spoilage rate depends on the speed with which the chemical reactions that cause their spoilage proceed. As is generally true for chemical reactions, the speed with which fish spoilage proceeds depends on the temperature of the system. The relationship between the rate of fish spoilage and temperatures has been widely observed and reported, and shelf life prediction devices have been constructed from some of these studies (Spencer and Baines, 1964; James and Olley, 1971; Charm et al., 1972; and Ronsivalli et al., 1973).

Although we are addressing the direct relationship between the spoilage of fish and the reaction rates of the enzymes, we do not want to ignore the fact that these enzymes are produced from bacteria and that the metabolic and numerical growth rates of bacteria are also enhanced by an increase in temperature (within limits). For example, while the generation time for Pseudomonas fragi, a common fish spoilage bacterium is about 12 hours at 32°F (0°C), it is only about 2 hours at 55°F (12.9°C) (Duncan and Nickerson, 1961). Obviously, the rate of production of bacterial enzymes is influenced by the metabolic rates and number of bacteria. While the roles of bacterial enzymes and bacterial numbers in fish spoilage are important and relevant to the subject of this paper, no further discussion will be made of these here. Instead, the reader is referred to Ronsivalli and Charm (1975), where a more detailed discussion already exists and additional references are given.

There is little doubt that the storage temperature is the most important variable influencing the spoilage of seafoods; and to optimize the preservative effect of lowering their temperature, it is helpful to understand the principles at work as well as the relationship between the temperature of a given seafood and its shelf life. Much work has been done to combine low temperature with other treatments such as the use of bacteriostats and bactericides (Windsor and Thomas, 1974), and some work has been done in vacuum (Liciardiello et al., 1967) and modified gas packaging (Veranth and Robe, 1979), but this discussion is limited only to the control of temperature.

For prolonging the quality of fish by simply controlling the temperature, the best results are obtained when the temperature control is applied immediately after the fish are caught. This is because the quality of fish is highest at point of catch and it undergoes irreversible quality losses with time at rates that are directly related to temperature.

Three categories of temperature control can be applied: Chilling, superchilling, and freezing. These control quality in somewhat different ways. The first category of temperature control is chilling. It is in the wet range of temperatures (where no freezing of the fish is desired). The chief control imposed by the temperature in this case is that it slows down the rates of the reproduction, growth, and metabolism of spoilage bacteria.
and the reaction rates of the bacterial enzymes. It slows the rate of enzymic spoilage simply because, as we stated earlier, spoilage involves chemical reactions whose rates are proportional to the temperature.

Superchilling, the second category, is in the narrow temperature range from 26.6° to 30.2 °F (from -3.0° to -1.0°C). In this range there is some freezing of the water in the fish tissues, and this is noticeable when an attempt to bend the fish is made. If the temperature is lower than this range, the fish will be frozen solid. If the temperature is above this range, there will be no freezing at all. The principle by which superchilling works is simply that the lowered temperature further slows the microbial metabolism and spoilage reaction rates. The formation of some ice also creates pockets of immobility insofar as bacterial activity is concerned.

In the third category of temperature control, freezing (0°F or -17.8 °C, or below), the product is frozen solid since most of its water is transformed to ice, and bacteria are completely immobilized. This is precisely the principle by which freezing protects fish quality. However, although freezing provides protection from microbial spoilage, other spoilage vectors such as oxygen and enzyme activity have to be controlled.

**Chilling**

Like other perishable foods, seafoods retain their initial quality for long periods when they are properly packaged and held properly frozen. However, there is a relatively high demand for fresh¹ (unfrozen) seafoods which command a significantly higher price at retail than frozen seafoods. The reason for the difference in price between fresh and frozen seafoods is attributed to the widely accepted belief that the quality of fresh seafoods is superior and much higher than the quality of frozen seafoods. Whether or not this notion is accurate, it does exist. Because of the high value of fresh seafoods and because of their relatively high rate of perishability, there is an economic reason to maximize their shelf life and to minimize the chance that their quality will deteriorate to the point that they lose their commercial value.

One of the best methods known for preserving the quality of fresh seafoods is to surround them with flaked or crushed ice, because this provides a quick way to bring their temperature to just above freezing.

**Use of Ice**

The preservation of the quality of seafoods by chilling them with ice was practiced as early as 1838 aboard New England trawlers. The principle employed was not different from that of the old domestic ice box: The ice was held in one compartment, the food was held in another, and both compartments were enclosed in a cabinet which served to keep the system separated from the environment. In fishing vessels, ice was kept in one pen, and fish were put in the other pens. This practice, while better than carrying no ice at all, was not effective, and it was not until fishermen began to mix the ice with the fish that icing aboard vessels made possible the landing of high-quality fish. The regular use of ice during overland shipments began from Boston to New York in 1858.

A major value of ice for preserving fresh seafoods is that it has a high latent heat of fusion² so that it is capable of removing large amounts of heat as it melts without changing its temperature at 32 °F (0°C). Of course, once it melts, the heat of fusion will have been absorbed, and its temper-

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¹In this context, fresh signifies never having been frozen.

²The latent heat of fusion is the amount of heat required to change a given weight of a solid to a liquid without changing its temperature. In the English system, the weight used is one pound (Btu). In the metric system, the weight used is one gram (calorie).
ature will begin to increase as it is exposed to more heat.

During the transition from ice to water, 1 pound (454 g) of ice absorbs 144 Btu (British thermal units). Since 1 Btu (252 calories) is defined as the amount of heat required to raise the temperature of 1 pound (454 g) of water by 1°F (0.56°C), then the removal of 144 Btu (36.3 Kcal) from a 6 pound (2.7 kg) fish, which contains about 75 percent water, will lower the temperature of that fish 32°F (17.8°C) from an ambient temperature of 144 Btu (36.3 Kcal) from a 6 pound (2.7 kg) fish, which contains about 75 percent water, will lower the temperature of that fish 32°F (17.8°C) from an ambient temperature of 64°F (17.8°C) to 32°F (0°C). The calculation involved is 144 ÷ (6 x 0.75).

This would suggest that fishermen should take about one-sixth as much ice as the weight of fish they expect to catch when the ambient temperature is about 64°F (17.8°C). However, we have to take into account the fact that the ice continually cools the pen walls as well as the air around it from the moment the ice is loaded on the vessel, and it is expected to keep removing heat from the system as well as the heat generated by the fish, once the fish are added, until such time as the fish are landed. The amount of extra ice needed for accommodating the heat which the system receives from the environment will vary depending on time of year, amount of insulation, length of trip, etc. This is bound to be quite high. At any rate, fishermen should take enough ice to maintain the fish temperature at about 32°F (0°C) at all times. The amount of ice taken on a trip will be best worked out for each vessel, but it would probably be from one-fourth to one-half the weight of the expected catch.

Since the spoilage of fish starts just after they die, and since the spoilage rate is largely dependent on the temperature, the sooner the fish can be cooled the better. This is precisely the reason that the quality of fish is preserved longer when there is an adequate amount of ice, and it is well dispersed among the fish. When the ice is in small particles, such as flakes, it does a more effective job of cooling than when it is in large pieces. This is because smaller ice particles give greater contact between fish and ice, and the rate of heat removal depends on the size of the contact area. Another advantage of small ice particles is that it avoids damaging fish in the lower part of the pen. Large pieces of ice can exert point forces (from the pressure developed in the lower part of the pens when they are filled) and thereby damage fish.

Although this paper does not cover the modification of ice with bacteriostats, it is important to point out that the ice must be sanitary. Obviously, both ice and water that come in contact with food must be of potable quality. The need to ensure the quality of the ice is not emphasized merely to meet legal compliance which is concerned with public health but rather to minimize the sources of bacteria and other agents of spoilage.

Use of Chilled Seawater

Chilled seawater (CSW) is discussed here because, in essence, it is an extension of the use of ice. That is, it is the end point to which can be carried the principle of maximizing surface contact (the smaller the ice particles, the greater the cooling rate, and molecules of cold water can be considered to behave as minute articles of ice).

In CSW, the fish are surrounded with a mixture of ice and water, thereby achieving maximum contact between fish and coolant. When enough ice is added to the system, it will bring the temperature of the water down to 32°F (0°C), and it will continue to remove the heat from the water, that the water, in turn, removes from the fish. The transfer of heat from the fish to the water and from water to ice will continue until the system is brought to a state of temperature equilibrium. Actually, a uniform temperature may never really be attained, because the system is dynamic, continually absorbing heat from the environment and from the bacteria in the fish. However, provided there is sufficient ice in the system, a point will be reached where the average temperature of the system cannot be reduced further.

CSW is effective because the water component of the CSW establishes maximum contact between the cooling medium and the fish. Therefore, the cooling rate of fish in CSW is higher than that of fish in ice.

CSW has sufficient advantages over ice alone to warrant its adoption by commercial fishermen for cooling their catch (Hulme and Baker, 1977). These authors reported that CSW cooling is fast, bringing the fish temperature down to 32°F (0°C) within 4 hours and maintaining the temperature quite uniformly. Temperature uniformity is enhanced by the thorough mixing due to the action of the sea, as one might expect. There is no need to declump ice at sea; however, seawater must be added to the ice as soon as possible. Otherwise, the ice tends to clump before a slush can be obtained. The fish are less damaged in CSW because of the buoyant effect of the water. Also, fish can be unloaded very quickly with pumps.

In our own work (Baker and Hulme, 1977), we observed that whiting, herring, and other fish may be scaled by the agitation to which they are subjected. This may be an advantage if the fish are to be scaled anyway, as they would be in most processing operations. On the other hand, if the fish were destined for a market that required the scales to remain on the fish, then CSW holding would not be suitable.

There have been reports of the development of discoloration of fish, of rancidity, and of salt absorption during their holding in refrigerated seawater which would have to hold true for CSW (Roach and Tomlinson, 1969; Peters, Carlson, and Baker, 1965). We did not encounter these problems, however. The one concern with CSW is that the holds must be of special construction to prevent the buildup of large surge forces in heavy seas. This may be prevented by the installation of perforated baffles (Baker and Hulme, 1977).

The ice requirements used in our studies were governed by an established ratio of one part ice, two parts...
seawater, and seven parts fish. Therefore, for every ton (0.9 t) of fish we expected to catch, we put into the hold 286 pounds (131 kg) of ice. At the first opportunity, 571 pounds (259 kg) (about 68 gallons or 257 liters) of seawater were added. Accordingly, if one had an insulated hold or compartment with a capacity of 10 tons (9 t), he would start out by putting 1 ton (0.9 t) of ice in the hold. He would add 2 tons (1.8 t) of seawater as soon as possible (not harbor water, because it is not clean enough). Two tons (1.8 t) of seawater are equal to about 480 gallons (1,817 liters). Then the hold would be filled to capacity with fish, resulting in a mixture of 1:2:7 (ice:seawater:fish). It should be noted that the reason why a relatively small amount of ice was adequate in our CSW work is because the holds of the vessel that we used were well insulated. Both insulation and ambient temperatures have major influences on ice requirements.

Refrigerated Seawater

In ordinary application of refrigerated seawater (RSW), the seawater is usually cooled by mechanical refrigeration. Thus, RSW, as opposed to CSW, is not as limited in its role of removing heat, and there is a reasonable control of temperature over a range that is not possible with CSW. In addition, it has all the advantages described for CSW and, unlike ice and CSW, it can be used for superchillng fish (see next section).

RSW systems may vary, but the basic components are a pump to bring seawater into the vessel and to circulate the RSW, a heat exchanger to remove heat from the seawater, a mechanical refrigerator to discharge heat from the system, a circulatory system for transporting the refrigerant between the heat exchanger and the refrigerator, and a sparging system for spraying the RSW over the catch or a tank to contain the fish and RSW. Auxiliary equipment can, and in some cases may have to be added; i.e., a filtering system, a holding tank for the chilled RSW, a system for controlling the sanitary quality of the water, and a system for removing fish oil.

The designs of a RSW system and its individual components are important (Peters, Slavin, Carlson, and Baker, 1965). Critical among these is the design of the heat exchanger. If it is not properly designed, the RSW may freeze and cause the system to fail. Even when the heat exchanger is of appropriate design, the RSW could conceivably freeze if its rate of flow is too slow. The pump(s) has to be corrosion resistant and have a relatively high capacity. The entire system must be designed, especially the circulatory system (pipes, fittings, valves, etc.), so as to prevent the growth of microbial colonies which can be the source of contamination that can easily be carried to the fish by the RSW. The system must be easily cleaned, especially the tanks that are used to hold the fish.

The earliest commercial use of RSW occurred in the early and middle 1920's to cool menhaden. It has been used to preserve the quality of sardines. In some cases, the brine has been made by the addition of salt to fresh water, especially when there was reason to believe that the available seawater was not satisfactory because of contamination or other deterrent. In the 1950's, Canadians used RSW for preserving the quality of salmon and halibut both on the vessel at sea and in trucks on shore (Roach et al., 1961). While RSW has many advantages, its use has by no means proliferated. It has advantages that result in stabilizing the quality of fish for periods of about 1 week. However, while RSW controls temperature exceedingly well, contact with the fish for periods longer than 1 week may have deleterious effects that result in undesirable changes in odor and flavor (e.g., rancidity) and in appearance (e.g., loss of pigment from skin).

Although RSW should have significant long term preservative effects, empirical data do not support the theory. Carbon dioxide (CO₂) has been added to RSW in recent experiments as an adjunct preservative. The CO₂ lowers the pH which has a beneficial effect on the quality of the fish; but because it does lower the pH, it then enhances the corrosiveness of RSW comonents to intolerable levels. The latter problem has been circumvented by using components that are coated with corrosion resistant materials. When this is done the RSW system containing CO₂ has shown an effective inhibition of bacterial growth and an increase of at least 1 week in the shelf life of the fish (Barnett et al., 1971).

Superchillng

Superchilling, as used for preserving seafoods, has been defined as the lowering of the temperature of the flesh to within the range from -3 ° to -1 °C (26.6-30.2 °F) (Carlson, 1969). The process also has been labeled “supercooling,” “light freezing,” “partial freezing,” and “very poor freezing.”

Pure water freezes at 0 °C (32 °F), but its freezing point is depressed when it contains dissolved substances. The water in biological systems (plants and animals) contains varying amounts of dissolved substances; therefore, the freezing of seafoods occurs below the freezing point of pure water. When the temperature of seafoods is lowered, the physical change to a hardened mass occurs gradually at rates that are fastest in the beginning and slower as the temperature drops. The water in the seafood is not spontaneously frozen at any given temperature. As the flesh temperature is lowered, the first water molecules are frozen at slightly below 0 °C (32 °F). Successively more is frozen as the temperature continues to fall. According to Power et al. (1969), as the temperature of fish muscle is lowered to -1 °, -2 °, -3 °, and -4 °C (30.2 °, 28.1 °, 26.6 °, and 24.4 °F), the percent of water frozen is 19, 55, 70, and 76, respectively.

At first, the rate of freezing of the water in fish is relatively rapid; and by the time the temperature is lowered to only -6 °C (21.2 °F), about 80 percent of the water is frozen and the flesh is rigid, even though the remaining 20 percent of the water is not frozen. At
The first record of superchilling was reported in about 1935 (Carlson, 1969), and it involved the use of brine (at about 26.6°F (-3°C) as the refrigerant, resulting in extended shelf lives for whole fish. In the first major use of superchilling, mechanical refrigeration was used to hold fish aboard fishing vessels at about 30°F (-1.1°C) (RanKen, 1963).

Reports on the preserving effectiveness of superchilling fish leave little doubt as to the considerable increase in the shelf life of the product. However, according to Carlson (1969), certain disadvantages surfaced in subsequent evaluations of the process by research teams from England and later by teams from Canada, The Federal Republic of Germany, and the United States. Degradation of appearance and texture and excessive drip loss were also found and confirmed (Power and Morton, 1965). Some of the quality degradation was attributed to the partial freezing that actually occurs during superchilling. The recommendations that derive from these subsequent evaluations are that superchilling is effective and practical, provided that the temperature does not fall below the point where freezing is discernible (about 28.4°F or -2°C) and that the time of holding does not exceed 12 days. The use of seawater with no added salt will insure that the temperature of the fish will not be lowered too much because seawater freezes at about 28.4°F (-2°C).

**Freezing**

The preserving of foods by freezing goes back into antiquity, having been used by such ethnic groups as Eskimos and Indians in certain cold areas. Fish caught in the winter months in cold climates were frozen and held frozen in the cold ambient air. Red meats were also frozen and held in natural, freezing, ambient conditions.

The industrial freezing of foods was introduced by Clarence Birdseye during the 1920's when he developed a process for freezing foods in small packages suitable for retailing. He found that the quality of a variety of foods, including fish, fruits, and vegetables could be preserved for months by freezing and low temperature storage. Subsequent development in freezing equipment and techniques has gradually evolved into the highly sophisticated frozen food and marketing distribution system available to us today. Important events in the development of the frozen food industry and a summary of its past and present are described by Fennema (1976). Much of the refrigeration equipment and techniques used in the frozen food industry has been connected with the preservation of fishery products.

While fresh seafoods are more acceptable to U.S. consumers and carry a higher retail value than frozen seafoods, this is an anomalous situation because the production costs of frozen seafoods are higher than for fresh seafoods. High quality seafoods are worth their extra production costs because they have a much longer shelf life than fresh seafoods, and after purchase they may be put into domestic frozen storage directly without the need to package them and to expend the energy required to freeze them.

Regardless of the comparative acceptabilities and values of fresh and frozen seafoods, much of the seafoods consumed in this country are frozen at one time or another before they reach the point where they are consumed. This is because of the long times involved in the distribution and especially holding of seafoods.

While the use of ice, CSW, or superchilling is adequate for preserving the quality of seafoods for short periods, none of these processes operates at low enough temperatures required to protect quality for long periods. Seafoods may retain their quality for many months if they are properly packaged and held at suitably low temperatures (below 0°F or -17.8°C). Numerous data demonstrate that many seafoods remain virtually unchanged in their quality for periods longer than 1 year when they are held at -40° (-40°F = -40°C). Even at -20°F (-28.9°C), long shelf
lives have been reported for seafoods. The need to thaw frozen seafoods prior to reprocessing in food plants or for domestic use is one undesirable aspect of freezing. Thawing is time consuming and, in some cases, is associated with loss of product quality. It normally takes longer to thaw food than to freeze it under similar heat transfer conditions. In other words, it takes longer for the temperature of a food to go from -10°F (-23.5°C) to 60°F (15.7°C) than it takes the temperature of the food to go from 60°F to -10°F. This is because the thermal conductivity of ice is about four times greater than that of water (Baumeister and Marks, 1966).

This difference in thermal properties affects the surface of the food which is frozen during most of the freezing cycle and unfrozen during most of the thaw cycle. Thus, during freezing, immobilization of surface microorganisms occurs early in the process before much deterioration can occur; conversely, in the thawing process the surface is thawed first and surface microorganisms are provided with good growing conditions for nearly the entire thawing period.

Foods packaged in small units defrost in a few hours at room temperature and during this time are not subject to an undesirable amount of decomposition due to bacterial growth. However, seafoods frozen in bulk (i.e., large fish blocks) may present a defrosting problem. Because bulk-frozen foods take a long time to defrost and because the rate at which the food defrosts depends on the temperature to which it is exposed, there may be a tendency to defrost the food at relatively warm temperatures. When this is done, the surface of the food is subject to microbial spoilage before the inner portions defrost.

Some methods have been developed to alleviate this problem. Refrigerator defrosting (holding at temperatures of 35-40°F or 1.7-4.5°C) is probably the best method of defrosting bulk-frozen foods when no fast method is available. This would apply to large whole fish since bacterial or mold growth would be limited under these conditions. However, in industrial processing, where bulk-frozen products are thawed as an intermediate step in the manufacture of the company's line of products, the refrigeration space required may be so large as to discourage this practice.

With microwave energy, food can be thawed rapidly and with virtually no quality loss. That is because microwaves, by their unique character, cause a temperature rise throughout the product almost simultaneously. The microwave beam penetrates foods with an alternating current. In alternating current, the charge alternates between positive and negative. Because water molecules are polar (i.e., they have positive and negative ends), they are put into a twisting motion due to the alternating current which attracts first the positive end of each molecule then the negative end at a rate of millions of times per second. The twisting action of the water molecules creates considerable friction which generates heat. Ice is not affected by microwaves, but neighboring unfrozen wa-
ter molecules (frozen foods contain some unfrozen water) generate the initial heat that melts adjacent ice to release more water which accelerates the heating.

Since the heat generated in foods by microwaves is quite rapid (about 10 times more rapid than by baking), when uneven heating in a frozen product does occur, the temperature differences within a food can become great. This, however, happens only under certain conditions, and it can be dealt with quite easily. For this condition, and also when one wants to ensure uniform temperature control, one solution is to apply the microwave energy in intermittent bursts. By this technique, the absorbed thermal energy generated during a burst of microwaves is allowed to be distributed by conduction during the intervals between the bursts, thereby permitting the temperature of the food to increase more uniformly albeit more slowly. Modern developments, such as wave guides, have improved the distribution of microwave energy.

The particular advantage of using microwave energy for thawing foods is that deterioration by microorganisms is not a factor. The feasibility and benefits of microwave thawing of frozen meats and fish have been adequately demonstrated, especially for thawing frozen shrimp blocks (Bezanson et al., 1973). Industrial microwave ovens are now used by both the meat and seafood industries.

One potential solution to the problems associated with thawing and the cell damage caused by ice crystals investigated by Charm et al. (1977) is worthy of mention and recommended for further investigation. Basically, the method involves the lowering of the temperature to below freezing (26.6°F or -3°C) without forming any ice by imposing a pressure of 272 atmospheres on the product. Lower temperatures are possible.

One aspect of seafood preservation that has variable importance is packaging. Packaging of seafood performs several basic functions (e.g., protection from contamination). In addition, the package has to serve additional functions, the critical one being gas impermeability (Nickerson and Ronisivalli, 1979). Preventing the frozen seafood from having direct contact with oxygen is highly important.

The rate at which foods are frozen is just as important as the temperature at which frozen foods are held and the range of fluctuation of the storage temperature. When foods are allowed to freeze slowly, water molecules, even though they are slow moving, have time to migrate to seed-crystals resulting in the formation of large ice crystals. When foods are made to freeze rapidly, the sluggish water molecules do not have enough time to migrate to ice crystals but instead are “frozen in their tracks,” so to speak, forming relatively small ice crystals made up of local water molecules. Rapid freezing may be effected by a variety of methods which include the use of liquid and gaseous refrigerants, cold-air blast, and cold-plate contact.

Liquid Refrigerants

Freezing is most rapid when the food is brought into direct contact with refrigerants (i.e., where the foods are immersed directly in a liquid refrigerant, sprayed with liquid refrigerants, or exposed to cold gases emanating from liquid refrigerants). This is because the removal of heat is proportional to the temperature differential at the food surface, and the direct contact between food and refrigerant tends to maintain the temperature differential at the highest possible value for the particular system.

Brine

Brine may be defined as a salt solution. Both the salt and its concentration may vary, depending on the intended application. The salt is generally sodium chloride, and the solvent is water. The principle that dissolved substances depress the freezing point of water makes brine an effective medium for freezing foods. Thus, salt solutions have lower freezing points than pure water, and brine can be made cold enough to freeze foods which are immersed in it while the brine itself remains fluid. The freezing point of brine is determined by the concentration of the salt.

At salt concentrations up to 23.3 percent, the higher the salt concentration, the lower the freezing point. When the concentration of the salt reaches a value of 23.3 percent by weight, the limit of the trend is reached at a temperature of -6°F (-21.2°C). This is the eutectic point for NaCl, and it is the lowest temperature that a NaCl solution will remain fluid. Any further increase in NaCl concentration tends to raise the freezing temperature of the brine.

When one wishes to avoid the use of sodium or when one wishes to depress the freezing point of the brine beyond the limit that can be reached with NaCl, then CaCl₂ may be used. It can be seen from Table 1 that, while there is little difference in freezing point depressions between the two salts up to concentrations of about 20 percent, at 25 percent concentration calcium chloride lowers the freezing point of water to a level that cannot be accomplished with sodium chloride at any concentration. Table 1 also shows that calcium chloride can depress the freezing point of water to as low as -67.0°F (-55.0°C), the eutectic point for calcium chloride. It can be seen that the difference between the

Table 1.—Effect of NaCl and CaCl₂ concentrations on the freezing point of water.

<table>
<thead>
<tr>
<th>Percent salt</th>
<th>Freezing point of aqueous solution of NaCl (°F)</th>
<th>Freezing point of aqueous solution of CaCl₂ (°F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>32.0</td>
<td>32.0</td>
</tr>
<tr>
<td>5</td>
<td>26.7</td>
<td>27.7</td>
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<td>20.2</td>
<td>22.3</td>
</tr>
<tr>
<td>15</td>
<td>12.3</td>
<td>13.5</td>
</tr>
<tr>
<td>20</td>
<td>2.3</td>
<td>-6.4</td>
</tr>
<tr>
<td>23.300</td>
<td>-6.0</td>
<td>-21.2</td>
</tr>
<tr>
<td>25</td>
<td>16.1</td>
<td>-21.0</td>
</tr>
<tr>
<td>25.200</td>
<td>32.0</td>
<td>-35.3</td>
</tr>
<tr>
<td>26.285</td>
<td>32.2</td>
<td>-5.1</td>
</tr>
<tr>
<td>26.308</td>
<td>38.0</td>
<td>-5.8</td>
</tr>
<tr>
<td>29.870</td>
<td>67.0</td>
<td>-55.0</td>
</tr>
</tbody>
</table>

1 Eutectic point for NaCl.
2 Transition point for NaCl.
3 Saturation point for NaCl.
4 Eutectic point for CaCl₂.
eutectic points for NaCl and CaCl₂ is considerable. While the data of CaCl₂ are not carried out, it should be noted that further increases in CaCl₂ tend to raise the temperature. Despite the versatility of calcium chloride, brine for cooling seafoods is produced from sodium chloride. Calcium chloride is used only when very low temperatures are needed to effect rapid cooling or when cooling bulky products.

From the middle 1910’s to the middle 1920’s, immersion of fish in brine was the only known method of quick freezing. While new methods for freezing have been developed since then, brine immersion freezing is still an effective and useful process because of its rapidity and because the fish do not lose water. However, the fish can absorb some salt which has a catalytic effect in oxidative deterioration of the quality of the fish during subsequent storage. Nevertheless, brine freezing is still employed in a variety of situations, including some U.S. vessels; however, in U.S. land-based operation, it has been replaced by other freezing methods. Many plants use brine to prechill fish.

One of the problems with the use of brines is their tendency to corrode equipment when their pH is allowed to fall below 7.0, becoming acidic, and when air enters the system. The pH of brine generally falls in the presence of air due to the carbon dioxide contained in air which dissolves in the brine to form carbonic acid which lowers the pH, and corrosion is enhanced due to the presence of oxygen in the air.

Both corrosion and salt absorption can be reduced without sacrificing the lowering of the freezing point by substituting sugar for some of the salt, provided that the present of sugar is neither restricted nor undesirable. There seems to be no significant conclusions regarding the use of salt/sugar brines except that they accomplish to some degree the objective for which they are used.

Cryogenic Liquids

Cryogenic liquids can be brought to very low temperatures without solidifying. They may be used in direct contact with foods in place of brines. These include liquid nitrogen at -320 °F (-196 °C), liquid carbon dioxide at -108 °F (-78 °C), and Freon-12 (dichlorodifluoromethane) at -21 °F (-29 °C). The number of refrigerants that can be used in direct contact with seafoods is limited because they are required by the Food and Drug Administration (FDA) to meet the same criteria that apply to foods, and only a few of these refrigerants can meet the criteria.

FDA requirements are not the only criteria imposed on the use of liquid refrigerants. Freon-12, although in use by industry for direct contact with foods under FDA sanction over a period of years is now under EPA (Environmental Protection Agency) scrutiny because of its perceived damage to the Earth’s atmospheric ozone layer which would lead to reduce protection from the Sun’s infrared radiation (Semling, 1979). This consideration is bound to affect future decisions as to choice of refrigerants. The EPA’s scrutiny directed at Freon-12 includes other halocarbons even though they may be used in closed systems and do not come in direct contact with foods.

While freezing food by various methods that involve direct contact between them and liquid refrigerants is practiced widely, the holding of frozen foods is largely done in rooms that are kept at freezing temperatures by systems that use any of a variety of fluid refrigerants in what are properly described as mechanical refrigeration systems. These will be described in the following section. However, at this point, we will continue with the discussion of the cryogenic liquids that are used in these systems.

The refrigerants used either in direct contact with food or in mechanical refrigeration systems are classified into three groups. Group 1 refrigerants, which are neither toxic nor flammable, include carbon dioxide, liquid nitrogen, and the fluorocarbons. Group 2 refrigerants are toxic, flammable, or both. Ammonia, which is used in some of the larger industrial installations, is a representative of this group. Group 3 refrigerants are highly flammable and explosive. They include propane, ethane, methane, ethylene, and propylene. This group has limited use and is used only where a flammability or explosion hazard is already present and their use does not add to the hazard. A description of some of the important refrigerants follows. In refrigeration jargon, which is mainly used to avoid contending with the unwieldly names of many of the refrigerants, they are given numbers with an “R,” the R meaning refrigerant (Table 2).

<table>
<thead>
<tr>
<th>Refrigerant</th>
<th>Chemical composition</th>
<th>Chemical formula</th>
<th>Boiling point °F</th>
<th>Freezing point °F</th>
<th>Heat of vaporization at boiling point kcal/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>R717 Ammonia</td>
<td>NH₃</td>
<td>-28</td>
<td>-33.3</td>
<td>-107.9</td>
<td>589.0</td>
</tr>
<tr>
<td>R12 Dichlorodifluoromethane</td>
<td>CCl₂F₂</td>
<td>-21.6</td>
<td>-29.8</td>
<td>-252</td>
<td>-157.8</td>
</tr>
<tr>
<td>R22 Monochlorodifluoromethane</td>
<td>CHClF₂</td>
<td>-41.4</td>
<td>-40.6</td>
<td>-256</td>
<td>-160</td>
</tr>
<tr>
<td>R502 Mixture of 48.8 percent R22 and 51.2 percent R115</td>
<td>CHClF/C₆ClF₁</td>
<td>-49.8</td>
<td>-45.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>R115 Monochloropentfluoromethane</td>
<td>C₅ClF₅</td>
<td>-38.4</td>
<td>-39.1</td>
<td>-159</td>
<td>-106.1</td>
</tr>
<tr>
<td>R728 Nitrogen</td>
<td>N₂</td>
<td>-320.4</td>
<td>-195.8</td>
<td>-415.5</td>
<td>-248.6</td>
</tr>
<tr>
<td>R744 Carbon Dioxide</td>
<td>CO₂</td>
<td>-109.2</td>
<td>-78.4</td>
<td>-69.9</td>
<td>-55.6</td>
</tr>
</tbody>
</table>
one of the best and most widely used refrigerants. It is used extensively in large commercial and industrial refrigeration plants. In small and medium-sized commercial plants, ammonia, which is a strong irritant of eyes, throat, nose, and lungs, is being replaced by Freon 12, 22, and 502, which are Group 1 refrigerants and have many advantageous physical properties, as well as being much safer.

R12. Dichlorodifluoromethane, or R12, has a boiling point of -21°F (-29.4°C) at atmospheric pressure and a latent heat of vaporization of 71 Btu/pound (39.5 calories/gram). Presently, it is the most widely known and widely used refrigerant. It is used in many small commercial refrigeration plants and has a multitude of applications, ranging from small household refrigerators and air conditioners to large centrifugal units for normal- and low-temperature plants and has been used to obtain temperatures as low as -130°F (-90°C) although other refrigerants are better suited to maintain temperatures in that range.

The disadvantage of R12 is that unlike ammonia, it is not compatible with moisture and care must be exercised to remove all air and moisture which otherwise would cause excessively high head pressure and freezing of expansion valves.

R22. Monochlorodifluoromethane, or R22, has a boiling point of -41°F (-40.6°C) at atmospheric pressure and a latent heat of vaporization of 100.5 Btu/pound (55.8 calories/gram). Its physical properties are similar to those of R12 except that it has a lower boiling point, and it operates at a higher discharge pressure than R12. It is used in place of R12 for low temperature applications.

R502. R502 is a mixture of monochlorodifluoromethane (48.8 percent) and monochloropentafluoroethane (51.2 percent) (R22 and R115, respectively). It is especially well suited to low temperature applications providing considerable capacity gain over R22 but with discharge temperatures comparable to R12. It has a boiling point of -50°F (-46°C) and a latent heat of vaporization of 76.5 Btu/pound (42.5 calories/gram). R502 is a recent addition to the refrigerant list but is rapidly becoming recognized and is replacing R22 in many applications.

R728. R728, liquid nitrogen, has a boiling point of -320°F (-196°C). The latent heat of vaporization of liquid nitrogen is 86 Btu/pound (47.8 calories/gram). However, the cold vapor is capable of absorbing another 80 Btu/pound (44.4 calories/gram) in warming up to -40°. Consequently, there is a usable heat-removal capacity of about 166 Btu/pound (92.2 calories/gram).

Both R728 and R744 are suitable for cryogenic freezing, and the choice is mainly an economic one, depending on availability and cost at the location.
Mechanical Systems
Using Liquid Refrigerants

A mechanical refrigeration system consists of an insulated area or room (the refrigerator) and a continuous, closed system consisting of a refrigerant, expansion pipes or radiator-type evaporator located in the refrigerator, a pump or compressor, and a condenser (Fig. I). The compressor and condenser are located outside the refrigerator. The refrigerant, such as ammonia or one of the freons, flows into the expansion pipes as a liquid. Here it evaporates to a vapor and in changing from the liquid to the vapor phase it absorbs heat through the evaporator. The vapor is pulled into the compressor by the suction action of the pump and is then compressed into a smaller volume of hot gas. The latter action causes the gas to heat up and this heat must be taken out. This is done by passing the compressed gas through a system of pipes or radiators usually cooled by water, or sometimes by forced air. Cooling the compressed gas liquefies it, whereupon it is then returned to the evaporator in the refrigerator. The conversion of the gas to a liquid also produces heat which is transferred to the water or air of the condenser. Special valves at both ends of the evaporator allow the required flow of liquid refrigerant in and of vapor out of the expansion system in the refrigerator.

There are a number of ways in which refrigeration may be applied to the insulated area which is to be cooled. Expansion pipes where the refrigerant is evaporated may be located along the walls of the freezer. In this case natural circulation of air (the cold air being heavier) may be depended upon to refrigerate areas within the room away from the expansion pipes, or some type of forced air circulation may be used. In some instances radiation-type evaporation units are used. A fan which blows air through the radiator fins provides circulation of cold air throughout the freezer.

A variety of methods are associated with the use of liquid refrigerants. The following discussion is limited to only some of the systems that are in current use.

Plate Freezing. In plate freezing (Fig. 2), layers of the packaged product are sandwiched between metal plates. The refrigerant (a fluorocarbon such as R12) is allowed to expand within the plates to provide temperatures of -28°F (-33.3°C) or below, and the plates are brought closer together mechanically so that full contact is made with the packaged product. In this manner the temperature of all parts of the product is brought to 0°F (-17.8°C) or below within a period of 1.5-4 hours (depending upon the thickness of the product). The packages are then removed, put into cases, and stored.

Continuous operating plate freezers are now in use. In one such system the freezer is loaded at the front and unloaded at the rear after completion of the freezing cycle. This is done automatically and continually. In another continuous system, the packages are fed automatically on belts which place them in front of eight levels of refrigerated plates. The packages are slid into the spaces between the plates and the plates closed to provide contact. As freezing proceeds, the packages are advanced by a system such that with each opening of the plates the packages are advanced by one row with a new set of packages entering the front row. By the time the packages reach the far side of the plates, they are completely frozen, and they are pushed out of the freezer and unloaded to be cased and stored.

The vertical plate freezer was developed mainly for freezing fish at sea. It is usually used in sodium chloride brine freezing wells and consists of a number of vertical plates forming partitions in a container with an open top. The product is simply dropped into the brine from the top. This type of freezing is limited to lean fish.
of freezer is widely used by the tuna industry. (Calcium chloride can be used when faster cooling times are desired.)

**Immersion Freezing.** Products either packaged or unpackaged can be frozen by direct immersion in cryogenic liquids. The products may be carried through the refrigerant by a submerged conveyer. When the product to be frozen is large (e.g., whole large tuna and swordfish), it may simply be immersed in a tank of refrigerant. There are not many choices for freezing large fish because of the relatively long freezing times required. Here, direct immersion effects rapid freezing.

**Spray Freezing.** The freezing of foods by direct sprays of cryogenic liquids (nitrogen and carbon dioxide) is widely used. In this process individual food portions are placed on a moving stainless steel mesh belt in an insulated tunnel where they are sprayed with liquid refrigerant (Fig. 3). Excess refrigerant is recovered, filtered, and recycled. The food leaves the freezer in the frozen state and is thereafter packaged, cased, and stored. This method provides very fast freezing and is being used especially for some marine products such as the various forms of frozen shrimp. When the liquid refrigerant is evaporated, the still cold vapors are used to precool and temper the product entering the freezer. The very high freezing rates associated with liquid nitrogen freezing results in improved texture, particularly in the case of certain fruits and vegetables.

In the case of carbon dioxide (CO₂) freezing, in order to utilize the liquid CO₂, it must first undergo a change of state to freeze the product at or near atmospheric pressure. Since liquid CO₂ cannot exist at pressures of less than 69.9 psia¹ (4.9 kg/cm²) when it expands from its storage pressure to atmospheric pressure, both gaseous CO₂ and solid dry ice are formed; and depending on the design of the equipment, either the production of CO₂ gas or CO₂ snow can be maximized. The CO₂ snow at -108°F (-78°C) then comes in contact with the product and, combined with the gases, effects the freezing process.

The liquid freon (LF) system is the newest system on the market and uses specially purified dichlorodifluoromethane (R12). The product is carried into the unit by a conveyer and dropped into a moving stream of R12 on a pan to separate and crust-freeze food particles as they are distributed and moved from the drop zone of the freeze belt. The freeze belt carries the food under sprays of refrigerant to complete the freezing process. A third conveyer then carries the food out of the freezer. R12, which has been vaporized as a result of heat extraction from the food, is recovered and reliquefied by contact with a condenser located above the freeze conveyer. Condensed refrigerant is collected in a sump and recycled to the spray nozzles. The system is very efficient because only minimal amounts of refrigerant are lost, about 0.5-0.7 kg per 45.5 kg (1-1.5 pounds per 100 pounds) of processed food. Most of the losses are residual amounts left on the food, and these evaporate very rapidly.

**Refrigerated Air**

Although air is fundamentally a poor conductor of heat, the fact that its density changes as its temperature changes permits its use as a contact refrigerant, albeit relatively slowly. Cold storage warehouses can lower the temperature of a food that is at higher temperature than the air within the cold room by conduction at the interface between the food (or its package or overwrap) and the air within the room which is put into motion as its specific gravity changes. That is, air made cold by the evaporator (or expansion pipes) is made more dense and tends to migrate to the floor of the cold room forcing the warmer air to migrate upward. Thus, the food surfaces are continually exposed to cooler, moving air molecules that acquire heat from the food by conduction, then are lifted by the buoyant force of the denser air molecules away from the food whereupon other cold molecules repeat the cycle. When foods are not protected by packaging or an ice glaze that is impermeable to water vapor, or otherwise prevents loss of moisture, the cold air which is also relatively dry will condense water molecules and tend to dehydrate the food as well as cool it. The water carried by the air is then condensed on the evaporator coils where is can be seen as “frost.”

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¹Pounds per square inch absolute. This means that when the pressure is measured with a pressure gauge, the value of the prevailing barometric pressure must be added to the gauge pressure to obtain psia.
**Sharp Freezers**

Sharp freezers employing the refrigerated air principle, were used in early installations and are still generally used on the Pacific coast and in Alaska. They are essentially cold storage rooms that cool the foods by air convection. In some of the early sharp freezers, shelves made of pipe grids or metal plates containing the refrigerating medium were installed on which the product to be frozen was placed. There is no rapidly circulating air so freezing is relatively slow depending on the size and shape of the product and the manner in which it was distributed on the shelves.

**Jacketed Freezers**

The jacketed freezer (Fig. 4) is designed so cold air circulates through an enclosed jacket completely surrounding the product storage space. It is simply a room within a room and allows storage at near 100 percent relative humidity and at a constant temperature. These conditions greatly reduce the weight loss of unpackaged foods and frost formation inside packaged frozen foods. The jacketed principle, although a good one, has not been accepted by the industry nor used to any great degree owing to prohibitive building costs.

**Blast Freezers**

Blast freezers are generally rooms or tunnels in which cold air is circulated by one or more fans through an evaporator and around the product to be frozen. Air blast freezers are generally preferred when unwrapped products of irregular size are involved (i.e., large fish in the round). The blast freezer may be of the batch type, semicontinuous or continuous, depending on whether the product is supported on racks, trucks, or moving belts (Fig. 5). Some of the latest designs are very efficient and space requirements are minimal due to a vertical spiral configuration of the continuous conveyor which moves the product through the freezer. These are known as belt freezers but, along with tunnel freezers, are still basically of the air blast variety.
Fluidized Bed Freezers

When particles of fairly uniform shape and size are subjected to an upward air stream, they are said to become fluidized. By this principle, food products of small uniform size, such as scallops and krill, can be frozen. Depending on the characteristics of the product particles and the air velocity, they will float in the air stream, each one separated from the other, surrounded by air and free to move. Under these conditions, the mass of particles behaves like a fluid. The product can then be frozen and simultaneously conveyed by air without the need of a mechanical conveyor. The advantage over belt freezing is that the product is truly individually quick frozen (I.Q.F.) and even applies to foods that tend to agglomerate.

Dehydrocooling

Dehydrocooling is the lowering of the temperature as a result of removal of water by evaporation. It is a practical method in current use for some applications, especially for cooling leafy vegetables. In practice, the process is a simple one involving the controlled evaporation of moisture from the surfaces of products to be cooled.

Water and substances containing it maintain a water-vapor pressure (that depends on temperature) above them in a state of equilibrium. Although the system is a dynamic one (i.e., water molecules are continually being vaporized while vaporized molecules are continually being condensed), the equilibrium is maintained for any given temperature. This is because the number of molecules being vaporized equals the number being condensed. In this condition, the heat lost by evaporation is regained by condensation.

This equality always exists until there is a change in conditions such as a change in temperature or pressure. A drastic disturbance to the system occurs when a vacuum is created in a chamber containing water or a substance containing water. The vacuum creates a reduction in vapor pressure which in turn creates a sudden drop in the condensation rate while simultaneously accelerating the evaporation rate. During this rate imbalance, the heat lost exceeds the heat gained, and there is a net cooling effect. If the vacuum is maintained, the cooling effect can be substantial, and foods can be cooled to below freezing temperatures relatively quickly.

Although dehydrocooling also can dehydrate the product, this can be nullified by the addition of water to the system through an internal water sparger. Employing a water sparger to prevent dehydration, Carver (1975) found that he could cool headed and gutted whiting from a temperature of about 59°F to 32°F (15°C to 0°C) in about 18 minutes (Fig. 6).

Beckman (1961) was granted a patent for “conserving fresh fish” aboard a vessel. By the Beckman process, the fish are eviscerated, washed, and placed into cylindrical tanks which are connected to a steam jet vacuum pump located in the engine room, which reportedly can reduce the pressure within each tank to about 2 mm of mercury. The tanks resemble vertical retorts and can be loaded and unloaded by baskets filled with fish and which fit into the tank. Each tank is designed to reduce heat gain and contains a water injection system for preventing dehydration of the product. The temperature of the product is brought down to 30.2°F (-1°C) and maintained at that temperature until brought to land. The advantages of low temperature holding and the elimination of oxygen, especially with treatment occurring just after the fish are caught, are obvious.

Use of Jet Aircraft at High Altitude

It is widely known that the temperature at altitudes used by commercial jet-powered aircraft is very low (Fig. 7). The use of jet altitude freezing was proposed as a means of transferring seafoods from the coastal areas of large underdeveloped areas like India to the interior of the country as a solution to transport protein foods from an area of abundance to an area of need where other means of temperature controlled transportation is unavailable.

By this proposed method, fresh landed fish are placed in special containers and loaded in specially designated aircraft and flown to inland airfields located more than 2 hours of flying time from coastal areas — sufficient time to freeze the product. The proposal, initiated by an NMFS technician, was evaluated by the Manager of New Products Investigations, the Boeing Company*, and given as a problem to the company’s engineering staff. Convinced of the potential of the idea, the Boeing group produced a design for a proto-

*Mention of trade names or commercial firms does not imply endorsement by the National Marine Fisheries Service, NOAA.
type system using a modified Boeing 727 (Fig. 8) and a special container (Fig. 9). Theoretical problems such as possible aerodynamic interference from the need to pass the outside air through the aircraft and inefficient heat removal by the rarefied atmosphere at jet altitudes were considered, analyzed, and discounted. Although we have not tested this concept, nor do we have any information that anyone else has, theoretically, it has been deemed entirely feasible, and there is no known impediment to its use. With the rising costs for energy to freeze foods, this concept has potential for foods that are destined for long distance transportation; because in these cases, the heat removal is done at little or no cost.

**Summary**

While there are a number of factors that affect the rate at which seafoods spoil, temperature control remains as a major one in the control of their quality. This paper has reviewed the principles, the methods, and the refrigerants used to chill seafoods (32°F or 0°C), superchill them (26.6 to 30.2°F or -3 to -1°C), or freeze them (0°F or -17.8°C or below).

For chilling seafoods, ice, with its high latent heat of fusion, is effective and widely used. When ice is in small particles (i.e., flaked), cooling rates are high and damage to the product is minimized. The amount of ice required varies with each situation, but it should be enough to maintain the product at 32°F (0°C) as long as necessary. In some instances, vessels require about one-fourth the weight of the expected catch or less. In other cases, the requirement could be as high as half the weight of the expected catch. Ambient temperature, length of trip, and degree of insulation are among the major factors that affect the weight of ice required.

Chilled seawater, a mixture of ice and water, chills fish more quickly than ice alone, and by its buoyant effect, prevents damage to the fish. The requirement, again, varies with each situation, but a ratio of 1:2:7 (weight of ice:weight of water:weight of expected catch) has been used successfully with an insulated vessel.

Refrigerated seawater (RSW) usually involves mechanical refrigeration, and, in this case, the product temperature can be lowered below 32°F (0°C) to the superchill range.
This system provides a better and more varied control, but it requires capital equipment and maintenance, and provisions have to be made to inhibit the corrosive effects of the seawater on the RSW components.

Because the seafood spoilage rate is directly related to the temperature, supercooling, which is in the range from 26.6 to 30.2°F (-3 to -1°C) provides the product with a longer shelf life than chilling (32°F or 0°C).

Freezing occurs over a broad range of temperatures below 26.6°F (-3°C). However, freezing is a stepwise process, and it is not until the temperature is lowered to 0°F (-17.8°C) that enough water is immobilized to effect a reasonable stabilization of product quality for about 1 year. At higher temperatures, chemical reactions involving enzymes and oxygen will eventually degrade the product quality. At lower temperatures the product quality will remain high for many months and even years.

Because salt lowers the freezing point of water, brine (usually a solution of sodium chloride) is used to freeze large products like whole tuna by direct immersion. Short brine dips are also used to chill fillets. Brines do impart salt to the product, the amount depending on a number of factors, and they do tend to corrode equipment.

Other freezing solutions that can be used for direct immersion of food include liquid nitrogen, liquid carbon dioxide, and a number of halocarbons such as R12 (dichlorodifluoro methane). The halocarbons, including R12, R22 (monochlorodifluoromethane), and R502 a mixture of R22 and R115 (monochloropentafluoroethane), are used in mechanical refrigeration systems where there is no direct contact with the food.

Conventional freezing techniques and equipment described include plate freezing which involves sandwiching the product between refrigerated plates; immersion freezing which simply involves the immersion of product in cryogenic liquids; spray freezing which occurs when cryogenic liquids or gases are sprayed directly on the product carried by a conveyor belt; refrigerated air, a slow process occurring when a product is simply placed in a chamber that is held at freezing temperatures (the sharp freezer is an example); the jacketed freezer which involves a double-walled chamber and controls humidity to 100 percent relative humidity is another variation of refrigerated air; blast freezing which involves refrigerated air that is driven across the product by powerful fans; and fluidized freezing which involves the suspension of product particles that are frozen as they are buoyed by cold air forced upwards. A conventional process in the agricultural industry, dehydrocooling, has a demonstrated potential for freezing seafoods. A theoretical, but apparently sound process, jet altitude freezing, has not yet been demonstrated but has a scientific basis for its consideration and has withstood analytical critiques regarding aerodynamic, economic, and technical feasibilities.

**Literature Cited**


