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<th>Recent R&amp;D on fish freezing with emphasis on cryoprotectants</th>
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Selected recent R&D findings on fish freezing are considered under six headings below. While most of the areas have been fairly extensively researched, the overall picture regarding fish freezing and storage is still incomplete. This may be due to the fact that the areas have been studied individually, rather than collectively, and important interactive effects and synergy have been missed and/or neglected. The freezing and storage of fish and shellfish has been reviewed recently by Morrison (1) and it is clear from the review that continued research on the long established PPP (product-process-package) and TTT (time-temperature-tolerance) factors (2) in combination with hazard analysis of critical control point (HACCP) (3) and quality systems (4) is the key to ensuring high quality frozen seafood products for the consumer. The findings from a recent survey (5) in the USA on consumer attitudes towards fresh and frozen fish showed that there is no room for complacency. Many of the consumers held a persistent belief that frozen fish is substantially inferior to fresh, i.e. less nutritious, more bones, and using only ‘offcuts’. This highlights the need for concerted efforts to rectify possible misunderstandings about frozen fish/fish products, including packing them in see-through packs so that consumers can actually see the fish they are buying.

1. **Fresh fish history:** A survey (6) on the R&D requirements of 819 food SMEs indicated that research on raw material quality was their top priority. Tests in Norway (7) have indicated that more attention should be paid to freshness than to freezing rate and that fish frozen in the pre-rigor state gave by far the best yield and quality. Rigor status of fish at time of freezing has major implications for gaping. Procedures for assessing fish freshness have been reviewed by Whittle *et al* (8) while Southey *et al* (9) have found large variations in quality indices both between and within three batches of good quality cod fillets. The upgraded Quality Index Method (10) is used as a sensory system for determining the freshness of thawed whole cod and is particularly relevant as much raw material (for further processing) is received as frozen fish.

2. **Freezing conditions:** Freezing and freezing methods have a major effect on water relations in fish and the consensus is that fast freezing (1°C/min) produces the best quality in that it induces small ice crystals, evenly distributed in the muscle. Slow freezing (5°C/hour) produces large damaging ice crystals (11). The effect of the type of material being frozen also has a major bearing on frozen/thawed quality as indicated by centrifugal drip loss values of 278, 267 and 345 g/kg for fillets from frozen fish, block frozen fillets and block frozen mince, respectively (12), i.e. mincing prior to freezing had a particularly adverse effect on the water-holding capacity of these samples of silver smelt (*Argentinus silus*). There is also considerable interest in two-stage freezing with the second stage being termed superfreezing (7) where the product is held at -50 to -60°C in order to give an extended shelf life. The first freezing (salmon fillets) was in a tunnel at -28°C to a core temperature of -22°C. The product was then transferred to a regional 'super freezing' low temperature cold store where the temperature was lowered to -50 to -60°C for long term storage. Some recent developments in freezing equipment include the AIR Products Cryo-Dip, and the Dybvad Stal Industri (DSI) range of horizontal plate freezers. The former has a capacity of up to 5 tonnes/hour, depending on the product, and allows companies easy
entry to IQF (liquid nitrogen) products because of its relatively low capital cost. The DSI plate freezers are easily cleaned and are convertible with short change-over times which benefits freezer trawlers and land based plants switching between herring and mackerel seasons (13).

3. **Storage conditions:** There are relatively few data in the literature on the effects of storage temperatures below -30°C on fish quality, although there is increasing evidence (7,14) that temperatures of -50 to -60°C are beneficial in terms of product quality, especially for fatty fish such as mackerel and herring. This relates to the two stage or 'super freezing' outlined under heading 2 above. Scudder (14) claims that the reason -18°C is used as a storage temperature is that it corresponds to 0°F. However, he stresses that the breakdown of triethylamine oxide (TMAO) to dimethylamine (DMA) and formaldehyde occurs readily at -18 to -20°C. The level of breakdown is reduced greatly below -24°C and becomes lower still below -30°C. The breakdown of TMAO to DMA and formaldehyde is of major significance in that the latter bonds with the fish proteins to cause toughening. These findings are supported by those of Howell (15) who showed that toughening due to protein aggregation increased more rapidly during storage at -20°C than at -30°C for cod, and especially for hake. Fluctuating cold storage temperatures below the freezing point also adversely affect the quality of frozen fish (11) due to recrystallisation and other effects. This topic will be studied in the ongoing EU concerted action on ‘The Preservation of Frozen Food Quality and Safety throughout the Distribution Chain’.

4. **Thawing conditions:** A thermal arrest (freezing plateau) occurs between 0 and -5°C, even in fast freezing of fish, and 5-10% of the muscle water has not formed ice crystals even at -20°C. This water is bound in the protein membrane structures and can still be active in chemical reactions (11). The glass transition state, where the whole fish forms a crystalline inert state, occurs when the temperature falls to -50°C or below. During thawing the opposite situation arises. The ice crystals turn to water
but with a longer thermal arrest as the heat transfer is faster in ice compared to water, and during thawing heat is transferred through a growing layer of water. The thawing process influences fish muscle structure and biochemistry (16) almost as much as freezing. Fast thawing does not allow ice crystal growth or recrystallisation to the same extent as slow thawing and gives a more intact appearance to the muscle structure and also a lower drip loss. Water heated to 40-60°C is usually used for defrosting, although forced humid air is also used, but to a lesser extent. Microwave and dielectric thawing systems are also under consideration.

5. **Double freezing:** Logistics often demand that fish are frozen ‘round’, and are then thawed, filleted and refrozen. Many processors also use fish from frozen fillet blocks which are thawed and are used for consumer fish products which are then refrozen, i.e. double freezing is common-place in today’s fish processing industry. A second freezing results in new ice crystal formation and a ‘repeat’ of the chemical changes occurring during the first freezing. However, ongoing research at The National Food Centre suggests that the second freezing is not as destructive in quality terms as the first, at least for some species.

6. **Cryoprotectants:** Extension of the shelf life of fish, and especially of fish mince, during frozen storage can be achieved by the incorporation of ingredients, e.g. cryoprotectants, that are able to prevent ice crystal growth and migration of water molecules from the protein, thus stabilising the protein in its native form during frozen storage (17). Recent research (18,19) at The National Food Centre investigated the use of nine dairy ingredients as potential cryoprotectants, in mince of cod, haddock, salmon and spent salmon which had been put through three freeze-thaw cycles. The ingredients (80 g/kg of fish mince), affected mince composition, colour, water holding capacity (WHC) and gel strength. There was an inverse relationship between the WHC of the thawed fish tissue and the compressive strength of fish gels prepared from the mince. Milk protein isolate and caseinates gave WHC values higher than the
controls for the four fish types. Whey protein concentrates gave the firmest fish gels and caseinates the softest. Fast freezing of cod mince resulted in higher WHC values and stronger gels than slow freezing. Different inclusions (20, 40, 80 g/kg of mince) of whey protein concentrate did not affect WHC values whereas sodium caseinate at the 80 g/kg inclusion level gave a much higher WHC value. These two dairy ingredients did not affect gel compression values for gels made from fast frozen mince; however, increasing inclusions gave stronger gels in the case of caseinates, and weaker gels in the case of whey protein concentrate, for samples of slow frozen mince. The addition of water greatly reduced gel strength, and whey protein concentrates or caseinates did not increase added-water gel strength values over those of the control. Taste panellists preferred cod nuggets containing whey protein concentrate over a control sample, while cod fish nuggets containing added water were downgraded.

Further research (20) at The National Food Centre is evaluating the cryoprotective effect of sodium caseinate and whey powder in minced frozen samples of 11 underutilised fish species. Whey powder fish gels had higher compression values than those with caseinates for six of the species but the reverse was the case for the five others, three of which were of the shark family. The gels are being examined by confocal microscopy to determine if there are major structural differences.

7. **Conclusions:** Fish freezing, frozen storage, and thawing are influenced by many factors, a number of which interact. The research items presented here are only a small selection of the overall recent R&D activity on the freezing of fish in Europe and world-wide. However, scanning the international literature confirms that much fish R&D still needs to be done.
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