Thermal Behavior during High Pressure Freezing
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ABSTRACT
This study focuses on heat transfer during high pressure (HP) freezing. HP depresses the initial freezing point of water below 220 MPa [1]. Pressure shift freezing (PSF) consists in creating a supercooling by a rapid pressure shift. The aim of PSF is to initiate fine nuclei in the whole volume of the sample. Experiments were realised in a 3 liters HP vessel. Cylindrical samples (4.2 cm diam.) were realised with a plastic film containing a high porosity (0.98) foam which was filled with pure water. Experiments pointed out the influence of the pressurisation rate on the duration of the first steps of the process.

HIGH PRESSURE AND FOOD TECHNOLOGY
Three domains of food processing are potentially interested in HP [2]: food texturation, food preservation and phase change. HP thawing and/or freezing were presented by Taylor [3] and then by [4] and [5]. HP thawing is one of the potential application of HP to food. The decreasing of the phase change temperature with pressure permits to shorten the thawing time. HP assisted freezing is an other potential application of HP to food.

THE PRESSURE SHIFT FREEZING PROCESS
Heat transfer phenomena during freezing are in relation with the quality of frozen foods. A slow freezing rate results in larger
ice crystals which might damage the texture of the food. Furthermore,
as the heat transfer is applied to a surface of the food, it causes
the ice crystals to grow aligned and perpendicular to that surface.
The mean size of the ice crystals is in relation with the freezing
rate. A high freezing rate can be obtained either by a high heat flux
rate or by supercooling. The ice-nucleation rate is enhanced in
increasing supercooling.

![Figure 1](image)

**Figure 1**

Key points of a pressure shift freezing process (pure water)

PSF consists in placing a food in a HP vessel whose temperature
is regulated below the initial freezing temperature of the food. The
vessel is closed and pressure increases (phase #1 in figure 1) up to
a pressure for which freezing is not possible. When the temperature
of the sample is close to the regulated temperature (phase #2),
the pressure is released (phase #3). Thus, water find itself in
supercooling condition and an homogenous ice nucleation is realised
at core. The latent heat is exchanged with the sensible heat of the
substance (pure water in our case). The percentage of frozen water
after the pressure shift can be roughly estimated in writing the
conservation of heat for the unit of mass of water. Equation (1) is
calculated in assuming heat of compression as negligible and
thermophysical properties as independent functions of pressure.

\[
m_{\text{WATER}} \cdot C \cdot \Delta T_{\text{SUPERCOOLING}} = L \cdot m_{\text{ICE}}
\]

With the specific heat of water \(C=4180 \text{ J.kg}^{-1}.\text{K}^{-1}\),
\(\Delta T_{\text{SUPERCOOLING}} \approx 20^\circ\text{C}\) (if \(P=200\text{MPa}\)), and the latent heat of solidification
of water \(L=333.10^3 \text{ J.kg}^{-1}\). The result of equation (1) is 25% of
frozen water. This amount of ice is made of numerous very fine nuclei
which will grow during phase #4. The freezing process is finished
whith the phase #5. Deuschi and Hayashi [4] presented thawing and
freezing of ice blocks. Kanda et al. [5] did a comparative study
between PSF and air blast freezing. The HP vessel was 460 ml (diam.
54mm). Sample were freeze dried and tissues were observed by S.E.M.
In the case of PSF, the particle size of ice crystals was comprised
between 50-150 \(\mu\text{m}\) (PSF at \(-10^\circ\text{C}\)) and 30-100 \(\mu\text{m}\) (PSF at \(-18^\circ\text{C}\)). By air
blast method at \(-18^\circ\text{C}\), they observed small ice crystals in the center
of the sample. The rest was a big long and slender ice crystal. They found no noticeable differences between Tofu before freezing and samples frozen by PSF method at -18°C in terms of appearance.

MATERIAL AND METHODS

The HP vessel (12 cm diam.) is presented in figure 2. One thermocouple (1.5 mm diam.) was placed at center of the sample to record the temperature. A 50% ethanol aqueous solution was used as pressurization fluid.

![Diagram of HP vessel](image)

Figure 2. Experimental HP vessel with the sample

The initial temperature of the sample was of 2°C. The vessel was maintained at a regulated temperature of -18°C and the pressure was elevated up to 200 MPa. An experimental plot of temperature versus time is presented in figure 3. In case #1 (T1), the pressure was elevated in 2 minutes up to 200 MPa. In case #2, the pressure was elevated at a constant rate of 5 MPa.min⁻¹ up to 200 MPa. In case #1, the temperature of the sample trended asymptotically to the ambient temperature (-18°C) after 60 minutes. In case #2, the sample temperature followed the linear pressure rise with respect to the phase change temperature up to -18°C and reached this temperature after 40 minutes. This shows that the excessive duration of the first steps of the process (up to phase 3) can be reduced in controlling the rate of the pressure rise. This experimental result might be explained as follow. On the first hand, an explanation based on heat transfer considerations could be proposed. Yet, the heat flux rate is controlled by natural convection in the annular gap located between the sample and the HP vessel. In case #1, the convective heat transfer coefficient decreased rapidly as the temperature difference (ΔT) between the hot wall (surface of the sample) and the cold wall (surface of the vessel) decreased rapidly. In case #2, the quasi linear temperature decrease of the sample corresponded to the phase change temperature with respect to pressure proposed by [1]. Thus, the temperature difference (ΔT) decreased slowly and the mean value of ΔT was higher in this latter case. This indicates too that a partial phase change was occurring during pressurisation. On the other hand, the increasing of the heat flux in case #2 could be explained by the fact that natural convection in a 50% ethanol aqueous solution
might be enhanced under moderate pressure. Complementary experiments should be realised to test these assumptions. Yet, this result corresponds to a convenient balance between convection in the annular gap and heat conduction in the sample. The convenient pressurization rate is a function of the geometry and of the thermal conditions.

![Figure 3 - Experimental Pressure shift freezing (phase #1)](image)

**CONCLUSION**

Pressure shift freezing experiments were realised with pure water. These experiments showed that the duration of the initial cooling at the start of the process can be reduced in controlling the pressurization rate. An explanation based on the influence of pressure and of phase change phenomenon on the convective heat transfer in the annular gap between the sample and the vessel is proposed.

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**LITERATURE CITED**

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