

# Structural Studies on Unpackaged Foods during Their Freezing and Storage

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**ABSTRACT:** During the freezing and frozen storage of unpackaged foods, their surface is exposed to mass transfer with the environment. Basically, ice sublimates and forms a dry, porous layer. This fact alters the sensory characteristics of the products and originates an important quality loss. In this work, a mathematical model was used to predict the thickness of the dehydrated layer, taking into account the influence of operating conditions and food characteristics. Based on the predictions of the numerical model, 2 regression equations were proposed to calculate the size of the dehydrated layer after freezing and storage, having the operating conditions and food properties as parameters. Besides, the frozen storage of the products was studied over different time periods (1, 2, and 3 mo) using beef cylinders and slices, as well as minced beef balls and hamburgers. The dimension of the dehydrated layer and the induced changes in the food surface structure were determined by image analysis and environmental scanning electron microscopy (ESEM). The experiments determined an increase in the depth of the dehydrated layer when storage times are longer, which could be adequately related to storage conditions through the predictions from the numerical model and the regression equations.

**Keywords:** freezing, frozen storage, ice sublimation, simplified prediction method, surface porous structure

## Introduction

Among many currently used methods for food preservation, those based in the action of low temperatures—refrigeration and freezing—are some of the most important. Freezing is particularly widespread because it does not require chemical agents or irradiation and assures long-time shelf life. Besides, nutrient losses are minimized when exposing the food to low temperatures, as opposed to what happens during thermal processing or hot-air drying (Cheftel and Cheftel 1991).

In spite of the numerous advantages of freezing with respect to other usual preservation methods, several sources of quality loss during this process must be considered: essentially, those derived from the influence of freezing rate on food structure. From a physical point of view, low freezing rates produce big ice crystals that damage tissues structure, inducing an important quality loss. Fast freezing generates a higher amount of smaller ice crystals, which produces a lower overall damage (Martino and others 1998).

In both freezing situations and during the later frozen storage, in the case of unpackaged foods, these undergo mass transfer with the environment. Therefore, apart from water freezing, surface ice sublimates, leaving holes in the food matrix, forming a dry, porous layer, and altering the sensory characteristics of the products. This leads mainly to quality decay—owing to weight loss—and to general appearance spoilage, for instance, changes in color, taste, and texture.

Related literature includes different publications in which the size of ice crystals is characterized as a function of operating conditions for different freezing methods (Bevilacqua and others 1979; Martino

and others 1998). However, none of these works analyzes the surface structure of foods subjected to the freezing process.

Literature also presents a few works that include experimental data of weight loss due to surface ice sublimation during freezing (Lambrinos and Aguirre Puente 1983; Campañone and others 2003) or during frozen storage (Lambrinos and Aguirre Puente 1983; Aguirre Puente and Sukhwal 1984; Pham and Willix 1984; Mendez Bustabad 1999; Campañone and others 2003). In none of the mentioned publications is weight loss related to the size of the dehydrated surface layer or to its structure. Only one publication was found (Chumak and Sibiriakov 1988) that provides data of sorption isotherms of frozen meat, which is fundamental for modeling and simulation.

For other food preservation processes, different from freezing, the influence of operating conditions on the resulting surface structure of food pieces was studied. For situations where water loss by evaporation or sublimation occurs, studies include drying (Wang and Brennan 1995; Krokida and others 1997), freeze-drying (King 1971; Krokida and others 1998), and osmotic dehydration (Barat and others 1998; Salvadori and others 1998). Research in this area is aimed at the characterization of food surfaces using certain parameters such as porosity, pore distribution, and tortuosity, which are specific of the process and the food and, for the same process, depend on the operating conditions. That is why the results of these processes are not directly extrapolated to food freezing and frozen storage.

Based on the previous considerations, it can be inferred that the structure of food surfaces during freezing and storage with simultaneous ice sublimation has not been adequately described or analyzed yet.

From the scope of mathematical modeling, freezing and frozen storage with surface dehydration have been satisfactorily described. Campañone (2001) and Campañone and others (2001) have presented a mathematical model that solves the differential equations arising from the coupled microscopic energy and mass balances during freezing and frozen storage. The model pays special attention to the generation and growth of a porous, dehydrated surface

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layer and to the specific characteristics of the heat and mass transfer phenomena in it. The implemented numerical solution predicts accurately freezing times and weight losses during freezing and frozen storage, the growth of the dried porous layer, and the behavior of the products exposed to fluctuating operating conditions. To our knowledge, this model constitutes the only tool to predict the depth of the dehydrated surface layer in function of operating conditions and process times.

Despite the fact that the numerical method provides general and basic information on the phenomena involved, from a practical point of view, it would be very useful to count on a simplified prediction method for the calculation of the depth of the dehydrated layer. Such prediction equations have already been developed for related situations, as the evaluation of freezing times and weight losses as a function of operating conditions and food characteristics (Cleland 1990; Salvadori and Mascheroni 1991; Campañone and others 2005a, 2005b). But, up to now, an equivalent prediction method has not been introduced to predict the thickness of the sublimated surface layer.

Based on the abovementioned needs and possibilities, the objectives of the present work include:

- The development of approximate prediction equations for calculating the size of the surface dehydrated layer as a function of food characteristics and freezing and storage conditions;
- The evaluation of the size and structure of the dehydrated layer, for different frozen meat samples stored during diverse time periods;
- The validation of the predictions from the developed equations against the experimental data obtained during this research.

## Materials and Methods

### Mathematical model

During freezing of unpackaged foods, 2 phase changes take place simultaneously: the free liquid water is frozen and the superficial frozen water sublimates. In the case of frozen storage, only 1 phase change takes place, the sublimation of the superficial ice.

From a physical point of view, food can be considered as a combination of a solid matrix, an aqueous phase, and a gaseous phase (air and water vapor). For the freezing process, the food can be divided into 3 zones: unfrozen, frozen, and dehydrated. During the storage, there are only 2 zones: frozen and dehydrated. From the mathematical point of view, the storage stage can be considered as a special case of the most general formulation (freezing stage) and needs no special mathematical development.

A complete mathematical model has to solve the heat transfer (freezing) and the mass transfer (weight loss) simultaneously. As the industrial freezing process begins with the food at temperatures higher than  $T_{if}$ , the model must also consider the weight loss by liquid water evaporation during the initial refrigeration step.

In previous works (Campañone 2001; Campañone and others 2001), a complete numerical modeling was performed for regular 1-dimensional shapes (slab, infinite cylinder, and sphere). The developed formulation accounts for each of these 3 geometries by means of the use of the geometric index  $GI$ . In brief, the microscopic heat and mass balances lead to Eq. 1 and 2, which are valid for all the food ( $0 \leq x \leq L/2$ ), where  $x$  is the axial or radial coordinate. Adequate initial and boundary conditions are considered:

$$\rho C_p \frac{\partial T}{\partial t} = \frac{\partial k}{\partial x} \frac{\partial T}{\partial x} + k \frac{\partial^2 T}{\partial x^2} + GI \frac{k}{x} \frac{\partial T}{\partial x} \quad (1)$$

$$\frac{\partial C}{\partial t} = \frac{\partial D}{\partial x} \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2} + GI \frac{D}{x} \frac{\partial C}{\partial x} \quad (2)$$

In each region (unfrozen/frozen/dehydrated), specific values for the thermal properties are needed. Besides, in the unfrozen and frozen regions the values of water concentration and diffusion coefficient considered are those of liquid water:  $C_w$  and  $D_w$ . Meanwhile, in the dehydrated zone, they are of water vapor:  $C_v$  and  $D_v$ .

When the surface is already frozen and sublimation begins, an additional balance is needed to evaluate the position of the sublimation front  $x_1$  and the thickness  $\delta$  of the dehydrated layer. In this sense, the model establishes that, at  $x = x_1$ ,

$$-m_s \frac{dx_1}{dt} = -D_v \frac{\partial C_v}{\partial x} \quad \text{where } m_s = \rho[w - f_{ads}(1 - Y_0)] \quad (3)$$

and at the food surface ( $x = L/2$ ):

$$-D_v \frac{\partial C_v}{\partial x} = k_m (C_v - C_{va}) \quad (4)$$

Then

$$\frac{dx_1}{dt} = \frac{D_v \frac{\partial C_v}{\partial x}}{\rho[w - f_{ads}(1 - Y_0)]} = \frac{k_m (C_{va} - C_v)}{\rho[w - f_{ads}(1 - Y_0)]} \quad (5)$$

That is to say: the mass of sublimated ice (left-hand side term in Eq. 3) equals the amount of water vapor that diffuses through the dehydrated layer (right-hand side of Eq. 3) and the amount of water vapor that is transferred from the food surface. So the movement of the dehydration front and its position can be related to mass transfer in food surface (Eq. 5), and the thickness of the dehydrated layer is evaluated by Eq. 6:

$$\delta = x_1 - L/2 \quad (6)$$

The system of coupled nonlinear partial differential equations (Eq. 1 to 3) was solved by an Implicit Finite-Differences Method (Crank-Nicolson centered method), coded in FORTRAN 90 (Fortran PowerStation 4.0, Microsoft Developer Studio, Microsoft Corp. 1994). In the dehydrated zone, a variable grid was applied to overcome the deformation of the original fixed grid due to the shift of the sublimation front (Campañone and others 2001). This numerical model was used in this work to generate the theoretical data of the depth of the dehydrated layer during freezing and storage, for different operating conditions. These data were later used to develop the simplified prediction equations. Further details on the development, implementation, and use of the numerical method can be found in the original publications (Campañone 2001; Campañone and others 2001).

### Experimental determinations

Each test consisted of the continuous measurement of weight and internal temperature of the samples along the different stages of the refrigeration process (initially unfrozen, later partially or completely frozen, and finally stored at low temperature). These experiments were performed in a prototype freezing-storage tunnel, which is able to have its operating conditions (air rate, relative humidity [RH], and temperature) varied within certain ranges. A complete description of the tunnel is presented elsewhere (Campañone and others 2003). Figure 1 shows a scheme of the test tunnel.

All the experiments involved the continuous measuring of weight loss and internal temperature of the various products during

freezing of unpackaged beef samples of different shapes and sizes and their storage (also unpackaged) during 3 mo.

Three replicates of each sample were used in each experimental series; 2 of them to measure weight variations and the remaining 1 to record the thermal history. The characteristics of the different samples were the following:

- Minced beef hamburgers, 1.5 cm thick and 10 cm dia;
- Beef slices (semitendinous muscle), approximately 2 cm thick and 8 cm dia;
- Beef cylinders (semitendinous muscle), 10 cm long and 2.5 cm dia. Both circular bases were isolated with polystyrene plates (5 mm thick) to avoid heat and mass transfer through these surfaces and to allow transfer only in the radial sense.
- Minced beef balls, 4 cm dia.

The initial water content was 66% for minced beef and 74% for whole beef.

To resemble real freezing situations, the initial food temperature was higher than the freezing temperature. This was accomplished by storing overnight the samples in a refrigerated chamber at 10 °C.

Samples and air temperatures were measured and recorded using type-T thermocouples linked to a data acquisition and control system (Keithley KDAC Series 500). Weight of samples was continuously monitored by hanging the sample-holders from strain gages mounted on top of the tunnel roof.

The average RH of the air during experiences was 75%, which was measured by an electronic hygrometer OMEGA HX48 (accuracy  $\pm 2\%$ , from 0% to 100% RH). Air rate was fixed at 1 m/s, measured with a vane anemometer Solomat MPM 2000 (full scale 40 m/s, accuracy 0.1% full scale, conformity 0.05 m/s).

The experiments were carried out according to the procedure detailed in Campañone and others (2003).

## Image analysis

Ice sublimation induces changes in the size and structure of the dehydrated layer. These studies aim at characterizing the size and properties of that layer. In that matter, beef samples of different sizes, shapes, and structures (whole or minced meat) were frozen and stored under different operating conditions of the refrigeration equipment. Later, the samples were characterized by photographic and microscopic studies.

Photographs of cuts performed on the frozen samples were taken using a digital camera. Using these images, approximate values of the average thickness of the dehydrated layer ( $\delta$ ) were determined

with the software Global Lab (Global Lab Image 2.1, Data Translation Inc., Marlborough, Mass., U.S.A.; Automatrix Inc. 1992).

To study the microstructure of the surface dehydrated layer, samples were taken after each month of storage and were analyzed with environmental scanning electron microscopy (ESEM), using an environmental electronic microscope (Philips XL 30 ESEM; Philips Electronic Optics, Eindhoven, The Netherlands).

## Results and Discussion

### Parametric study using the numerical model

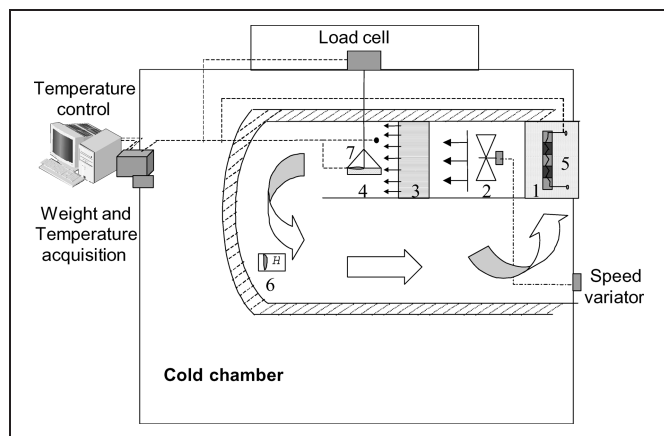
The mathematical model is an adequate tool for evaluating the variation of the size of the dehydrated layer  $\delta$  as a function of food characteristics and operating conditions. Figure 2 shows the prediction of the increase in predicted  $\delta$  (Eq. 6) with time, for a beef slab with the following characteristics and operating conditions:  $L = 3$  cm,  $T_i = 0$  °C,  $T_a = -30$  °C,  $v_a = 3.5$  m/s, RH = 75%. The figure also includes the predicted variation of food surface temperature.

As it can be seen, the rates of ice sublimation and growth of the dehydrated layer are higher at short times, but after about 100 to 160 min of refrigeration a decrease in the slope of the curves appears and both processes become slower. This is due to the fact that the surface temperature reduces faster reaching ambient air temperature; so the contribution of the difference between food surface and ambient temperature to the driving force for ice sublimation disappears. From this moment onward, the only driving force is the difference in water vapor pressure between food surface and the surroundings.

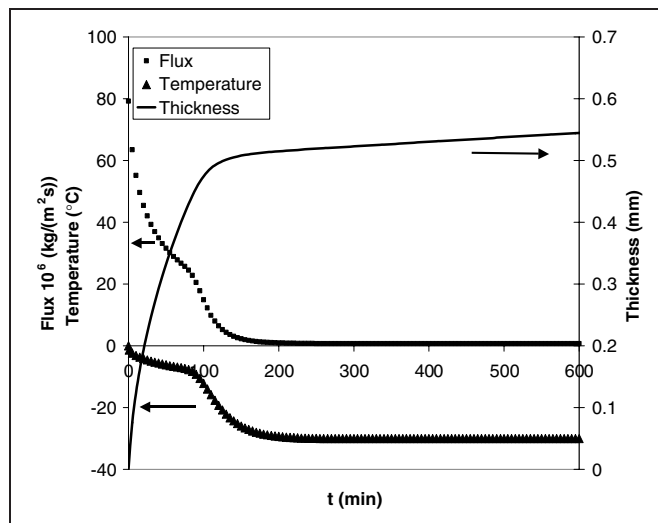
### Effect of operating conditions

The analysis of the influence of the operating conditions during freezing and frozen storage was developed for a particular shape but it is deemed as representative of what happens for any food shape. Slab and beef were chosen because beef hamburger, meat loaf, and steaks are the most often frozen unpackaged foods.

The following operative parameters were considered in this study: temperature, velocity and RH of air, food size, and initial temperature. To study the individual influence of each variable only 1 of the parameters was varied during each study, while the remaining conditions were kept at the following standard conditions:  $L = 3$  cm,  $T_i = 5$  °C,  $T_a = -30$  °C,  $v_a = 3$  m/s, RH = 70%.



**Figure 1**—Scheme of the freezing tunnel: (1) evaporator, (2) blowers, (3) flow straightener, (4) measuring sector, (5) heaters, (6) humidity sensor, (7) sample



**Figure 2**—Predicted variation with time of mass flux (■), temperature (▲), and thickness of the dehydrated layer (full line)

The same procedure was followed to study the storage stage. The selected standard conditions were  $L = 3$  cm,  $T_a = -25$  °C,  $v_a = 1$  m/s, RH = 70%, st = 2 months. Besides, it is supposed that all the stored samples were frozen under slow freezing conditions (as defined by the International Institute of Refrigeration [IIR 1972], e.g., a freezing rate lower than 0.2 cm/h):  $T_i = 15$  °C,  $T_a = -20$  °C,  $v_a = 1$  m/s, RH = 75%.

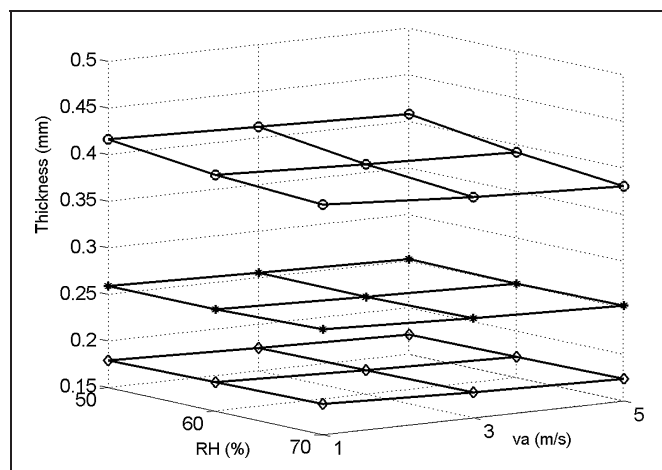
The results of the parametric analysis are summarized in Figure 3 and 4. They show the variation of thickness when compared with ambient RH, with air temperature and velocity as parameters. From their study, the following features are deduced.

**Air temperature.** It is the most important parameter in freezing and frozen storage. For freezing, when air temperature lowers, the process is accelerated, since the driving force for energy transfer increases almost linearly with the temperature difference between the surroundings and the food surface. As freezing time lowers, the same happens to mass flow by sublimation, because the time the food surface is exposed to dehydration is also lower and the surface temperature diminishes more rapidly. Figure 3 shows the predicted results from the numeric model.

In the case of frozen storage, air temperature strongly influences mass transfer with the surroundings. In Figure 4, it can be observed that, when lowering air temperature, the surface dehydrated layer is also smaller. This happens because of the minor driving force for mass transfer. As an example, the driving force for sublimation (difference between vapor pressure at food surface and in the environment) lowers from 24.50 to 9.04 N/m<sup>2</sup> when air temperature varies from  $-20$  to  $-30$  °C, maintaining RH = 75%.

**Air velocity.** Air velocity plays a less important role in the development of the dehydrated surface layer. During freezing, if air velocity is augmented, the same happens to the heat transfer coefficient, inducing a decrease in the freezing time. At the same time, the mass transfer coefficient increases in a similar amount to that of the heat transfer coefficient. This phenomenon augments the sublimation rate. This is counterbalanced by the low freezing time. The final result on the thickness of the dehydrated layer is determined by the relative importance of both phenomena, plus the influence of the structure of the dehydrated food on the effective diffusion coefficient of water vapor in this layer. In this particular case, a slight diminution in the thickness of the dehydrated layer can be observed with the increase in the air velocity (see Figure 3).

During frozen storage, the situation is simpler: Any increase in air velocity means a related increase in weight loss and in the thickness



**Figure 3** – Influence of air rate, relative humidity, and temperature on the predicted thickness of dehydrated layer during freezing. Air temperature:  $\circ$   $-20$  °C,  $\diamond$   $-30$  °C,  $\square$   $-40$  °C.

of the dehydrated layer, but this increase is not steep. This is due to the fact that in this stage mass transfer is clearly prevailing over heat transfer (ambient temperature is constant) and higher air velocities mean higher mass transfer coefficients, favoring water loss. But this is strongly counterbalanced by the resistance to water vapor diffusion of the dehydrated layer (Figure 4).

**Ambient relative humidity.** Figure 3 presents also the effect of RH on thickness of the dehydrated layer during freezing. The lower RH is the higher is the driving force for mass loss. This loss induces a lowering in the freezing time due to the additional refrigerating effect of ice sublimation, which is more evident at higher air temperatures (Campañone 2001).

The dependence of  $\delta$  with RH is strongly influenced by  $T_a$ . For high values ( $-20$  °C), dehydration increases at low RH due to the slow freezing rate, which induces high surface temperatures during part of the freezing period. Contrarily, lower  $T_a$  ( $-30$  °C or less) imply a quick decrease of temperature, with the correlative loss of driving force for sublimation (lower overall weight loss). In this situation, the value of RH is almost irrelevant, and there is even a very slight increase of  $\delta$  with RH.

During frozen storage, external control for mass transfer exists, so the lower the RH is the higher is the thickness  $\delta$  of the dehydrated layer (Figure 4).

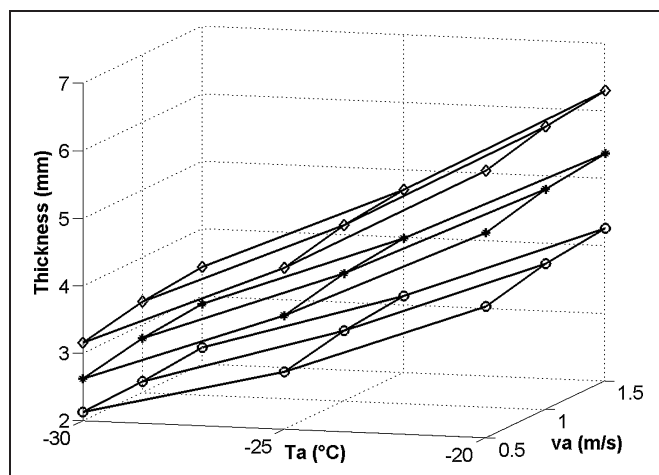
**Food particular conditions.** Food size  $L$  and its initial temperature  $T_i$  were considered. Experiments and model predictions show that freezing time increases with  $T_i$  and  $L$ . In both situations, the period that food surface is exposed to mass exchange also increases, with the resulting augmentation of  $\delta$ , which is depicted in Figure 5.

When comparing the influence of both parameters, it can be seen that  $L$  plays a much more important role on the value of  $\delta$  than  $T_i$ .

Food size  $L$  has almost null influence on the cumulative value of  $\delta$  after frozen storage. This is so because during storage, mass transfer is strongly dependent on vapor diffusion through the dehydrated layer. The thicker  $\delta$  originated in higher  $L$  during freezing hampers diffusion during storage and weight loss (and dehydrated layer) grows slower, balancing the effect of  $L$  during both periods.

### Simplified prediction method

One of the objectives of this work was to develop simplified prediction equations to calculate  $\delta$  as a function of food characteristics and process conditions for both stages, freezing and frozen storage.



**Figure 4** – Influence of air rate, relative humidity, and temperature on the predicted thickness of dehydrated layer during frozen storage. Relative humidity:  $\diamond$  60%,  $\square$  70%,  $\circ$  80%.

**Freezing.** To count on the necessary information about the dependence of  $\delta$  on food characteristics and freezing conditions, 730 runs of the previously developed numeric model (Campañone and others 2001) were performed for each simple shape using physical properties of beef. For each run of the model, the variation of  $\delta$  with time and its value at the end of freezing were calculated using Eq. 6. The range of operative conditions studied is detailed in Table 1.

Previous developments for the prediction of freezing time and weight loss during freezing and frozen storage, and results of the parametric analysis presented in this work, were taken into account to describe the dependence of  $\delta$  with the relevant process variables. Its dependence is inspired in dimensional analysis, using typical dimensionless numbers as Re and Bi, food characteristics ( $L$ ,  $Y_0$ , and  $T_i$ ) and air operating conditions ( $T_a$ , RH). The best-fit equation form is similar to simplified empirical equations exhaustively tested by the authors in preceding works (Salvadori and Mascheroni 1991; Campañone and others 2005a, 2005b). Therefore, the following empirical equation is proposed to evaluate the growth of  $\delta$  during freezing:

$$\delta_f = a_f(L)^{b_f} Re^{c_f} \left(\frac{1}{Bi}\right) (-1 - T_a)^{d_f} (f_f - RH)^{e_f} (1 + g_f T_0) Y_0^{h_f} \quad (7)$$

where constants  $a_f$ ,  $b_f$ ,  $c_f$ ,  $d_f$ ,  $e_f$ ,  $f_f$ ,  $g_f$ , and  $h_f$  are the parameters of this regression, which are shown in Table 2. These were obtained using software for nonlinear regression (NONLIN and SYSTAT). In all cases, very high values of the correlation coefficients  $r^2$  were obtained, also presented in Table 2.

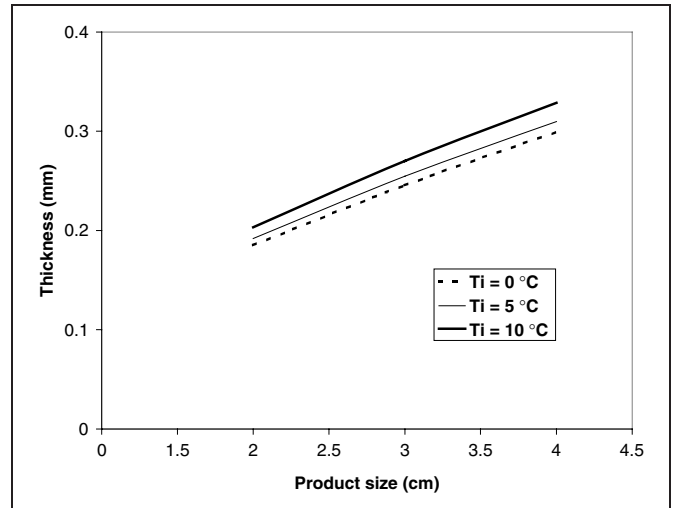
Figure 6 presents the comparison of predicted  $\delta_f$  (by Eq. 7) against numerical results for the 3 shapes. As can be seen, predicted values lie on a narrow band centered on the 45° line, without any bias. Values predicted by Eq. 7 have very little differences with numeric ones. Average relative errors between predicted and numeric values are 0.80% for plates, 0.82% for cylinders, and 0.83% for spheres.

**Frozen storage.** A similar procedure was performed for the development of a prediction equation for the size of the dehydrated layer during frozen storage. Numerous results of the numeric model (9150 data) were obtained, using thermal properties of meat products and 90 days of total storage time. The range of process conditions studied is detailed in Table 1.

Based on the results provided by the mathematical model, the following empirical nonlinear equation is proposed for the prediction of the thickness of the dehydrated surface layer:

$$\delta_s = a_s(L)^{b_s} Re^{c_s} (-T_a)^{d_s} (f_s - RH)^{e_s} st^{i_s} \quad (8)$$

$$\delta = \delta_f + \delta_s \quad (9)$$



**Figure 5—Influence of initial temperature and product size on the predicted thickness of dehydrated layer during freezing**

**Table 1—Range of operating conditions of the numerical runs**

Parameter	Freezing	Frozen storage
$T_a$ (°C)	-40 to -20	-30 to -20
$v_a$ (m/s)	1 to 5	0.5 to 1.5
RH (%)	50 to 90	60 to 80
$L$ (m)	0.02 to 0.04	0.02 to 0.04
$Y_0$	0.7 to 0.8	—
$T_i$ (°C)	0 to 10	—
Re	$1.7 \times 10^3$ to $2 \times 10^4$	$8.5 \times 10^2$ to $5.5 \times 10^3$

where  $\delta_f$  is the thickness generated during freezing, calculated using Eq. 7, and st (day) is the storage time. Constants  $a_s$ ,  $b_s$ ,  $c_s$ ,  $d_s$ ,  $e_s$ ,  $f_s$ , and  $i_s$  are the parameters of this regression which are also presented in Table 2. Very high values of the correlation coefficients  $r^2$  were obtained, also presented in Table 2.

Figure 7 presents the comparison between predicted  $\delta$  by Eq. 8 and 9 against numerical results for the three shapes.

Predicted results are in very good accordance with numeric ones. Average relative errors between them are 4.24% for plates and cylinders and 6.60% for spheres.

Equation 7, 8, and 9 can be used to analyze the effect of food shape in the value of  $\delta$  during freezing and frozen storage. This analysis was performed considering equal operating conditions and food characteristics (initial water content, size, and temperature). Calculations showed that the dehydrated thickness for cylindrical geometry is 0.888 times that for spherical geometry, while the relation between

**Table 2—Parameters for the prediction Eq. 7 and 8 for the 3 shapes**

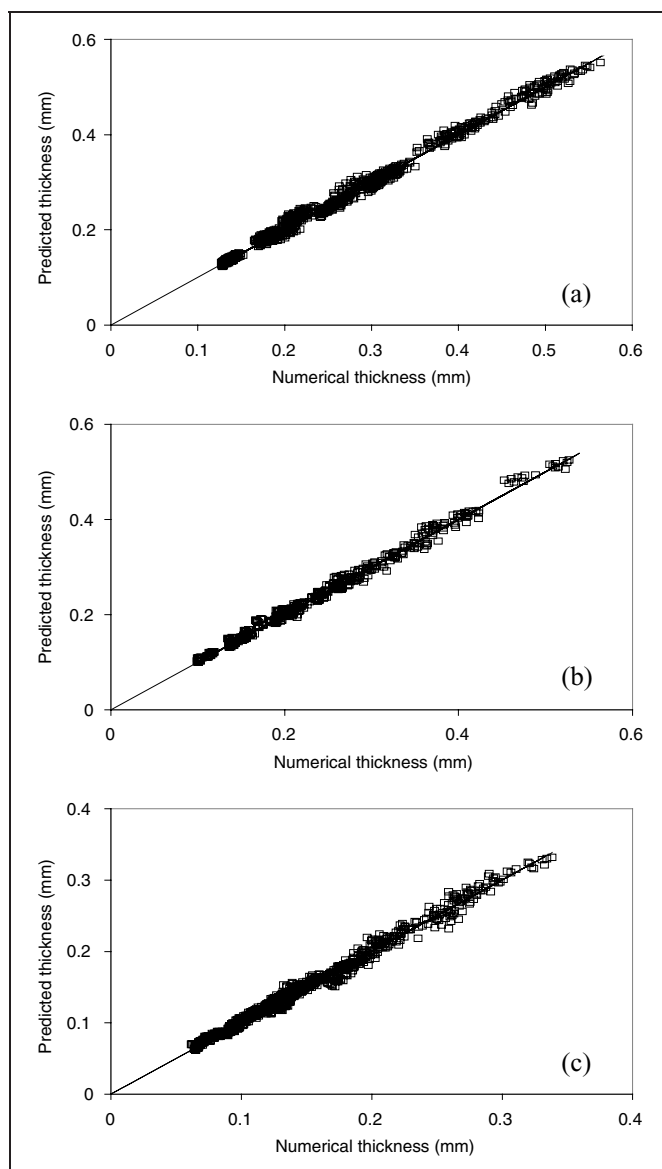
Parameter	Slab		Cylinder		Sphere	
	Freezing	Storage	Freezing	Storage	Freezing	Storage
$a$	165.58	27.388	4.482	18.172	4.807	22.722
$b$	1.414	-0.127	1.000	-0.197	0.978	-0.157
$c$	0.311	0.067	0.412	0.080	0.378	0.067
$d$	-1.203	-1.526	-1.013	-1.493	-1.092	-1.434
$e$	0.021	0.549	0.006	0.540	-0.010	0.522
$f$	1	0.978	1	0.977	1	0.981
$g$	0.009	—	0.002	—	-0.005	—
$h$	-0.524	—	-0.780	—	-1.097	—
$i$	—	0.648	—	0.640	—	0.608
$r^2$	0.999	0.999	0.999	0.999	0.989	0.999

depths for slabs and spheres is 0.859. This means that, during freezing and later frozen storage, under equal operating conditions, a food with spherical shape generates thicker dehydrated layers than the other geometries. This implies higher quality losses for the same process. This phenomenon is fundamentally owed to the higher specific area (area by unit of volume) of spheres.

### Structural analysis

Figure 8a–c shows a representative selection of the photographs obtained for the different types of samples (beef cylinders and steaks, minced beef hamburgers and balls) after diverse storage periods. In particular, Figure 8a includes transversal cuts of beef cylinders (perpendicular to the main axis). Figure 8b presents frontal views of cuts done across the diameters of transversal slices taken from beef steaks. Equivalent results (not shown here) were obtained for hamburgers. Figure 8c shows frontal views of perpendicular cuts performed across the center of meat balls (a quarter of a sphere).

In all the figures, zones with different values of gray scale can be distinguished: the inner region (frozen and not dehydrated) is

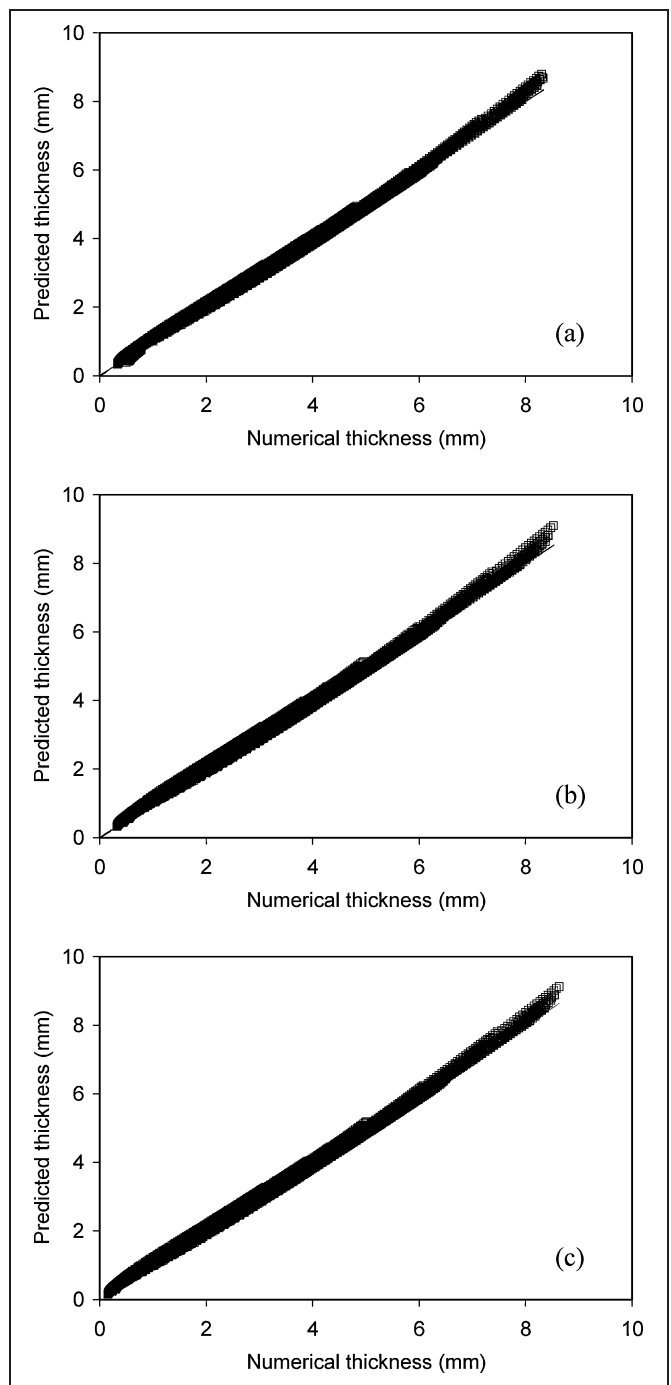


**Figure 6** – Predicted (symbols) compared with numerical (line)  $\delta_i$ , for different geometries: (a) slab, (b) cylinder, (c) sphere

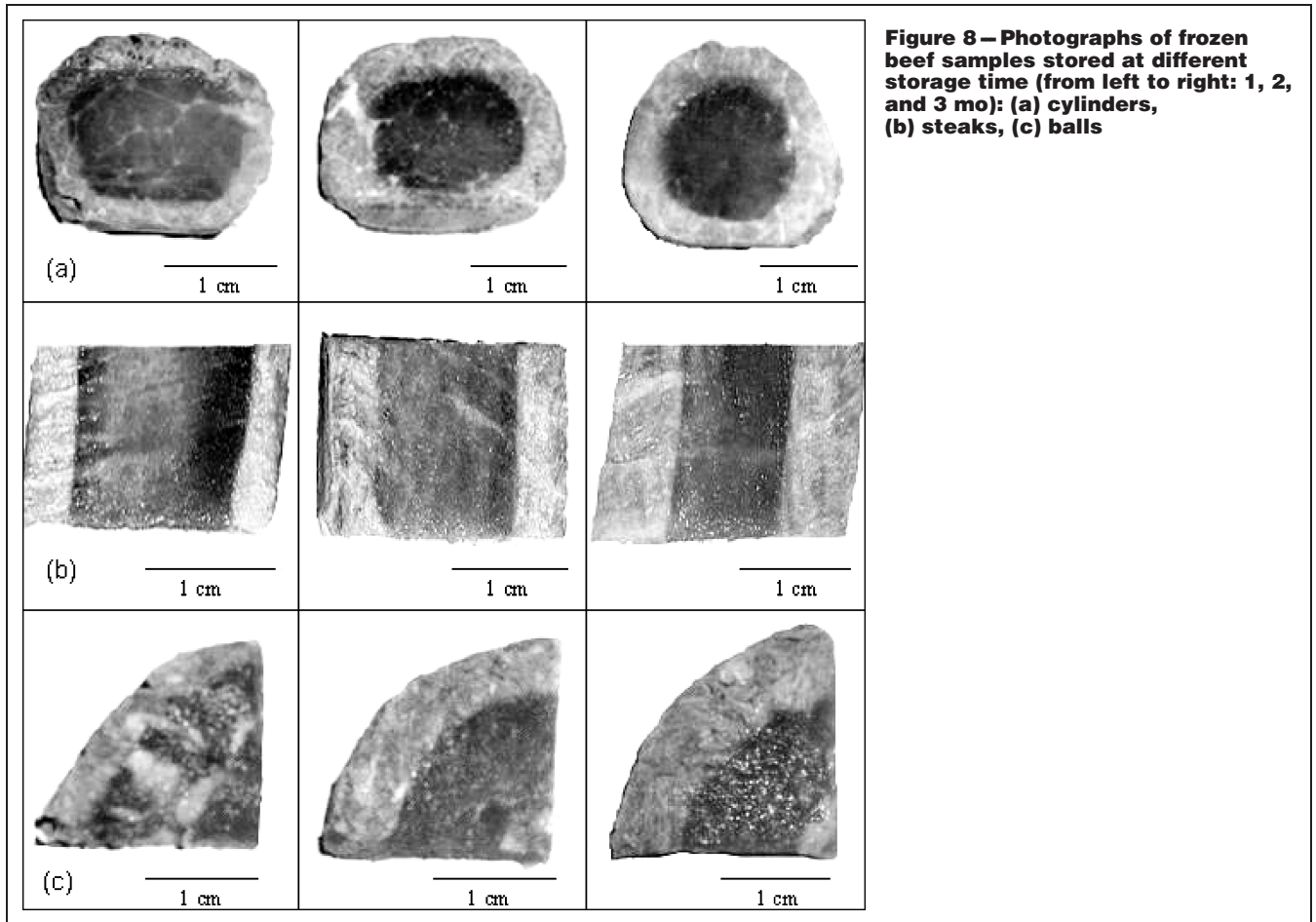
darker than the outer (surface) region (dehydrated). This fact implies that meats change their color and appearance when surface ice sublimation takes place, due mainly to changes in structure.

A well-defined front that separates the frozen and dehydrated zones can also be distinguished. This fact verifies one of the most important hypotheses done in the development of the mathematical model: that phase change (sublimation) takes place on a defined moving front that divides the frozen and dehydrated regions, and not along a partially dehydrated zone.

Experimental values for the evolution of  $\delta$  with storage time were obtained with Global Lab for the different types of samples. These



**Figure 7** – Predicted (symbols) compared with numerical (line)  $\delta$ , for different geometries: (a) slab, (b) cylinder, (c) sphere



**Figure 8 – Photographs of frozen beef samples stored at different storage time (from left to right: 1, 2, and 3 mo): (a) cylinders, (b) steaks, (c) balls**

values were used to verify the predictions of Eq. 7 and 8 and those of the numerical model. Results are shown in Figure 9. It can be observed that the prediction equations adequately describe the general trend of the experimental variation of  $\delta$  with storage time. The average relative error and absolute relative error between experimental and predicted values (given by Eq. 7 and 8) is 0.22% and 15.09%, respectively, without any type of bias in predicted values. In the same sense, the average relative error and absolute relative error between experimental and numerical values is 11.03% and 17.50%, respectively.

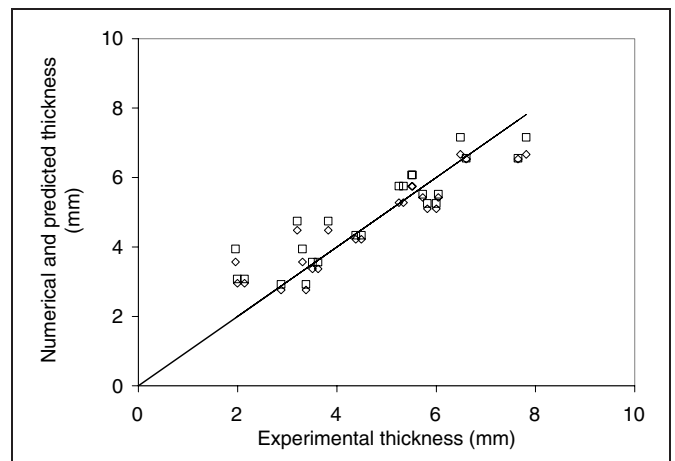
Figure 10 shows micrographs obtained from cuts of beef cylinders after different periods of storage (1, 2, and 3 mo). Cuts were done on a sense normal to cylinder axis and to fiber direction.

Zones of different gray tones can be distinguished within the surface layer: 1 clear zone that belongs to meat and dark sectors that correspond to the holes left by ice sublimation. It can be observed that the structure of the layer is porous and that pore size increases with storage time.

Photographs and micrographs enable us to conclude that, as storage time goes, the size of the dehydrated layer increases continuously, with the correlated damage to the structure of the frozen food.

### Conclusions

The effect of operating conditions and food characteristics on the rate of growth of the surface dehydrated layer of frozen un-packaged foods could be predicted using a numerical model for heat and mass transfer in food freezing and storage. Numerical results allow determining the dependence of the thickness of the dehydrated layer with food size, shape, and initial water content and with air

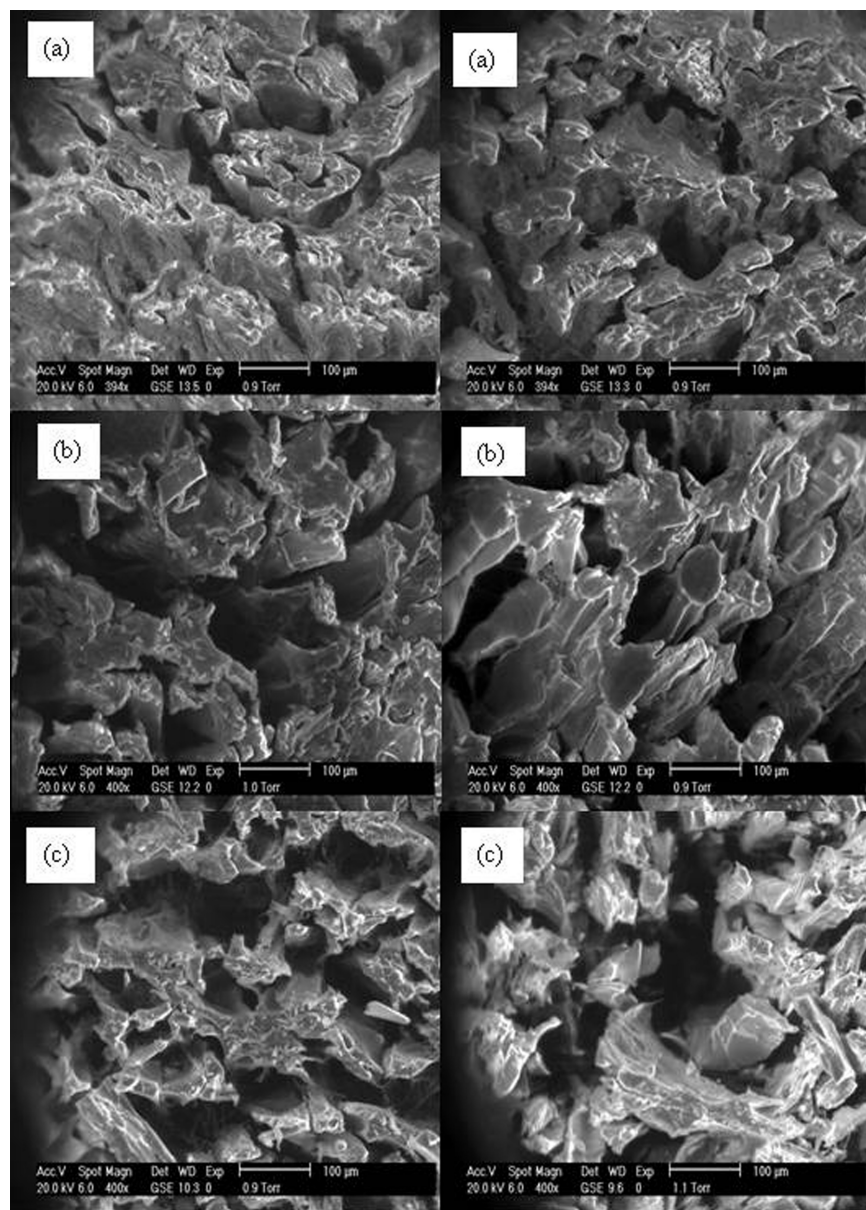


**Figure 9 – Predicted ( $\diamond$ ) and numerical ( $\square$ )  $\delta$  compared with experimental values ( $*$ ), after different periods of frozen storage for beef samples: cylinders, steaks, balls, and hamburgers**

characteristics specified by its RH and by Biot and Reynolds numbers.

Two simplified equations for the prediction of the thickness of the dehydrated layer during freezing and storage were proposed, and their characteristic coefficients were determined using predicted numerical data as input. High correlation coefficients were obtained for the regressions. Predictions from these equations were validated against experimental data of the thickness of the

**Figure 10 – Micrographs of beef cylinder samples (cuts on a sense normal to cylinder axis): (a) 1, (b) 2, and (c) 3 months of frozen storage (2 samples for each storage period)**



dehydrated layer in diverse samples of different beef products (cylinders, steaks, hamburgers, and balls) frozen and stored during our tests. The comparison between experimental, predicted, and numerical thickness of the dehydrated layer shows that the prediction equations adequately describe the general trend of the experimental behavior, without any type of bias in predicted values.

Using photographs and micrographs of the partially dehydrated samples, the size of the dehydrated layer and its structure could be studied for the different food types at diverse storage times. These results show that on growing the depth of the sublimated layer along frozen storage, structural damage has a correlated increase with higher depth of dehydrated, distorted, and discolored tissues.

### Nomenclature

Bi Biot number,  $h_c L / (2k)$   
 C Molar concentration,  $\text{mol}/\text{m}^3$   
 Cp Specific heat,  $\text{J}/(\text{kg} \text{ } ^\circ\text{C})$   
 D Diffusion coefficient,  $\text{m}^2/\text{s}$

$f_{\text{ads}}$  Adsorbed ice fraction,  $\text{kg}$  of ice/ $\text{kg}$  of dried solid  
 GI Geometric index, its value is 0 for slabs, 1 for cylinders and 2 for spheres  
 $h_c$  Heat transfer coefficient,  $\text{W}/(\text{m}^2 \text{ } ^\circ\text{C})$   
 $k$  Thermal conductivity,  $\text{W}/(\text{m} \text{ } ^\circ\text{C})$   
 $k_m$  Mass transfer coefficient (referred to vapor water driving force),  $\text{m}/\text{s}$   
 L Food thickness or diameter,  $\text{m}$   
 $m_s$  Sublimated mass by unit volume,  $\text{kg}/\text{m}^3$   
 Re Reynolds number,  $\rho v L / \mu$   
 RH Relative humidity, %  
 st Frozen storage time, day  
 t Time, s (or min, day or month)  
 T Temperature,  $^\circ\text{C}$   
 v Velocity,  $\text{m}/\text{s}$   
 w Ice content,  $\text{kg}$  of ice/ $\text{kg}$  of food  
 x Spatial coordinate,  $\text{m}$   
 $x_1$  Moving sublimation front position,  $\text{m}$   
 $Y_0$  Initial water content,  $\text{kg}$  of water/ $\text{kg}$  of food



## Greek symbols

$\rho$	Density, kg/m <sup>3</sup>
$\mu$	Viscosity, Pa s
$\delta$	Dehydrated layer thickness, mm (or m)

## Subscripts

a	Air
f	Freezing
i	Initial
if	Initial freezing
s	Frozen storage
v	Water vapor in food
va	Water vapor in ambient air
w	Liquid water in food

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## References

- Aguirre Puente J, Sukhwil RN. 1984. Sublimation of ice in frozen dispersed media. Proceedings of the Third International Offshore Mechanics and Arctic Engineering Symposium, 1984, Houston, Tex. Vol III, p 38–44.
- Barat JME, Chiralt A, Fito P. 1998. Equilibrium in cellular food osmotic solution systems as related to structure. *J Food Sci* 63:836–40.
- Bevilacqua A, Zaritzky NE, Calvelo A. 1979. Histological measurements of ice in frozen beef. *J Food Technol* 14:237–51.
- Campañone LA. 2001. Transferencia de calor y materia en congelación y almacenamiento de alimentos, sublimación de hielo, calidad, optimización de condiciones de proceso [DPhil thesis]. Argentina: Facultad de Ingeniería, Universidad Nacional de La Plata. p 197. Available from: Universidad Nacional de La Plata, Argentina.
- Campañone LA, Salvadori VO, Mascheroni RH. 2001. Weight loss during freezing and storage of unpackaged foods. *J Food Eng* 47:69–79.
- Campañone LA, Roche LA, Salvadori VO, Mascheroni RH. 2003. Monitoring of weight losses in meat products during freezing and frozen storage. *Food Sci Tech Int* 8(4):229–39.
- Campañone LA, Salvadori VO, Mascheroni RH. 2005a. Food freezing with simultaneous surface dehydration. Approximate prediction of freezing time. *Int J Heat Mass Transfer* 48(6):1205–13.
- Campañone LA, Salvadori VO, Mascheroni RH. 2005b. Freezing and frozen storage with simultaneous surface dehydration. Approximate prediction of weight losses. *Int J Heat Mass Transfer* 48(6):1195–204.
- Cheftel JC, Cheftel H. 1991. Introducción a la bioquímica y tecnología de los alimentos II. España: Editorial Acribia. p 404.
- Chumak IG, Sibiriakov PV. 1988. Influence of air parameters in a frigorific chamber on water content of meat surface during refrigeration (in Russian). *Izvestia vuzov, Pischevaia tehnologua* 2:54–6.
- Cleland AC. 1990. Food refrigeration processes. Analysis, design and simulation. London: Elsevier Applied Science Publishers Ltd. p 284.
- [IIR] International Institute of Refrigeration. 1972. Recommendations for the processing and handling of frozen foods. Paris: International Institute of Refrigeration. p 82.
- King CJ. 1971. Freeze-drying of foods. Londres: CRC Press. p 86.
- Krokida MK, Karathanos VT, Maroulis ZB. 1998. Effect of freeze-drying conditions on shrinkage and porosity of dehydrated agricultural products. *J Food Eng* 35: 369–80.
- Krokida MK, Zogzas NP, Maroulis ZB. 1997. Modelling shrinkage and porosity during vacuum dehydration. *Int J Food Sci and Technol* 32:445–58.
- Lambrinos GP and Aguirre Puente J. 1983. Deshydratation des milieux dispersés congelés. Influence des conditions d'entreposage sur les pertes de masse. Proceedings of XVI International Congress of Refrigeration, 1983, Paris, France. Vol II, p 567–74.
- Martino MN, Otero L, Sanz PD, Zaritzky NE. 1998. Size and location of ice crystals in pork frozen by high pressure assisted freezing as compared to classical methods. *Meat Sci* 50(3):303–13.
- Méndez Bustabad O. 1999. Weight loss during freezing and the storage of frozen meat. *J Food Eng* 41:1–11.
- Pham QT, Willix J. 1984. A model for food desiccation in frozen storage. *J Food Sci* 49:1275–81.
- Salvadori VO, Mascheroni RH. 1991. Prediction of freezing and thawing times of foods by means of a simplified analytical method. *J Food Eng* 13: 67–78.
- Salvadori D, Andrés A, Alborns A, Chiralt A, Fito P. 1998. Structural and compositional profiles in osmotically dehydrated apple. *J Food Sci* 63:606–10.
- Wang N, Brennan JG. 1995. Changes in structure, density and porosity of potato during dehydration. *J Food Eng* 24:61–76.