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Multicomponent diffusion during Prato cheese ripening: mathematical modeling using the finite element method

Difusão multicomponente durante a maturação de queijo Prato: modelagem matemática usando o método de elementos finitos

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Abstract

The partial replacement of NaCl by KCl is a promising alternative to produce a cheese with lower sodium content since KCl does not change the final quality of the cheese product. In order to assure proper salt proportions, mathematical models are employed to control the product process and simulate the multicomponent diffusion during the reduced salt cheese ripening period. The generalized Fick's Second Law is widely accepted as the primary mass transfer model within solid foods. The Finite Element Method (FEM) was used to solve the system of differential equations formed. Therefore, a NaCl and KCl multicomponent diffusion was simulated using a 20% (w/w) static brine with 70% NaCl and 30% KCl during Prato cheese (a Brazilian semi-hard cheese) salting and ripening. The theoretical results were compared with experimental data, and indicated that the deviation was 4.43% for NaCl and 4.72% for KCl validating the proposed model for the production of good quality, reduced-sodium cheeses.

Keywords: ripening; Prato cheese; finite element method; multicomponent diffusion.

Resumo

A substituição parcial do NaCl pelo KCl é uma alternativa promissora para produzir queijos com um teor reduzido de sódio, desde que não se altere sua qualidade final. Para assegurar uma proporção adequada dos sais, a utilização de modelos que simulam a difusão multicomponente durante a maturação de queijos com teor reduzido de NaCl é importante para o controle do processo e qualidade do produto. A segunda lei de Fick generalizada para dois solutos é um dos modelos mais utilizados para este fim, e o sistema de equações diferenciais resultante foi resolvido através do Método de Elementos Finitos (MEF). No presente trabalho, foi simulada a difusão dos sais NaCl e KCl durante a maturação de queijo prato utilizando uma salmoura estática 20% (m/m) contendo 70% de NaCl e 30% de KCl. Em seguida, os resultados estimados foram comparados com os dados experimentais. O desvio percentual obtido entre os dados experimentais e os estimados resultou em 4,43% para o NaCl e 4,72% para o KCl, indicando que o modelo proposto é válido para a produção de queijos de qualidade e com teor reduzido de sódio.

Palavras-chave: maturação; queijo Prato; método de elementos finitos; difusão multicomponente.

1 Introduction

The direct relationship between the sodium content of food and arterial hypertension is leading consumers to choose foods with reduced sodium contents. As such, the production of reduced-sodium foods is needed. As NaCl is believed to play an important role in the final quality of most food products, the complete replacement of all NaCl is not recommended (KATSIARI et al., 1998; LYNCH, 1979). The partial replacement of NaCl by other salt forms has become an accepted alternative, as long as this change does not alter the sensory, physicochemical, and microbiological characteristics of the product. KCl is an adequate substitute for NaCl since its chemical and physical properties are similar to those of NaCl. A 30-45 mmol increase in potassium intake was associated with an average reduction in systolic blood pressure of 2-3 mmHg

(HE; MACGREGOR, 2001). Cheese is a heavily-consumed product in Brazil, and among the most popular varieties are Prato, Mozzarella, Cottage, Minas, Parmesan, and Ricotta (GOROSTIZA et al., 2004).

Sodium chloride diffusion has been studied by various authors for cheese varieties such as Cottage cheese (BRESSAN et al., 1982), Cuartirolo Argentino cheese (LUNA; BRESSAN, 1986, 1987), Gouda cheese (LUNA; CHAVES, 1992; GOMES; VIEIRA; MALCATA, 1998; PAYNE; MORRISON, 1999), Cheddar cheese (MORRIS; GUINEE; FOX, 1985; SCHROEDER et al., 1988), and Fynbo cheese (ZORRILLA; RUBIOLO, 1998). Molecular or Fickian diffusion in the fluid phase is widely accepted as the primary mass transfer mechanism within solid

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foods, in which the driving force toward the diffusion process is the concentration or chemical activity gradient (AGUILERA, 2005; LI, 2006). The Fick's Second Law depends on initial conditions such as the distribution of the solute within the solid before diffusion and on the boundary conditions, including concentration variations at the limit of the control region (the surface). Frequently, the apparent diffusion coefficient (D*) is considered to be constant and uniform (CRANK, 1975). Morris, Guinee and Fox (1985) studied the NaCl diffusion in the salting of Cheddar cheese, and found D* 0.12 cm²/ day. Luna and Bressan (1987) mathematically modeled the mass transfer of NaCl in the diffusion process which occurs in Cuartiolo Argentino cheese during salting and ripening, and established an effective diffusion coefficient of 0.30 cm²/ day. The multicomponent diffusion in foods occurs not only due to their intrinsic characteristics, but also because many additional components, including solutes, are added to them. Moreover, experimentally measuring the concentration of each species individually is often inconvenient and very difficult (ZORRILLA; RUBIOLO, 1994a, 1994b). When two solutes diffuse simultaneously, the generalized Fick's Second Law is adopted. In this case, in addition to the main diffusion coefficient, the cross diffusion coefficients, which determine the influence of one solute in the flow of another, are also required. In general, for fully dissociable ions such as Na+ and K⁺, the values of the cross coefficients are ten times lower than those of the main coefficients (GERLA; RUBIOLO, 2003; MEDINA-VIVANCO et al., 2002). Several authors have studied diffusion in food using the Fick's laws for binary and ternary systems, including diffusion during the salting of Prato cheese (BONA et al., 2007) and Pategras cheese (GERLA; RUBIOLO, 2003); salting (ZORRILLA; RUBIOLO, 1994a) and ripening (ZORRILLA; RUBIOLO, 1994b) of Fynbo cheese; osmotic dehydration of pieces of meat (DJELVEH; GROSS; EMAM-DJOMEH, 2001), potatoes cubes (KHIN; ZHOU; PERERA, 2006), tissues of plants (LI, 2006), pumpkins (MAYOR et al., 2006), and tomatoes (TELIS; MURARI; YAMASHITA, 2004).

The Finite Element Method (FEM) is a set of powerful numerical techniques for solving differential equations frequently used in food science, which allows the simulation of systems under realistic conditions (WANG; SUN, 2003). The FEM can provide solutions for differential equations that simulate phenomena such as heat and/or mass transfer, radiation, fluid dynamics, and elasticity, as well as chemical and biological processes responsible for the loss of food quality (MARTINS, 2006). According to Puri and Anantheswaran (1993), the primary advantages of FEM include: (i) easier handling of spatial variation of material properties, (ii) more accurate modeling of irregular regions, (iii) ready indication for non-linear problems, (iv) easy variation of element size, (v) more meaningful spatial interpolation, and (vi) easier handling of mixed-boundary-value problems. Several authors have studied the FEM in foods. Lomauro and Bakshi (1985) used this technique to predict the humidity content of several foods (flour, nonfat dried milk, freeze-dried apple, cookies, and raisins) with different geometries. Silva, Borsato and Silva (1998) analyzed the NaCl transfer through cheese (three-dimensional solid matrix) with the use of the Fick's equation. Payne and Morison (1999) investigated the loss of salt and humidity of Gouda cheese during salting by employing Maxwell-Stefan's equation. Bona et al. (2005) simulated the multicomponent diffusion during mixed salting (NaCl+KCl) in Prato cheese based on the generalized Fick's Second Law for both solutes in static brine. However, to the best of our knowledge, there are no reports on the use of FEM for the simulation of the multicomponent diffusion in cheese during ripening through the generalized Fick's equation. To this end, the objective of the present work was to study and model the multicomponent diffusion of NaCl and KCl during the Prato cheese ripening.

2 Materials and methods

2.1 Salting

Two pieces of cheese measuring $24 \times 10 \times 12$ cm (Queijo Prato Lanche DI CARLO from Campina Alta dairy plant, located in Manoel Ribas - PR, Brazil) were used for the study. After pressing, the cheese was taken to the laboratory in the same mold where the curd had been pressed. The cheese was stored under refrigeration (10 ± 1 °C) for 12 hours prior to the beginning of the experimental procedure. After this period, it was removed from the mold and cut into twelve smaller pieces ($4\times8\times10.5$ cm) for the salting process. Three of these samples were used to determine fat, moisture, and initial sodium and potassium content.

Nine samples of the cheese were salted in static condition for 5 hours (BONA et al., 2007) in a brine mixture consisting of $13.59\,g\,NaCl.100\,g^{-1}_{NaCl+KCl+water}\,and\,5.06\,g\,KCl.100\,g^{-1}_{NaCl+KCl+water}$ at 10 ± 1 °C using an adapted domestic refrigerator (CONTINENTAL 560 L). Twenty liters of brine were prepared according to a literature procedure (FURTADO, 1991), which suggested a saline concentration of 20% (w/w) and an average pH of 5.5 (adjusted with HCl). To prevent loss of Ca²⁺ and the subsequent loss of rigidity, 0.5% (w/w) of CaCl, was also added (FURTADO, 1991). The brine volume used was approximately 6 times greater than the cheese volume to ensure that the brine concentration remained constant throughout the salting period (GERLA; RUBIOLO, 2003). Before and after salting, samples of brine were removed to quantify salt content. For studying the multicomponent diffusion, 70% NaCl and 30% KCl were used to avoid significant modifications in sensorial qualities of the cheese (RAPACCI, 1989).

Due to the lower density of cheese relative to brine, the cheese was immobilized by a network of cotton threads within the salting recipient $(34 \times 49 \times 15 \text{ cm})$, as illustrated in Figure 1a. This network guaranteed that none of the samples touched one another, and that all the surfaces were in contact with the brine, allowing for uniform salting.

2.2 Ripening

After a 5 hour salting period, the samples were removed from the brine and left to dry in a refrigerator for 2 hours. Next, all samples were packed up in a SELOVAC vacuum seal machine model 120-B to start the ripening process.

The nine cheeses were left to ripen for 40 days under a refrigeration temperature of 10 ± 1 °C. After each ripening period (0, 1, 5, 10, 15, 20, 25, 30, and 40 days), one sample was removed for physicochemical analyses. The initial ripening (day 0) refers to the 5-hour salting period.

2.3 Sampling

The sampling procedure consisted of removing two cylindrical samples, each 1.5 cm in diameter and 4 cm in height, as illustrated in Figure 1b. Two cylindrical samples were removed to determine whether there was variability in the salt concentration during the extraction and quantification processes. After removal, the cylinders were cut into half to produce four cylindrical samples, as shown in Figure 1c. The cylinders belonging to the same face were analyzed together, and the samples were removed for analysis.

2.4 Moisture, fat, and salts

Moisture was determined by drying in an oven at 105 °C to a constant weight (ASSOCIATION..., 1984; RICHARDSON, 1985). Fat content was determined by the Soxhlet method (CECCHI, 2003).

Sodium and potassium content were determined by atomic emission using a flame photometer FC-280 (*CELM – Cia.*

Equipadora de Laboratórios Modernos, Barueri - SP, Brazil) after incinerating the samples and extracting the salts with 0.5 mol.L⁻¹ HCl (ASSOCIATION..., 1984).

2.5 Modeling the multicomponent diffusion

This study considered the simultaneous three-dimensional mass transfer of two solutes in a cheese sample that occupied a volume of $\Omega \subset \mathbb{R}^3$, where $\bar{\Omega} \equiv [-R_1, R_1] \times [-R_2, R_2] \times [-R_3, R_3]$, associated with a system of Cartesian coordinates x, y, z with the origin located at the geometric center of the cheese. It was assumed that diffusion was the predominant mechanism operating, so the convective mass transfer into the cheese pores was negligible (WELTI-CHANES; VERGARA-BALDERAS; BERMÚDEZ-AGUIRRE, 2005). The effective or apparent diffusion coefficients in the cheese ripening were not necessarily equal to those in salting since the process occurs under isothermal conditions, and sample contraction was negligible. Under these conditions, the multicomponent diffusion during ripening at a constant temperature of 10 °C was modeled.

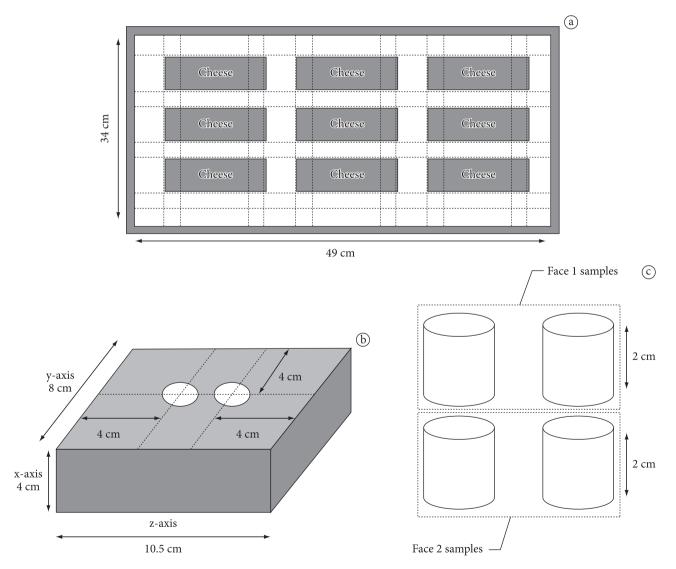


Figure 1. a) Schematic upper view of the experimental system showing cheese pieces; The dotted lines represent the network of cotton threads. b) Sampling used to determine NaCl and KCl contents; c) Section of the samples in four identical cylinders.

The $C_1(x, y, z, t)$ and $C_2(x, y, z, t)$ concentrations of the solutes NaCl and KCl, respectively, defined at point $P \equiv (x, y, z) \in \Omega$ and at time t, can be described by the Onsager's equations for the solute concentrations (ONSAGER, 1945) (Equation 1):

$$\begin{split} &\frac{\partial C_1}{\partial t} = D_{11} \nabla^2 C_1 + D_{12} \nabla^2 C_2 \\ &\frac{\partial C_2}{\partial t} = D_{21} \nabla^2 C_1 + D_{22} \nabla^2 C_2 \end{split} \tag{1}$$

The initial and boundary conditions used for the salting process in brine at rest, known as the Cauchy boundary conditions, are, in mathematical terms, essential, and are given by Equation 2 and 3:

$$C_1(x, y, z, 0) = C_{1,0}$$

 $x, y, z \in \Omega$ (2)
 $C_2(x, y, z, 0) = C_{2,0}$

$$\frac{\partial C_1(\pm R, t)}{\partial \eta} = \frac{h_m}{\lambda_m} \left[C_1 - C_{1,s} \right]$$
with $x, y, z \in \partial \Omega, t > 0$ (3)

$$\frac{\partial C_2(\pm R,t)}{\partial \eta} = \frac{h_m}{\lambda_m} \left[C_2 - C_{2,s} \right]$$

The coefficients $h_{_m}$ and $\lambda_{_m}$ are related to the Biot mass-exchange number by Equation 4:

$$Bi = \frac{h_m \cdot R_i}{\lambda_m} \qquad \qquad for \ i = 1, 2, 3 \tag{4}$$

The partial differential equation formed by equation (1) and conditions (2) and (3) was solved by FEM employing the generalized Galerkin formulation (BONA et al., 2007), and the Crank-Nicolson implicit scheme was used for time discretization (BICKFORD, 1990). The full resolution of the three-dimensional salting model used in this work, the adjusted values for the apparent diffusion coefficients, and the Biot number have all been reported by Bona et al. (2007).

The FEM allowed us to simulate the ripening period of the Prato cheese using a differential equation (1). It also required the substitution of the boundary condition for Neumann (Equation 5):

$$\frac{\partial C_1(\pm R, t)}{\partial \eta} = 0$$
with $x, y, z \in \partial \Omega$, $t > 0$

$$\frac{\partial C_2(\pm R, t)}{\partial \eta} = 0$$
(5)

Which specifies the value of the normal derivative corresponding to the dependent variables (C_1 and C_2) on the cheese surface. The initial condition represents the NaCl and KCl present in the cheese at the end of the salting process.

This change allowed the method to simulate the ripening process as a function of the cheese size since equation (5) was equal to zero. This indicated that the entrance of salt from the salting process had been interrupted. The required adaptations (incorporation of the ripening procedures) were performed with the software previously described (BONA et al., 2007).

2.6 Statistical test

The estimated and experimental values for the NaCl and KCl concentrations in the brine were compared by percentage deviation (TELIS; MURARI; YAMASHITA, 2004), represented by Equation 6, in order to assess the accuracy of the fit.

$$\% deviation = 100 \sqrt{\sum_{i=1}^{N} \left[\left(\frac{\overline{C}_{est} - \overline{C}_{exp}}{\overline{C}_{exp}} \right)_{i} \right]^{2} \frac{1}{N}}$$
 (6)

2.7 Fit of the diffusion coefficients for ripening

The diffusion coefficients were fitted by the Simplex optimization method (WALTERS et al., 1999) associated with the desirability functions (DERRINGER; SUICH, 1980), and the optimization algorithm proposed combinations for the diffusion coefficients (BONA et al., 2000). These values were assessed by FEM. The simulated NaCl and KCl concentrations were then compared to those of the experimental results by a statistical test (Equation 6). The calculated percent deviations were reassessed by the optimization method, which resulted in new value combinations with the objective of minimizing the deviation among the estimated and the experimental values. The procedure was repeated until the calculated values for the deviations and diffusion coefficients were constant.

3 Results and discussion

Table 1 shows data for the humidity, fat content, NaCl content, and KCl content for cheese samples prior to salting, obtained directly from the dairy industry. The nine cheese samples were immersed in brine for a period of 5 hours. At the end of the salting period, the NaCl and KCl concentrations and the brine pH were determined. All showed no measurable changes related to the values from the beginning of the salting period (Table 2).

Table 1. Relevant Prato cheese chemical composition before brining^a.

Moisture	Fat	NaCl	KCl
$(g.100 g^{-1})$	$(g.100 g^{-1})$	$(g.100 g^{-1})$	$(g.100 g^{-1})$
wet basis)	dry basis)	NaCl+KCl+water)	NaCl+KCl+water)
43.67 ± 0.34	52.80 ± 1.00	0.1821 ± 0.0060	0.2459 ± 0.0080

 $[\]ensuremath{^{\text{a}}}$ Average from duplicates and standard deviation.

Table 2. Initial brine characteristics^a.

Temperature (°C)	рН	$\begin{array}{c} {\rm CaCl_2} \\ {\rm (g.100~g^{-1}}_{\rm NaCl+KCl+\acute{a}gua}) \end{array}$	$\begin{array}{c} \text{NaCl} \\ \text{(g.100 g}^{-1} _{\text{NaCl+KCl+\acute{a}gua}}) \end{array}$		Salt ratio	Brine volume/ total cheese volume
10 ± 1	5.3	0.5	13.59	5.06	72.9% NaCl: 27.1% KCl	6.6

^aThe initial and end brining characteristics were the same.

The calculation of the concentration units (g.100 g $^{-1}$ NaCl+KCl+water) was carried out according to the procedure of Pajonk, Saurel and Andrieu (2003) to represent the ternary system. As mentioned, a 5 hour salting period was used due to the optimal results obtained with the computational simulation performed by Bona et al. (2007) for salting experiments using Prato cheese. In these experiments, the concentrations of salts were within the recommended values for avoiding sensorial alterations (RAPACCI, 1989).

Apart from the beginning of the ripening period (day 0, 5 hour salting period), the average salt ratio remained constant at approximately 65% for NaCl, and 35% for KCl. The experimental ratio of KCl was determined to be similar to that verified by both Rapacci (1989) and Bona et al. (2007), who reported a NaCl/KCl replacement of 37% for Prato cheese, under otherwise identical conditions to our method. Varying ratios may occur due to different characteristics between the experiments including salting period, cheese composition, and total salt concentration, as previously reported (FITZGERALD; BUCKLEY, 1985; KATSIARI et al., 1998; LINDSAY; HARGETT; BUSH, 1982).

After the experimental determination of NaCl and KCl concentrations, the Simul 3.0 software associated with the Simplex optimization method was employed for iterative adjustments of the diffusion coefficients in the ripening process (BONA et al., 2007). Each ripening simulation took approximately 23 minutes when a Celeron D° 2.8 GHz processor with 1.0 Gb RAM computer was used.

With a define mesh and time discretization scheme, the diffusion coefficients were estimated using the Simplex optimization method. Figure 2 shows the convergence and stabilization of the values for the responses of the deviations from the experimental NaCl and KCl data, as well as the fitted parameters for the diffusion coefficients. All deviations stabilized after approximately 33 iterations of the optimization algorithm, reaching minima at 4.43% for NaCl and 4.72% for KCl. The stabilization of the apparent diffusion coefficients was achieved after 25 iterations. Table 3 shows the deviations and estimated values for the diffusion coefficients in Prato cheese ripening process. The estimation for the apparent (or effective) diffusion coefficient for NaCl was in agreement with the values previously reported, falling between 0.18 and 0.25 cm²/day (FURTADO,

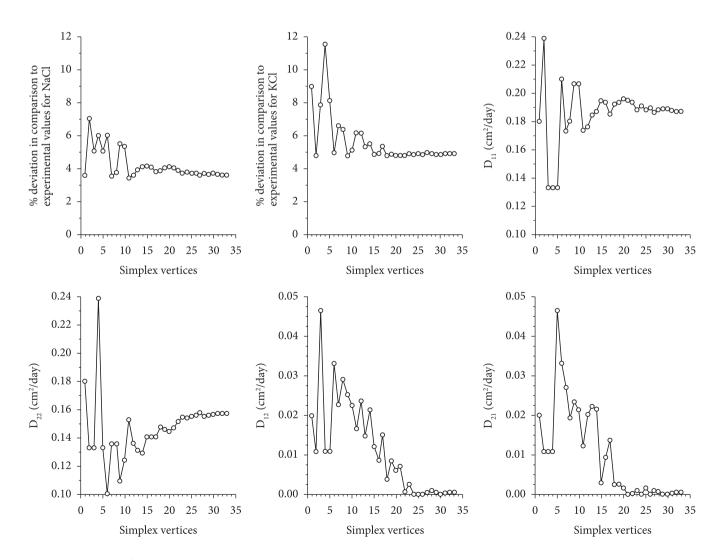


Figure 2. Percentage of deviation and parameter estimation during the simplex method.

1991). The corresponding estimated coefficient for KCl in the Prato cheese ripening has not been previously reported.

The values of the diffusion coefficients, adjusted through the Simplex optimization method for the salting process (BONA et al., 2007), were higher than those adjusted for the ripening process of Prato cheese (Table 3). The reduction in these values indicates that the hypothesis that reactional diffusion medium and structural changes cannot be excluded during the ripening process. The ripening process accounts for a number of chemical and biochemical transformations including proteolysis, lipolysis, and glycolysis. These processes, together, transform cheese into a product rich in flavor and taste with characteristic consistencies, texture, and coloration (ALVES, 1995; FOX, 1989; GUINEE; FOX, 1987; KILCAWLEY; WILKINSON; FOX, 1998; SORENSEN; BENFELDT, 2001). The biochemical changes that occur during ripening may modify the cheese matrix and therefore, the porosity and diffusion coefficients during ripening (GOMES; VIEIRA; MALCATA, 1998). Guinee (2004) has recognized that it is difficult to establish the direct effect of different compositional parameters in salt diffusion. These parameters affect the volume fractions of the fat and protein phases, which in turn determine the tortuosity effects of fat globules and protein particles and the sieve effect of the protein matrix on migrating salt molecules. Nevertheless, little research has been undertaken to determine the factors that influence the diffusion of salt in cheese after the removal from the brine because continued physicochemical and structural changes during ripening may alter cheese matrix. For Prato cheese, Cichoscki et al. (2002) showed that the salting-moisture ratio has a significant increase (p < 0.05) in the first month of ripening reaching average values of 3.4% (w/w). Salt addition at levels up to 1.4% (w/w) enhances protein hydration and the water-binding capacity of the protein matrix. Therefore, the diffusion rate decreases because not all moisture in cheese is free and available. The increase in protein tortuosity and reduction in relative pore geometry would be expected to reduce the diffusion coefficients significantly (GUINEE, 2004). The total content of free amino acids increased approximately 8 times throughout ripening (GOROSTIZA et al., 2004). The movements of ions from a region of high concentration to a low concentration one within the cheese are impeded by protein aggregates around. The ions must proceed by tortuous routes, and thereby travel an extra path length on proceeding from one region to another (GUINEE, 2004).

The values of the crossed coefficients were far lower (Table 3) than those of the main coefficients, indicating that self diffusion is much more important than diffusion due to interactions among the solutes, which are likely fully dissociated.

Figure 3 shows the profile of the experimentally concentration values obtained and the values estimated by the application of the FEM for both NaCl and KCl. The experimental values for both salts showed nearly analogous behavior in relation to the values estimated through FEM, and the mean deviations, up to 40 ripening days, are indicated in Table 3. It was also observed that the use of FEM enabled simulation of the diffusion of salts during the Prato cheese ripening. The simulated results showed

a deviation value of less than 5%, which means a good predictive capacity in relation to the experimental data, further validating the application of FEM for a multicomponent diffusion in the Prato cheese ripening.

Figure 4 shows the saline distribution profiles for NaCl and KCl along the x-axis of the removed cylinders, analogous to those shown in Figure 1b during 40 days of ripening period, both estimated by FEM. Each curve was generated using 320 points interpolated on the central axis of the sampling cylinder (Figure 1b). A higher salt concentration was observed near the borders of all samples on the first ripening day indicating that during the salting process and at the beginning of ripening, a large amount of salt was found at the cheese surface. After the tenth ripening day, the concentration gradient along the x-axis was no longer observed since the saline distributions were homogeneous.

Based on the simulation, a uniform saline distribution for NaCl should occur after 20-30 ripening days (Figure 4), data corroborated by findings from Silva, Borsato and Silva (1998). Figure 4 shows the simulated saline distribution profile for KCl during 40 ripening days, with an analogous behavior obtained for NaCl. It was also observed that 20-30 ripening days would be sufficient to assure a homogeneous salt distribution in the cheese. The simulated ripening time (20-30 days) is similar to that of most traditional Prato cheese producers (FURTADO, 1991).

Table 3. Diffusion coefficients and deviation percentages obtained during the ripening period for NaCl and KCl.

	NaCl	KCl
Main coefficients (cm²/day)	0.1867	0.1570
Cross-coefficients (cm ² /day)	0.0005	0.0005
% deviation	4.43	4.72

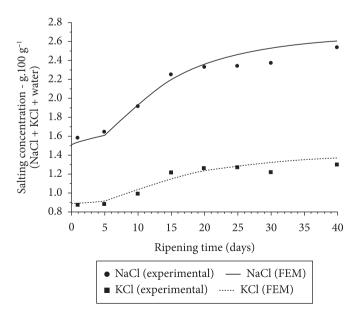
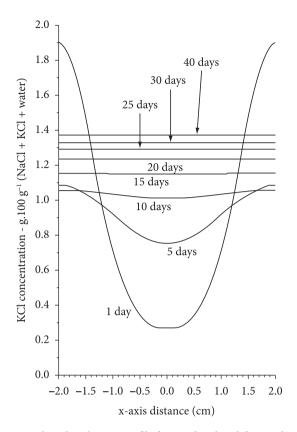


Figure 3. Experimentally-determined and FEM-estimated values for cylindrical samples.



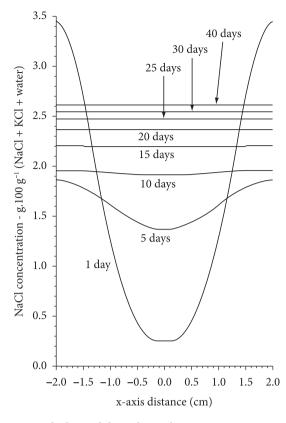


Figure 4. Saline distribution profile for NaCl and KCl during the 40-day ripening period, obtained through simulation.

4 Conclusions

The estimation for the main apparent diffusion coefficient for NaCl and KCl were 0.19 and 0.16 $\rm cm^2/day$, respectively. The corresponding estimated coefficient for KCl in the Prato cheese ripening has not been previously reported. The values of the diffusion coefficients adjusted for the ripening process were lower than those adjusted for the salting process for the same cheese.

Employing the generalized Fick's Second Law by FEM, we successfully simulated the multicomponent diffusion (deviation was less than 5%) during Prato cheese ripening with the NaCl-KCl-water system. The data simulated during the ripening period were in agreement with experimental results, which validated the application of the finite element method toward solving the multicomponent diffusion problem during this process.

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Nomenclature

Bi: Biot mass-exchange number

 \bar{C} : mean concentration (g.100 g⁻¹ NaCl + KCl + water)

 $ar{C}_{
m est}$: mean concentration estimated by FEM (g.100 g $^{-1}$ NaCl + KCl + water)

 $\bar{C}_{\rm exp}$: experimental mean concentration (g.100 g⁻¹ $_{\rm NaCl+KCl+Mex}$

 $C_{i,0}$: initial concentration of component i (g.100 g $^{-1}$ NaCl + KCl + water)

 $C_{i,s}$: component i concentration in brine (g.100 g⁻¹ NaCl + KCl + Water)

 $C_i(x,y,z,t)$: specific mass concentration (g.100 g⁻¹ NaCl + KCl + water)

D_{ii}: effective main diffusion coefficient (cm²/day)

D_{ii}: effective cross-diffusion coefficient (cm²/day)

h_m: film mass transfer coefficient (g/cm²/hour)

N: number of observations used to calculate %deviation

 $\pm R_1$, $\pm R_2$, $\pm R_3$: characteristic length (cm)

t: time (hours)

x, y, z: spatial coordinates (cm)

 ∇^2 (.): Laplacian operator

 $\partial/\partial\eta$: normal derivative operator

 $\partial\Omega$: set of surface points on the cheese

%deviation: percentage of deviation between predicted and experimental data

Greek symbols

 λ_m : mass conductivity (g/cm/hour)

 Ω : cheese volume or domain (cm³)

Sub indices

i: component i

j: component j

1: NaCl

2: KCl

References

- AGUILERA, J. M. Why food microstructure? **Journal of Food Engineering**, v. 67, n. 1-2, p. 3-11, 2005.
- ALVES, G. Parâmetros físico-químicos envolvidos na padronização e no rendimento de queijo Prato: modelagem matemática. Dissertação (Mestrado em Ciência de Alimentos)-Universidade Estadual de Londrina, Londrina, 1995.
- ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS AOAC. Official Methods of Analysis, 14. ed. Arlington, VA, USA: AOAC International, 1984. p. 1141.
- BICKFORD, W. B. A first course in the finite element method. Boston: Irwin, 1990. 649 p.
- BONA, E. et al. Aplicativo para otimização empregando o método simplex seqüencial. Acta Scientiarum, v. 22, n. 5, p. 1201-1206, 2000.
- BONA, E. et al. Difusão multicomponente durante a salga mista de queijo Prato. **Ciência e Tecnologia de Alimentos**, v. 35, n. 2, p. 394-400, 2005.
- BONA, E. et al. Multicomponent diffusion modeling and simulation in Prato cheese salting during brine at rest: the finite element method approach. **Journal of Food Engineering**, v. 79, n. 3, p. 771-778, 2007.
- BRESSAN, J. A. et al. Modeling of isothermal diffusion of whey components from small curd Cottage cheese during washing. **Journal of Food Science**, v. 47, n. 1, p. 84-88, 1982.
- CECCHI, H. M. Fundamentos teóricos e práticos em análise de alimentos. Campinas: Editora da Unicamp, 2003. p. 36-59.
- CICHOSCKI, A. J. et al. Characterization of Prato cheese, Brazilian semi-hard cow variety: evolution of physico-chemical parameters and mineral composition during ripening. **Food Control**, v. 13, n. 4-5, p. 329-336, 2002.
- CRANK, J. **The mathematics of diffusion**. 2. ed. London: Oxford University, 1975. 441 p.
- DERRINGER, G.; SUICH, R. Simultaneous optimization of several response variables. **Journal of Quality Technology**, v. 12, n. 4, p. 214-219, 1980.
- DJELVEH, G.; GROSS, J-B.; EMAM-DJOMEH, Z. Osmotic dehydration of foods in a multicomponent solution. Part II. Water loss and solute uptake in agar gels and meat. LWT, v. 34, n. 5, p. 319-323, 2001.
- FITZGERALD, E.; BUCKLEY, J. Effect of total and partial substitution of sodium chloride on the quality of cheddar cheese. **Journal of Dairy Science**, v. 68, n. 12, p. 3127-3134, 1985.
- FOX, P. F. Proteolysis during cheese manufacture and ripening. **Journal of Dairy Science**, v. 72, n. 6, p. 1379-1400, 1989.
- FURTADO, M. M. A arte e a ciência do queijo. 2. ed. São Paulo: Globo, 1991. 297 p.

- GERLA, P. E.; RUBIOLO, A. C. A model for determination of multicomponent diffusion coefficients in foods. **Journal of Food Engineering**, v. 56, n. 4, p. 401-410, 2003.
- GOMES, A. M. P.; VIEIRA, M. M.; MALCATA, F. X. Survival of probiotic microbial strains in cheese matrix during ripening: simulation of rates of salt diffusion and microorganism survival. **Journal of Food Engineering**, v. 36, n. 3, p. 281-301, 1998.
- GOROSTIZA, A. et al. Changes in soluble nitrogenous compounds, caseins and free amino acids during ripening of artisanal Prato cheese; a Brazilian semi-hard cows variety. **Food Chemistry**, v. 85, n. 3, p. 407-414, 2004.
- GUINEE T. P.; FOX, P. F. Salt in cheese: physical, chemical e biological aspects. In: FOX, P. F. **Cheese**: chemistry, physical and microbiology. New York: Elsevier Applied Science, 1987. v. 1, cap. 7, p. 215-297.
- GUINEE, T. P. Salting and the role of salt in cheese. **International Journal of Dairy Technology**, v. 57, n. 2-3, p. 99-109, 2004.
- HE, F. J.; MACGREGOR, G. A. Fortnightly review: beneficial effects of potassium. **British Medical Journal**, v. 323, n. 7311, p. 497-503, 2001.
- KATSIARI, M. C. et al. Manufacture of Kefalograviera cheese with less sodium by partial replacement of NaCl with KCl. **Food Chemistry**, v. 61, n. 1-2, p. 63-70, 1998.
- KHIN, M. M.; ZHOU, W.; PERERA, C. O. A study of the mass transfer in osmotic dehydration of coated potato cubes. **Journal of Food Engineering**, v. 77, n. 1, p. 84-95, 2006.
- KILCAWLEY, K. N.; WILKINSON, M. G.; FOX, P. F. Enzime-modified cheese: review. International Dairy Journal, v. 8, n. 1, p. 1-10, 1998.
- LI, L. Y. Numerical simulation of mass transfer during the osmotic dehydration of biological tissues. Computational Materials Science, v. 35, n. 2, p. 75-83, 2006.
- LINDSAY, R. C.; HARGETT, S. M.; BUSH, C. S. Effect of sodium/potassium (1:1) chloride concentrations on quality of cheddar cheese. **Journal of Dairy Science**, v. 65, n. 3, p. 360-370, 1982.
- LOMAURO, G. J.; BAKSHI, A. S. Finite-element analysis of moisture diffusion in stored foods. Journal of Food Science, v. 50, n. 2, p. 392-396, 1985.
- LUNA, J. A.; BRESSAN, J. A. Mass transfer during brining of Cuartiolo argentino cheese. **Journal of Food Science**, v. 51, n. 3, p. 829-831, 1986.
- LUNA, J. A.; BRESSAN, J. A. Mass transfer during ripening of Cuartiolo argentino cheese. Journal of Food Science, v. 52, n. 2, p. 308-311, 1987.
- LUNA, J. A.; CHAVEZ, M. S. Mathematical model for water diffusion during brining of hard and semi-hard cheese. **Journal of Food Science**, v. 57, n. 1, p. 55-58, 1992.
- LYNCH, N. M. In search of the salty taste. Food Technology, v. 33, n. 12, p. 57-59, 1979.
- MARTINS, R. C. Simple finite volumes and finite elements procedures for food quality and safety simulations. **Journal of Food Engineering**, v. 73, n. 4, p. 327-338, 2006.
- MAYOR, R. L. et al. Kinetics of osmotic dehydration of pumpkin with sodium chloride solutions. **Journal of Food Engineering**, v. 74, n. 2, p. 253-262, 2006.
- MEDINA-VIVANCO, M.; SOBRAL, A.; HUBINGER, M. D. Osmotic dehydration of tilapia fillets in limited volume of ternary solutions. Chemical Engineering Journal, v. 86, n. 1-2, p. 199-205, 2002.
- MORRIS, H. A.; GUINEE, T. P.; FOX, P. F. Salt diffusion in Cheddar cheese. **Journal of Dairy Science**, v. 68, n. 8, p. 1851-1858, 1985.

- ONSAGER, L. Theories and problems of liquid diffusion. **Annals of the New York Academy of Sciences**, v. 46, n. 5, p. 241-265, 1945.
- PAJONK, A. S; SAUREL, R.; ANDRIEU, J. Experimental study and modeling of effective NaCl diffusion: coefficients values during Emmental cheese brining. **Journal of Food Engineering**, v. 60, n. 4, p. 307-313, 2003.
- PAYNE, M. R.; MORISON, K. R. A multi-component approach to salt and water diffusion in cheese. **International Dairy Journal**, v. 9, n. 12, p. 887-894, 1999.
- PURI, V.M.; ANANTHESWARAN, R. C. The finite element method in food processing: a review. **Journal of Food Engineering**, v. 19, n. 3, p. 247-274, 1993.
- RAPACCI, M. Efeito da substituição do cloreto de sódio por cloreto de potássio nas características do queijo Prato. Dissertação (Mestrado em Ciência de Alimentos)-Universidade Estadual de Londrina, Londrina, 1989.
- RICHARDSON, G. H. (Ed.). **Standard methods for examination of dairy products**. 5. ed. Washington: American Public Health Association, 1985. 412 p.
- SCHROEDER, C. L. et al. Reduction of sodium chloride in Cheddar cheese: effect of sensory, microbiological and chemical properties. **Journal of Dairy Science**, v. 71, n. 8, p. 2010-2020, 1988.
- SILVA, R. S. S. F.; BORSATO, D.; SILVA, L. H. M. Difusão do cloreto de sódio no processo de salga de queijos: modelagem matemática com o emprego do método de elementos finitos. Ciência e Tecnologia de Alimentos, v. 18, n. 1, p. 87-92, 1998.

- SORENSEN, J.; BENFELDT, C. Comparison of ripening characteristics of Danbo cheeses from two dairies. **International Dairy Journal**, v. 11, n. 4-7, p. 355-362, 2001.
- TELIS, V. R. N.; MURARI, R. C. B. D. L.; YAMASHITA, F. Diffusion coefficients during osmotic dehydration of tomatoes in ternary solutions. **Journal of Food Engineering**, v. 61, n. 2, p. 253-259, 2004.
- WALTERS, F. H. et al. **Sequential simplex optimization**. Karskrona, Sweden: Licensed eletronic reprint by Multisimplex AB, 1999. 403 p.
- WANG, L.; SUN, D. Recent developments in numerical modeling of heating or cooling processes in the food industry a review. **Trends in Food Science and Technology**, v. 14, n. 10, p. 408-423, 2003.
- WELTI-CHANES, J.; VERGARA-BALDERAS, F.; BERMÚDEZ-AGUIRRE, D. Transport phenomena in food engineering: basic concepts and advances. **Journal of Food Engineering**, v. 67, n. 1-2, p. 113-128, 2005.
- ZORRILLA, S. E.; RUBIOLO, A. C. Fynbo cheese NaCl and KCl changes during ripening. **Journal of Food Science**, v. 59, n. 5, p. 972-975, 1994a.
- ZORRILLA, S. E.; RUBIOLO, A. C. Modeling NaCl and KCl movement in Fynbo cheese during salting. Journal of Food Science, v. 59, n. 5, p. 976-980, 1994b.
- ZORRILLA, S. E.; RUBIOLO, A. C. Modelling average concentrations of salt and salt substitute in partial or total volumes of semihard cylindrical cheeses. **International Journal of Food Science and Technology**, v. 33, n. 6, p. 501-508, 1998.