SIMULATION OF NaCl AND KCl MASS TRANSFER DURING SALTING OF PRATO CHEESE IN BRINE WITH AGITATION: A NUMERICAL SOLUTION

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Abstract - The association of dietary NaCl with arterial hypertension has led to a reduction in the levels of this salt in cheeses. For salting, KCl has been used as a partial substitute for NaCl, which cannot be completely substituted without affecting product acceptability. In this study a sensorially adequate saline solution (NaCl/KCl) was simultaneously diffused during salting of Prato cheese in brine with agitation. The simultaneous multicomponent diffusion during the process was modeled with Fick's second generalized law. The system of partial differential equations formed was solved by the finite element method (FEM). In the experimental data concentration the deviation for NaCl was of 7.3% and for KCl of 5.4%, both of which were considered acceptable. The simulation of salt diffusion will allow control and modulation of salt content in Prato cheese, permitting the prediction of final content from initial conditions.
Keywords: Multicomponent diffusion; Finite element method; Biot mass-exchange number.

INTRODUCTION

Sodium chloride is an important component in cheese production because it gives flavor, produces physical alterations in cheese proteins that influence texture, and also helps to control microbial growth and the activity of several enzymes in the cheese (Guinne and Fox, 1984). However, a portion of the population avoids cheese consumption to reduce salt intake due to problems related to arterial hypertension (Jameson, 1986; He and MacGregor, 2001).

An alternative proposed by Rapacci (1989) is to substitute some of the NaCl by KCl in the cheese formulation. According to the same author, the substitution of up to 30% of the NaCl by KCl does not produce significant differences in sensorial, physical, and chemical properties (p>0.05) from traditional cheese salted with sodium chloride.

Salt transport in cheese can be simply described by Fick's second law, but many cheese and brine properties can affect the process. When several solutes diffuse simultaneously, Fick's second

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generalized law can be assumed (Onsager, 1945; Cussler, 1976), and in this case, in addition to the self-diffusion coefficient, cross diffusion coefficients are included to take into account the influence of a solute on the flow of the other one. Generally, for highly dissociable solutes the cross terms are smaller than the main ones (Gerla and Rubiolo, 2003). It seems to be well established that an appropriate salt concentration and its uniform distribution are important factors in cheese ripening (Guinne and Fox, 1984). Consequently, models that estimate saline concentrations as a result of processing could be useful when more than one component is considered in the salting.

Nowadays with the development of high-performance computers, it is possible to simulate a process close to reality using numerical techniques such as the finite element method, or FEM (Puri and Anantheswaran, 1993; Wang and Sun, 2003). Mass and heat transfer and solid and fluid mechanics are among the typical applications of this method (Bickford, 1990). According to Puri and Anantheswaran (1993), the main advantages of FEM are as follow: the spatial variation in material properties can be easily manipulated, irregular regions can be modeled with great precision, it is the best for nonlinear problems, the dimensions of the elements can be easily altered, the spatial interpretation is very realistic, and problems with the most diverse boundary conditions can be easily studied. However, the reliability of the solution obtained using FEM is directly related to the discretization of the model (Lyra, 1993). Silva et al. (1999) showed that due to the order of magnitude of the diffusion coefficient in cheese salting, the oscillation in the results could be dampened (Britz et al., 2002), optimizing the spatial and temporal discretization (Bona, 2004). This method has been applied successfully in simulating NaCl diffusion in cheese using Fick's second law as the theoretical support for this phenomenon (Silva et al., 1998, 1999) and in simulating simultaneous NaCl and KCl diffusion in static brine (Bona, 2004).

The objective of this study was to present an analysis of multicomponent mass transfer during salting with agitation for the NaCl-KCl-water system in Prato cheese using FEM.

MATERIAL AND METHODS

Salting

A piece of cheese measuring 24cm × 12cm × 9cm (Queijo Prato Lanche DI CARLO from Campina Alta dairy plant, located in Manoel Ribas – PR, Brazil) was 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 ($10\pm1^{o}C$) for approximately 12 hours before the experimental procedure. After this period it was removed from the mold and cut into smaller pieces (4cm × 9cm × 12cm) for the salting process. One of these samples was used to determine the fat, moisture, and initial sodium and potassium concentrations.

The cheeses were kept in stirred brine at $10\pm1^{o}C$ using an adapted domestic refrigerator (CONTINENTAL 560L). A pump (Motor Pump SARLO Better S520) with a 520L/h circulation flow was used for agitation purposes. Twenty liters of brine were prepared in accordance with Furtado (1990), who suggested a saline concentration of about 20% (w/w) and an average pH of 5.5 adjusted with HCl. To prevent Ca^{2+} loss from the cheeses and the consequent loss of rigidity, 0.5% (w/w) of $CaCl_2$ was added. The brine volume used was approximately five times greater than the cheese volume to ensure that the brine concentration remained constant throughout the salting period (Gerla and Rubiolo, 2003). Before salting, a sample of brine was removed to quantify the salt contents, and another sample was removed at the end of the salting period. For studying multicomponent diffusion, approximately 70% NaCl and 30% KCl was used, as suggested by Rapacci (1989).

Because the cheese density was lower than the brine density, the cheese was immobilized by a network of cotton thread within the salting recipient (34cm × 49cm × 15cm), (Figure 1). This network guaranteed that none of the samples touched and all the surfaces were in contact with the brine, permitting uniform salting.
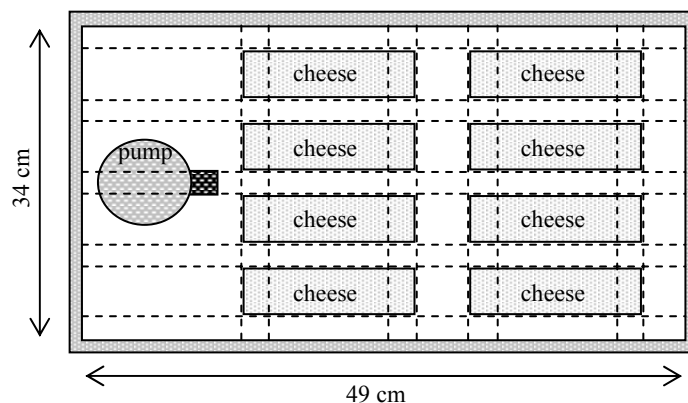
Figure 1: Schematic upper view of the experimental system showing cheese pieces
and the pump. The dotted lines represent the network of cotton threads.

Sampling

The sampling procedure consisted of removing two cylindrical samples, each 1.5cm in diameter and 4cm in height, located as illustrated in Figure 2.

After removal, the cylinders were cut half to produce four cylindrical samples, as shown in Figure 3.

The cylinders belonging to the same face were analyzed together. The samples were removed for analysis after 1, 2, 3, 4, 5, and 7 hours of salting.

The dimensions shown in Figure 2, which were 4.5cm for the Y axis and 4.0cm for the Z axis, were sufficient to guarantee a one-dimensional approach to the problem (Gerla and Rubiolo, 2003; Luna and Bressan, 1986) because maximal NaCl penetration was estimated to be about 1.5cm for the salting time considered (Silva et al., 1998).

Two samples were removed to determine whether there was variability in the salt concentration during the extraction and quantification processes.
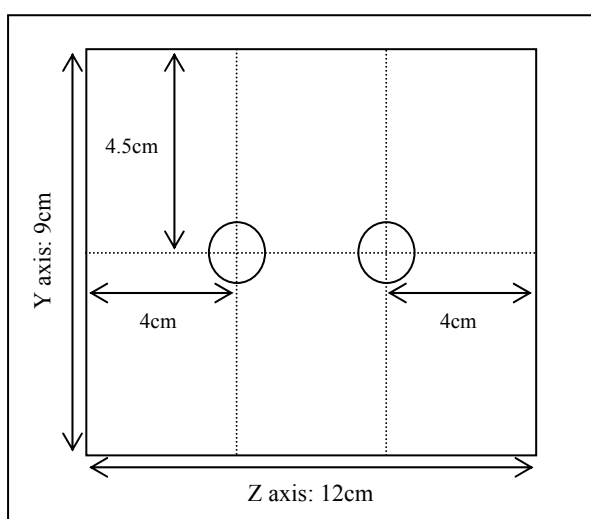

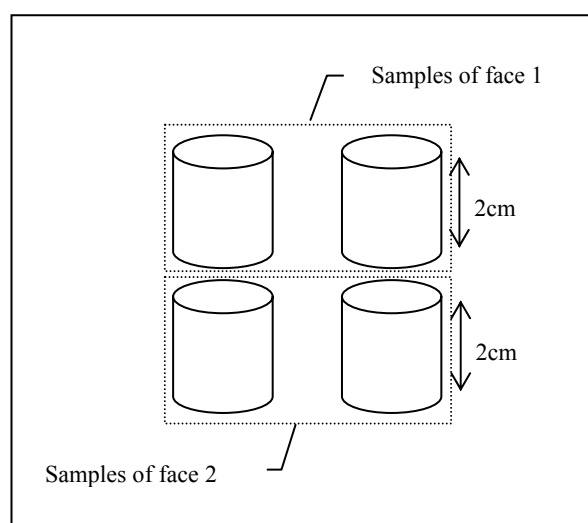**Figure 2:** Sampling used to determine the NaCl and KCl contents.

Figure 3: Section of the samples in four identical cylinders.

Moisture and Fat

Moisture was determined by drying in an oven at 105°C to constant weight (Richardson, 1985; AOAC, 1984) and fat, by the Soxhlet method (Cecchi, 1999).

Sodium and Potassium

Sodium and potassium content was determined by atomic emission (flame photometry), using a Celm FC-280 flame photometer, after incinerating the samples and extracting the salts with 0.5 mol/L HCl.

MATHEMATICAL MODEL

Finite Element Formulation

This study considered the simultaneous three-dimensional mass transfer of two solutes in a cheese that occupied a volume of $\Omega \subset R^3$, 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 there were no chemical reactions; diffusion was the predominant mechanism, so there was no convective mass transfer into the cheese pores, only diffusion; the effective or apparent diffusion coefficients were constant (did not depend on concentration or coordinates); and the sample contraction was negligible. Under these conditions, multicomponent diffusion during salting in brine with agitation at a constant temperature of 10°C was modeled. With well-stirred brine we can assume that the inter-phase concentration equilibrium of the brine/cheese is instantaneously established after immersion of the cheese (Luna and Bresan, 1986).

The classical theory of transport phenomena is difficult to apply to biological materials because of their peculiar characteristics, structure, properties, etc. (Welti-Chanes et al., 2005). The effect of food microstructure on the diffusion coefficient is discussed in Aguilera and Stanley (1999). Actually, even considering cheese as a food matrix with saline solution occluded in the pores, parameters such as porosity, tortuosity, and phase ratios are not sufficient to describe the extraction/impregnation process accurately (Crossley and Aguilera, 2001). It is very probable that the quantification of food microstructures using image analysis will result in a more fundamental approach to studying mass transfer phenomena in foods and other biological materials (Aguilera, 2005). Meanwhile, many research publications on mass transfer in food engineering are oriented to solving Fick's law or other derivations of this law for some specific process (Welti-Chanes et al., 2005).

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 instant t, can be described by the Onsager equations (1945) for the solute concentrations:

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

where $\nabla^2(.) = \nabla.\nabla(.)$ is the Laplacian operator and D_{ii} are the main diffusion coefficients and D_{ij} are the crossed diffusion coefficients that combine the flows.

The boundary conditions used for the salting process in well-stirred brine are, in mathematical terms, essential and are called Dirichlet boundary conditions and are given by

$$C_1(x, y, z, t) = C_{1,S}$$
$$C_2(x, y, z, t) = C_{2,S} \qquad x, y, z \in \partial\Omega, \text{and } t \geq 0 \tag{2}$$

The initial conditions used were

$$C_1(x, y, z, 0) = C_{1,0}$$
$$C_2(x, y, z, 0) = C_{2,0} \qquad x, y, z \in \Omega \tag{3}$$

where $C_{1,S}$ and $C_{2,S}$ are respectively the NaCl and KCl concentrations in brine and $\partial\Omega$ is the set of points on the surface of the cheese, conditions (2). $C_{1,0}$ and $C_{2,0}$ are respectively the initial NaCl and KCl concentrations in the cheese, conditions (3).

The partial differential equation system formed by equation (1) and by conditions (2) and (3) is difficult to solve analytically, even under the assumptions made regarding the process. One way of solving it is by using a transformation obtained with eigenvalues and eigenvectors in a matrix of differential operators that appears on the right-hand side of equation (1). The disadvantages of this method are mainly due to restrictions in system geometry. In addition, the transformed variables have no physical meaning (Bona et al., 2005).

Another alternative that does not have these restrictions and can also be applied in this study is the numerical solution of the system by a finite element method. A generalized Galerkin formulation was used (Buchanan, 1994; Huebner et al., 1995) to obtain the equation to be discretized by finite elements. The main steps are synthesized as follows:

1. The equation for the weighted residues formed for the system (1) is

$$\int_{\Omega} \begin{bmatrix} \phi & 0 \\ 0 & \psi \end{bmatrix} \begin{Bmatrix} \dfrac{\partial C_1}{\partial t} \\ \dfrac{\partial C_2}{\partial t} \end{Bmatrix} d\Omega = \int_{\Omega} \begin{bmatrix} \phi & 0 \\ 0 & \psi \end{bmatrix} \begin{bmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{bmatrix} \begin{Bmatrix} \nabla^2 C_1 \\ \nabla^2 C_2 \end{Bmatrix} d\Omega \qquad (4)$$

where ϕ and ψ are weighting functions that are null in $\partial\Omega$;

2. The right side of equation (4) is integrated by parts to obtain the following:

$$\int_{\Omega} \begin{bmatrix} \phi & 0 \\ 0 & \psi \end{bmatrix} \begin{Bmatrix} \dfrac{\partial C_1}{\partial t} \\ \dfrac{\partial C_2}{\partial t} \end{Bmatrix} d\Omega = -\int_{\Omega} \begin{bmatrix} \dfrac{\partial\phi}{\partial x} & 0 & \dfrac{\partial\phi}{\partial y} & 0 & \dfrac{\partial\phi}{\partial z} & 0 \\ 0 & \dfrac{\partial\psi}{\partial x} & 0 & \dfrac{\partial\psi}{\partial y} & 0 & \dfrac{\partial\psi}{\partial z} \end{bmatrix} \begin{bmatrix} D_{11} & D_{12} & 0 & 0 & 0 & 0 \\ D_{21} & D_{22} & 0 & 0 & 0 & 0 \\ 0 & 0 & D_{11} & D_{12} & 0 & 0 \\ 0 & 0 & D_{21} & D_{22} & 0 & 0 \\ 0 & 0 & 0 & 0 & D_{11} & D_{12} \\ 0 & 0 & 0 & 0 & D_{21} & D_{22} \end{bmatrix} \begin{Bmatrix} \dfrac{\partial C_1}{\partial x} \\ \dfrac{\partial C_2}{\partial x} \\ \dfrac{\partial C_1}{\partial y} \\ \dfrac{\partial C_2}{\partial y} \\ \dfrac{\partial C_1}{\partial z} \\ \dfrac{\partial C_2}{\partial z} \end{Bmatrix} d\Omega \qquad (5)$$

The discretization continues following the next steps:

3. A partition of the domain in to some subdomains called finite elements is adopted;

4. N nodes are attributed to each element, and each node has two degrees of freedom (one for each solute). The variables of the problem are interpolated locally by the interpolation equations associated with the nodes. Therefore, equation (5) can be rewritten in matrix form (local stiffness matrix) for each element as

$$\mathbf{A}_{2N \times 2N} \dot{\mathbf{C}}_{2N} = -\mathbf{B}_{2N \times 2N} \mathbf{C}_{2N} \qquad (6)$$

where

$$\mathbf{A}_{2N \times 2N} = \int_{\Omega} \begin{bmatrix} \phi_1 & 0 \\ 0 & \psi_1 \\ \phi_2 & 0 \\ 0 & \psi_2 \\ \vdots & \vdots \\ \phi_N & 0 \\ 0 & \psi_N \end{bmatrix} \begin{bmatrix} \phi_1 & 0 & \phi_2 & 0 & \cdots & \phi_N & 0 \\ 0 & \psi_1 & 0 & \psi_2 & \cdots & 0 & \psi_N \end{bmatrix} d\Omega \qquad \mathbf{C}_{2N} = \begin{Bmatrix} C_1 \\ C_2 \\ \vdots \\ C_1 \\ C_2 \end{Bmatrix} \qquad \dot{\mathbf{C}}_{2N} = \begin{Bmatrix} \dfrac{\partial C_1}{\partial t} \\ \dfrac{\partial C_2}{\partial t} \\ \vdots \\ \dfrac{\partial C_1}{\partial t} \\ \dfrac{\partial C_2}{\partial t} \end{Bmatrix}$$

$$\mathbf{B}_{2N \times 2N} = \int_{\Omega} \begin{bmatrix} \dfrac{\partial\phi_1}{\partial x} & 0 & \dfrac{\partial\phi_1}{\partial y} & 0 & \dfrac{\partial\phi_1}{\partial z} & 0 \\ 0 & \dfrac{\partial\psi_1}{\partial x} & 0 & \dfrac{\partial\psi_1}{\partial y} & 0 & \dfrac{\partial\psi_1}{\partial z} \\ \dfrac{\partial\phi_2}{\partial x} & 0 & \dfrac{\partial\phi_2}{\partial y} & 0 & \dfrac{\partial\phi_2}{\partial z} & 0 \\ 0 & \dfrac{\partial\psi_2}{\partial x} & 0 & \dfrac{\partial\psi_2}{\partial y} & 0 & \dfrac{\partial\psi_2}{\partial z} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \dfrac{\partial\phi_N}{\partial x} & 0 & \dfrac{\partial\phi_N}{\partial y} & 0 & \dfrac{\partial\phi_N}{\partial z} & 0 \\ 0 & \dfrac{\partial\psi_N}{\partial x} & 0 & \dfrac{\partial\psi_N}{\partial y} & 0 & \dfrac{\partial\psi_N}{\partial z} \end{bmatrix} \begin{bmatrix} D_{11} & D_{12} & 0 & 0 & 0 & 0 \\ D_{21} & D_{22} & 0 & 0 & 0 & 0 \\ 0 & 0 & D_{11} & D_{12} & 0 & 0 \\ 0 & 0 & D_{21} & D_{22} & 0 & 0 \\ 0 & 0 & 0 & 0 & D_{11} & D_{12} \\ 0 & 0 & 0 & 0 & D_{21} & D_{22} \end{bmatrix} \begin{bmatrix} \dfrac{\partial\phi_1}{\partial x} & 0 & \dfrac{\partial\phi_2}{\partial x} & 0 & \cdots & \dfrac{\partial\phi_N}{\partial x} & 0 \\ 0 & \dfrac{\partial\psi_1}{\partial x} & 0 & \dfrac{\partial\psi_2}{\partial x} & \cdots & 0 & \dfrac{\partial\psi_N}{\partial x} \\ \dfrac{\partial\phi_1}{\partial y} & 0 & \dfrac{\partial\phi_2}{\partial y} & 0 & \cdots & \dfrac{\partial\phi_N}{\partial y} & 0 \\ 0 & \dfrac{\partial\psi_1}{\partial y} & 0 & \dfrac{\partial\psi_2}{\partial y} & \cdots & 0 & \dfrac{\partial\psi_N}{\partial y} \\ \dfrac{\partial\phi_1}{\partial z} & 0 & \dfrac{\partial\phi_2}{\partial z} & 0 & \cdots & \dfrac{\partial\phi_N}{\partial z} & 0 \\ 0 & \dfrac{\partial\psi_1}{\partial z} & 0 & \dfrac{\partial\psi_2}{\partial z} & \cdots & 0 & \dfrac{\partial\psi_N}{\partial z} \end{bmatrix} d\Omega$$

5. The global stiffness matrix is the assemblage of all local stiffness matrices and it results in a system of ordinary differential equations;

6. The solution of this system is obtained by an implicit process of finite differences supplying the values of the concentrations at the element nodes. Local interpolation can determine the concentration profile at any point in the cheese at any time during salting.

Spatial Discretization

The spatial domain was represented by a set of hexahedral elements of the C^0 type, shown in Figure 4. Each element has 20 nodes with two degrees of freedom (one for each solute) on the intersecting lines and vertices, totaling forty degrees of freedom (Silva et al., 1998). Figure 4a shows the nodes and the local enumeration. The spatial orientation of the elements and enumeration of the surfaces used in the computer procedure are shown in Figures 4b and 4c. The element is defined in standard Cartesian coordinates, that is $-1 \leq \xi, \eta, \zeta \leq 1$ (Chung, 1978).
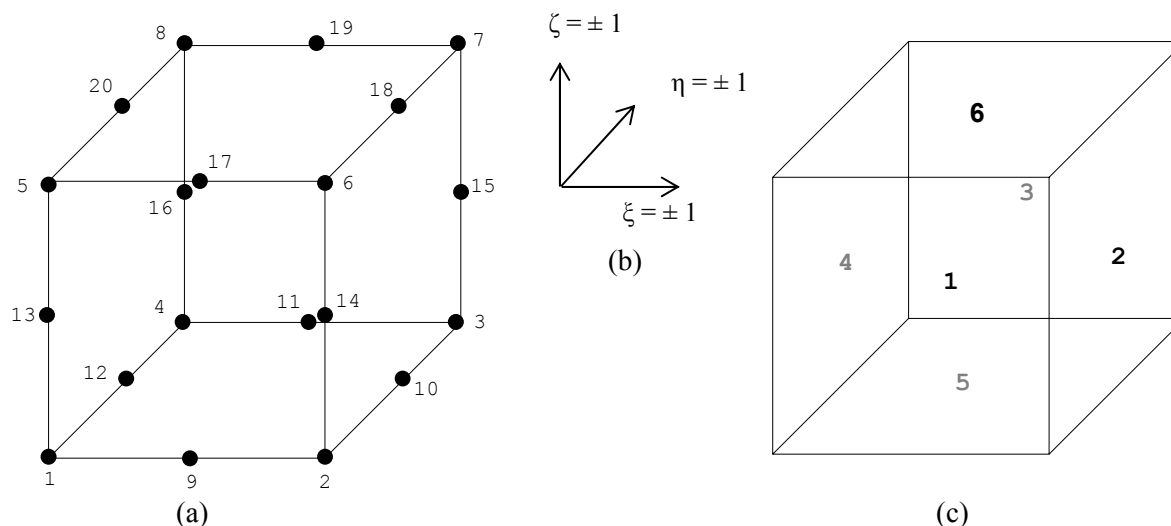

Figure 4: (a) Standard hexahedral element with 20 nodal points, (b) standard orientation, and (c) enumeration of the surfaces. The bold numbers represent the visible faces and the gray numbers, the invisible ones.

The interpolation functions, represented by equations 7 to 10, preserve the continuity among the elements (Chung, 1978; Akin, 1982). The interpolation functions used for the nodal points of the vertices, i = 1, 2, 3, ..., 8 were

$$\phi_i = \frac{1}{8}\left(1 + \xi\xi_i\right)\left(1 + \eta\eta_i\right)\left(1 + \zeta\zeta_i\right)$$

$$\left(\xi\xi_i + \eta\eta_i + \zeta\zeta_i - 2\right)$$

(7)

at midside nodes, i = 9, 10, 11, ..., 20.

$$\phi_i = \frac{1}{4}\left(1 + \xi^2\right)\left(1 + \eta\eta_i\right)\left(1 + \zeta\zeta_i\right) \quad \text{where}$$

$$\xi_i = 0, \eta_i = \pm 1 \text{ and } \zeta_i = \pm 1$$

(8)

$$\phi_i = \frac{1}{4}\left(1 + \xi\xi_i\right)\left(1 + \eta^2\right)\left(1 + \zeta\zeta_i\right) \quad \text{where}$$

$$\xi_i = \pm 1, \eta_i = 0 \text{ and } \zeta_i = \pm 1$$

(9)

$$\phi_i = \frac{1}{4}\left(1 + \xi\xi_i\right)\left(1 + \eta\eta_i\right)\left(1 + \zeta^2\right) \quad \text{where}$$

$$\xi_i = \pm 1, \eta_i = \pm 1 \text{ and } \zeta_i = 0$$

(10)

where ϕ_i is the isoparametric function (Brebbia and Ferrante, 1975; Chung, 1978; Cook, 1981; Bickford, 1990) and ξ, η, and ζ are local coordinates of the standard element. In the formulation proposed $\psi_i = \phi_i$ was used.

Procedure for Integration in Time

The Crank-Nicholson implicit algorithm, or the central difference scheme was used for time discretization. For application of the implicit scheme in the domain, $\dot{C}_{2N}$ and C_{2N} were discretized from equation (6) as follows:

$$\mathbf{A_{2Nx2N}}\left(\frac{\mathbf{C_{2N}^1} - \mathbf{C_{2N}^0}}{\Delta t}\right) = -\mathbf{B_{2Nx2N}}\left(\frac{\mathbf{C_{2N}^1} + \mathbf{C_{2N}^0}}{2}\right) \quad (11)$$

where Δt is a discrete increase in time; $\mathbf{C_{2N}^0}$ is the solute concentration vector, which is already known for each node of the element before adding time; and $\mathbf{C_{2N}^1}$ represents the concentration vector that will be calculated after adding time (Δt). Organizing the terms of the equation (11) we have

$$\left(\frac{\mathbf{A_{2Nx2N}}}{\Delta t} + \frac{\mathbf{B_{2Nx2N}}}{2} \right) \mathbf{C_{2N}^1} =$$
$$= \left(\frac{\mathbf{A_{2Nx2N}}}{\Delta t} - \frac{\mathbf{B_{2Nx2N}}}{2} \right) \mathbf{C_{2N}^0} \qquad (12)$$

Equation (12) represents the system of equations, written in matrix form, for each element. By overlapping the elements, a global system of linear equations of the $\mathbf{AX} = \mathbf{B}$ type is obtained. The boundary conditions (2) are imposed next, and the system can be solved by any technique compatible with the size and characteristics of matrix $\mathbf{A}$.

Solving the System of Linear Equations

When choosing a method for this system resolution, care should be taken with respect to two problems (Sperandio et al., 2003): the first concerns the propagation of round-off errors, that is, the numerical stability of the method compared to its sensitivity in accumulating round-off errors; the second concerns the form of storage of matrix $\mathbf{A}$, which should be in line with the algorithm used.

The LU decomposition method (Sperandio et al., 2003) was used to solve the system of linear equations (12). For a linear system of equations, LU factorization produces $\mathbf{A} = \mathbf{LU}$ where $\mathbf{L}$ and $\mathbf{U}$ are the lower and upper triangular matrices, respectively. Therefore $\mathbf{LUX} = \mathbf{B}$, and assigning $\mathbf{UX} = \mathbf{Y}$, another linear system is formed as

$$\begin{cases} \mathbf{LY} = \mathbf{B} \\ \mathbf{UX} = \mathbf{Y} \end{cases} \qquad (13)$$

The $\mathbf{L}$ and $\mathbf{U}$ matrices were generated using the Doolittle method (Sperandio et al., 2003). The computational implementation of the method was carried out by a set of subroutines (DLSLRB and DLFCRB) based on the LINPACK package (Cline et al., 1979; Dongarra et al., 1979). The DLSLRB subroutine solves linear equation systems stored in a band without using interactive refinement. This subroutine uses another subroutine (DLFCRB), which estimates the condition number of the matrix and performs the LU decomposition, and the DLFSRB routine solves the system formed by the $\mathbf{L}$ and $\mathbf{U}$ matrices.

Mesh

A mesh generating subroutine was applied because the practical application of the finite element method requires a lot of input data. The global enumeration and the coordinates of the nodes were obtained automatically for rectangular domains. This procedure simplified node position identification, allowing sampling at any point or region of the mesh, making the computer program more versatile (Bona, 2004).

Computational Programming

Simul 3.0 software (Bona, 2004) in Fortran language, configured to apply the Dirichlet boundary condition, was used to simulate multicomponent diffusion during the salting with agitation. The minimal requirement for its use is a Pentium III processor and 256Mb of ram memory.

Integration and Interpolation

The experimental values obtained represented the mean NaCl and KCl concentrations for the cylindrical sample (Figure 3). As FEM gives point concentrations, it was necessary to interpolate the simulated points on the imaginary axis located at the center of the sample removed. The average was calculated by the integration of these points using the following equation:

$$\overline{C} = \frac{\int_V C_i(x, y, z, t)\, dV}{\int_V dV} \quad \text{for } i = 1 \text{ or } 2 \qquad (14)$$

The integral was calculated numerically by a Gauss quadrature formula (Sperandio et al., 2003) and the abscissas and weights were obtained from Davis and Polonsky (1965).

Statistical Test

The estimated and experimental values of the NaCl and KCl concentrations in the brine were compared by percentage deviation (Heldman, 1974),

represented by equation (15), in order to assess the goodness of fit.

$$\%\text{deviation} = 100 \sqrt{\sum_{i=1}^{N}\left[\left(\frac{\overline{C}_{est} - \overline{C}_{exp}}{\overline{C}_{exp}}\right)_i\right]^2 \frac{1}{N}} \quad (15)$$

where $\overline{C}_{est}$ is the average concentration estimated by the numerical solution, $\overline{C}_{exp}$ is the experimental average concentration, and N is the number of observations considered.

RESULTS AND DISCUSSION

The initial brine and cheese characteristics are shown in Tables 1 and 2, respectively.

The parameters used (three steps) were obtained by optimization of the spatial temporal discretization applied to the simulation of multicomponent diffusion (Bona, 2004): (i) the simulation by finite elements was performed with a mesh of 504 elements; (ii) two 0.05h, three 0.30h, and six 1.00h intervals were used for the time discrete partitions because shorter time intervals at the start are essential (Lyra, 1993) to dampen the oscillations that damage FEM refinement; and (iii) the effective diffusion coefficients (Table 3) used in the simulation were obtained from Bona (2004) for brine at rest. Slightly different values for the diffusion coefficients were found through a one-dimensional analytical solution (Bona et al., 2005). However the deviations among the respective main coefficients were comparable with those found in published data (Zorrilla and Rubiolo, 1994). The fact that the KCl main coefficient was larger than the NaCl coefficient was due to its greater mobility in an aqueous solution (Schwartzberg and Chao, 1982). The main coefficients were greater than the cross coefficients, indicating that diffusion in relation to its own gradient was more important than diffusion due to interaction among solutes (Zorrilla and Rubiolo, 1994).

Figure 5 shows the experimental and simulated saline distribution profiles of NaCl and KCl diffusion in Prato cheese using brine with agitation. The average values for both faces (Figure 3) were used as experimental data.

Table 1: Initial brine characteristics[*].

Temperature (ºC)	10 ± 1
pH	5.3
CaCl$_2$ (g/100g $_{NaCl + KCl + water}$)	0.5
NaCl (g/100g $_{NaCl + KCl + water}$)	13.59
KCl (g/100g $_{NaCl + KCl + water}$)	5.06
Salt ratio	72.9% NaCl : 27.1% KCl
Brine volume/total cheese volume	5.0

[*]The initial and end brining characteristics were the same.

Table 2: Relevant Prato cheese chemical composition before brining[*].

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

[*]Average and standard deviation.

Table 3: Diffusion coefficients used for simulation (Bona, 2004).

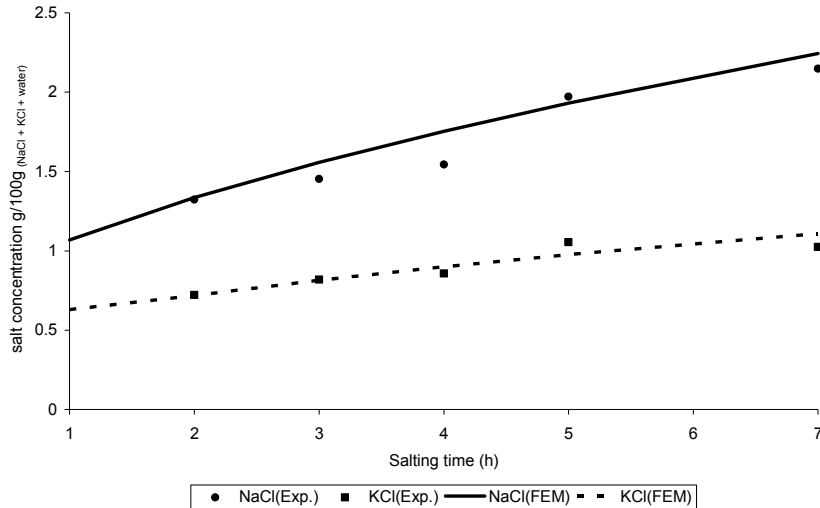|	NaCl	KCl
Main coefficient (cm^2/day)	0.242 (D$_{11}$)	0.254 (D$_{22}$)
Cross coefficient (cm^2/day)	0.019 (D$_{12}$)	0.039 (D$_{21}$)

Figure 5: Saline distribution profile for NaCl and KCl during salting in stirring brine.

Salting in brine at rest is different from salting with agitation due to the existence of an external resistance that hinders diffusion of the salts in the cheese. This resistance is inversely proportional to an adimensional number called the mass transfer Biot number (Loncin and Merson, 1979; Fryer et al., 1997). It can be expressed as

$$Bi = \frac{h_m \cdot R_i}{\lambda_m} \qquad \text{for } i = 1, 2, 3 \qquad (16)$$

where h_m (g/cm² h) is the film mass transfer coefficient, λ_m (g/cm h) is the mass conductivity, and R_i is the characteristic length (cm). For brine with agitation this resistance can be neglected (Luna and Bressan, 1986).

Simul 3.0 software was also used to assess the efficiency of the agitation, assuming that the salting was static. Results were simulated with Biots of 33.154 (Bona, 2004), 50, and 100. Table 4 shows the percentage of deviation for different Biot numbers using a Cauchy boundary condition, equation (17), and for the absence of external resistance using the Dirichlet boundary condition in the salting simulation.

$$\frac{\partial C_1 (\pm R, t)}{\partial \eta} = \frac{h_m}{\lambda_m} \Big[C_1 - C_{1,s} \Big]$$

$$\frac{\partial C_2 (\pm R, t)}{\partial \eta} = \frac{h_m}{\lambda_m} \Big[C_2 - C_{2,s} \Big] \qquad (17)$$

with $x, y, z \in \partial\Omega, t > 0$

Table 4: Percentage of deviation, equation (15), of the simulations by FEM with different Biot numbers, in relation to the X axis.

	Deviation (%)	
	NaCl	**KCl**
Biot = 33.154[*]	19.6	10.8
Biot = 50	14.2	7.6
Biot = 100	8.7	6.3
No resistance	7.3	5.4

[*](Bona, 2004)

The simulation with no resistance compared to that with a Biot number of 100 (Table 4) indicated that the agitation applied to the brine in this case was sufficient to reduce external resistance in a way that did not interfere with saline diffusion in the cheese. These statements are in line with Schwartzberg and Chao (1982), who reported that Biot numbers over 100 mean that the diffusion

process is little influenced by external resistance.

The theoretical profiles for the well-stirred brine (no external resistance) fall rapidly toward the initial concentration at values less than 1.2cm (Figure 6). This fact needs to be taken into account when sampling cheese to obtain experimental data for comparison with theoretical data.
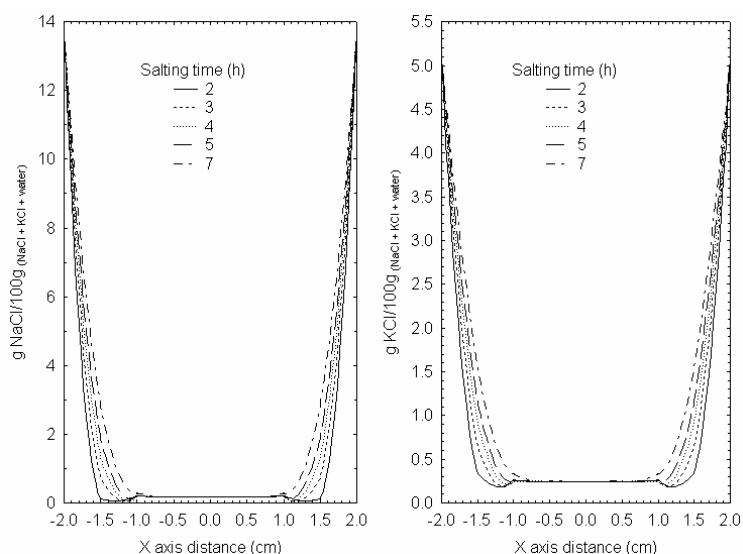
Figure 6: Theoretical spatial concentration profiles for brining of Prato cheese assuming no external resistance.

The curve shapes in Figure 6 are in line with other experiments on brining cheeses such as Emmental (Pajonk et al., 2003), Cuartirolo (Luna and Bressan, 1986), and Romano (Guinne and Fox, 1984).

The oscillation verified up to the fifth hour is normally expected when FEM is applied to diffusion problems dealing with food solids (Silva et al., 1999) because mass diffusivity is very low, on the order of 10^{-9} m^2/s (Loncin and Merson, 1974). Furthermore, the concentration gradient is very large during all brining processes. In spite of this, the oscillation was reduced applying the Crank-Nicolson scheme and spatial-time refinements (Bona, 2004).

The average concentration of the salts in whole cheeses can be calculated with equation (14). This procedure permits estimation of the ideal salting time for a desired salt content. Figure 7 shows a simulation of the total saline profile (NaCl and KCl) as a function of time, obtained from the data generated by the Simul 3.0 software. According to Furtado (1990), the salt content of Prato cheese consumed in Brazil is normally 2.0%. Based on this information, salting without agitation would take about 5.8 hours, which is twice the time necessary to salt the same Prato cheese when the brine is agitated (Figure 7).
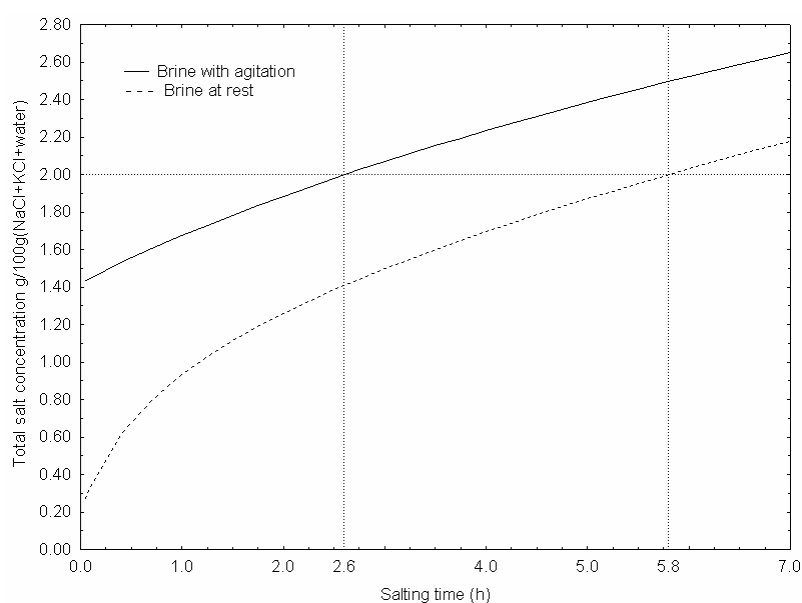

Figure 7: Saline distribution profile simulated by FEM using Simul 3.0.

CONCLUSIONS

By FEM it was possible to simulate multicomponent diffusion during the salting of Prato cheese in well-stirred brine. The data simulated were in line with experimental results, validating the application of FEM in this case. The deviation of experimental concentration data was 7.3% for NaCl and 5.4% for KCl, both of which were considered acceptable. For sodium and potassium chloride it was evident that an increase in the Biot number reduced the deviation from the experimental data. The system developed to simulate salt diffusion will allow for the control and modulation of salt content in Prato cheese (widely consumed in Brazil), predicting the final content from the initial conditions. Thus, a better quality cheese with proper salt concentrations can be produced by solely controlling the salting time. The possible reduction in salting time will allow an increase in productivity without additional investments in the process.

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NOMENCLATURE

Bi	Biot mass-exchange number	(-)
$\overline{C}$	average concentration	(g/100g $_{NaCl+KCl+water}$)
$\overline{C}_{est}$	average concentration estimated by FEM	(g/100g $_{NaCl+KCl+water}$)
$\overline{C}_{exp}$	experimental average concentration	(g/100g $_{NaCl+KCl+water}$)
$C_{i,0}$	initial concentration of component i	(g/100g $_{NaCl+KCl+water}$)
$C_{i,s}$	component i concentration in brine	(g/100g $_{NaCl+KCl+water}$)
$C_i(x,y,z,t)$	specific mass concentration	(g/100g $_{NaCl+KCl+water}$)
D_{ii}	effective main diffusion coefficient	(cm^2/day)
D_{ij}	effective cross-diffusion coefficient	(cm^2/day)
h_m	film mass transfer coefficient	(g/cm^2 h)
N	number of observations	(-)

	used to calculate %deviation	
p	statistical significance	(p-level)
$\pm R_1, \pm R_2, \pm R_3$	characteristic length	(cm)
t	time	(hours)
x, y, z	spatial coordinates	(cm)
$\nabla^2(.)$	Laplacian operator	(-)
$\partial/\partial\eta$	normal derivative operator	(-)
$\partial\Omega$	set of surface points of the cheese	(-)
$\int_\Omega f(\Omega)d\Omega$	integration on the domain	(-)
$\int_V f(V)dV$	integration on the volume	(-)
%deviation	percentage of deviation between predicted and experimental data	(-)

Greek Symbols

ϕ, ψ	weighting or interpolation functions	(-)
λ_m	mass conductivity	(g/cm h)
ξ, η, ζ	standard Cartesian coordinates	(-)
ξ_i, η_i, ζ_i	nodal standard cartesian coordinates	(-)
Ω	cheese volume or domain	(cm^3)

Sub Indices

i	component i	
j	component j	
1	NaCl	
2	KCl	

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